Polymerization

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Crystalline Isotactic Polar Polypropylene from the Palladium-Catalyzed Copolymerization of Propylene and Polar Monomers

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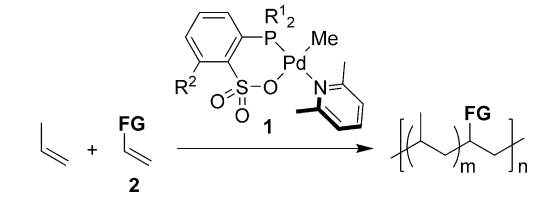
Abstract: *Moderately isospecific homopolymerization of propylene and the copolymerization of propylene and polar monomers have been achieved with palladium complexes bearing a phosphine-sulfonate ligand. Optimization of substituents on the phosphorus atom of the ligand revealed that the presence of bulky alkyl groups (e.g. menthyl) is crucial for the generation of high-molecular-weight polypropylenes ($M_w \approx 10^4$), and the substituent at the ortho-position relative to the sulfonate group influences the molecular weight and isotactic regularity of the obtained polypropylenes. Statistical analysis suggested that the introduction of substituents at the ortho-position relative to the sulfonate group favors enantiomorphic site control over chain end control in the chain propagation step. The triad isotacticity could be increased to mm = 0.55–0.59, with formation of crystalline polar polypropylenes, as supported by the presence of melting points and sharp peaks in the corresponding X-ray diffraction patterns.*

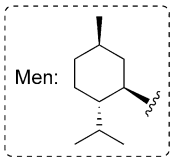
Since the discovery of chromium[1] and titanium[2] catalysts for propylene polymerization, polypropylene has been one of the most widely used commodity plastics in the world.[3] The most important parameter to control the macroscopic properties of the resultant polypropylene is its stereoregularity. For example, highly isotactic crystalline polypropylene is used as a rigid material and exhibits high toughness.[3] Polypropylene with low levels of isotacticity shows good elastomeric properties,[4] while syndiotactic polypropylene displays other unique properties, such as high impact strength and optical clarity.[5] Therefore, control over regio- and stereoregularity is crucial in any type of propylene polymerization. Accordingly, it is hardly surprising that substantial efforts have been devoted to the understanding and control of mechanistic details in the metal-catalyzed polymerization of propylene.[3a,6]

In addition to the homopolymerization of ethylene or propylene, the late transition metal catalyzed copolymerization of olefins and polar monomers has recently emerged as a powerful method for the synthesis of functional polyolefins.[7] Despite the substantial progress in this area, most catalytic systems are still restricted to the copolymerization of ethylene and polar monomers, and examples of the copolymerization of propylene and polar monomers remain scarce. The first copolymerization of propylene and a polar monomer, methyl acrylate, was reported by Brookhart and coworkers, who used palladium/α-diimine catalysts.[8] However, the obtained copolymer contained significant amounts of "chain-straightening" units, generated by a formal 3,1-insertion of propylene, that is, a 2,1-insertion of propylene followed by β-hydride elimination and a reinsertion in the opposite direction. We have recently disclosed a novel palladium/imidazo[1,5-*a*]quinolin-9-olate-3-ylidene (Pd/IzQO) catalyst system,[9] which represents the first general method for the polymerization of propylene and the copolymerization of propylene with various polar monomers in the absence of any formal 3,1-insertion of propylene. However, the obtained polypropylenes exhibited an atactic stereoregularity, which may render this catalytic system less attractive. In the present study, we accomplished the moderately isospecific homopolymerization of propylene and the copolymerization of propylene with polar monomers through the use of palladium/phosphine-sulfonate catalysts. The incorporation of bulky menthyl substituents,[10] derived from (−)-menthol, into the catalysts generates polypropylenes with high molecular weights and high levels of regioregularity (Scheme 1). Furthermore, the introduction of substituents at the *ortho*-position relative to the sulfonate group favors enantiomorphic site control over chain end control in the chain propagation step, thereby leading to crystalline isotactic polar polypropylene (iPPP) with high triad ratios ($mm \leq 0.59$).



2a: FG = CH_2OAc **2b**: FG = CH_2CN **2c**: FG = CH_2Cl **2d**: FG = CO_2Me

1a: R^1 = 2-$MeOC_6H_4$, R^2 = H
1b: R^1 = 2-(2',6'-$MeO_2C_6H_3$)C_6H_4, R^2 = H
1c: R^1 = Cy, R^2 = H
1d: R^1 = Men, R^2 = H
1e: R^1 = Men, R^2 = $SiMe_3$
1f: R^1 = Men, R^2 = $SiPh_2Me$
1g: R^1 = Men, R^2 = Ph
1h: R^1 = Men, R^2 = C_6F_5



Scheme 1. Copolymerization of propylene and polar monomers with palladium/phosphine-sulfonate catalysts.

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Table 1: Propylene polymerization using palladium/phosphine-sulfonate catalysts.[a]

Entry	Catalyst	Yield [g][b]	Activity [g mmol^{-1} h^{-1}]	M_n [kg mol^{-1}][c]	M_w/M_n[c]	[*mm*][d]	[*mr*][d]	[*rr*][d]	4[*mm*][*rr*]/[*mr*]^2	2[*rr*]/[*mr*]	regiodefects [%][e]	T_g[f] [°C])	T_m[g] [°C]	ΔH[h] [J g^{-1}]
1	**1a**	0.03	0.1	0.7	1.2	0.23	0.47.	0.30	1.25	1.28	nd	nd	nd	nd
2	**1b**	0.41	1.7	0.6	1.2	0.12	0.47	0.41	0.89	1.74	nd	nd	nd	nd
3[i]	**1c**	0.48	2.0	1.0	1.8	0.27	0.48	0.25	1.17	1.04	nd	nd	nd	nd
4	**1d**	1.81	7.5	14	2.1	0.49	0.40	0.11	1.35	0.55	0.8	−10.2	–	–
5	**1e**	2.38	9.9	24	2.0	0.57	0.32	0.11	2.45	0.69	0.9	−9.3	43.5, 62.0	11.6
6	**1f**	1.83	7.6	20	2.0	0.55	0.33	0.12	2.42	0.73	1.3	−9.9	44.4, 61.6	3.7
7	**1g**	1.41	5.9	21	1.9	0.59	0.29	0.12	3.37	0.83	0.9	−9.6	46.6, 63.9	17.8
8	**1h**	1.47	6.1	7.0	2.2	0.51	0.37	0.12	1.79	0.65	1.3	nd	nd	nd

[a] A mixture of catalyst **1** (0.020 mmol) and propylene (6.0 g) in toluene (10 mL) was stirred for 12 h at 50 °C in a 50 mL stainless-steel autoclave; nd: not determined. [b] Yields of isolated products after passing the reaction mixture through a short pad of silica gel (entries 1–3) or after evaporation of solvents and reprecipitation from methanol (entries 4–8). [c] Molecular weights determined by size-exclusion chromatography analysis using polystyrene standards and corrected by universal calibration. [d] Triad ratios determined by ^{13}C NMR analysis. [e] Regiodefects determined by quantitative ^{13}C NMR analysis. [f] Glass transition temperatures determined by DSC analysis. [g] Melting temperatures determined by DSC analysis. [h] Heats of fusion determined by DSC analysis. [i] As a result of the strong overlap of signals, triad ratios are only approximate.

Initially, we focused on the homopolymerization of propylene with palladium/phosphine-sulfonate catalysts **1a**–**1d** to investigate the effect of the phosphorus-bound substituents on the catalytic performance (Table 1). Palladium catalyst **1a**, widely used in the copolymerization of ethylene with polar monomers,[7d] yielded merely oligopropylenes (entry 1). As a consequence of the low molecular weight, it was difficult to accurately determine their tacticity and regiodefects,[11] but the triad ratio was consistent with an almost atactic stereoregularity (Figure S19). Catalyst **1b**, bearing bulky biaryl groups on the phosphorus atom,[12] also furnished oligomers, and an increase in the molecular weight could not be observed (entry 2). Replacing the substituents with alkyl groups (**1c**)[13] led to a slightly increased catalytic activity and molecular weight, although no improvement in terms of tacticity was observed (entry 3, Figure 1a). In contrast, the use of catalyst **1d** with bulky menthyl groups[10] dramatically improved the catalytic performance[14] and afforded high-molecular-weight polypropylene ($M_n > 10^4$; entry 4).[15] Analysis of the obtained polymer by ^{13}C NMR spectroscopy revealed that the control over regioregularity was almost absolute.[16,17] According to our preliminary theoretical calculations,[18] the high regioregularity can be attributed to the selective 1,2-insertion of propylene. It is worth noting that other, previously reported, propylene polymerization catalysts based on Group 10 metals, for example, nickel complexes,[19,20] require low temperatures (< −60 °C) to achieve control over the regioregularity. Moreover, the stereoregularity of the polypropylene obtained with **1d** (entry 4) was much improved (*mm* = 0.49; Figure 1b) relative to that obtained with **1a** or **1c** (entries 1 or 3).

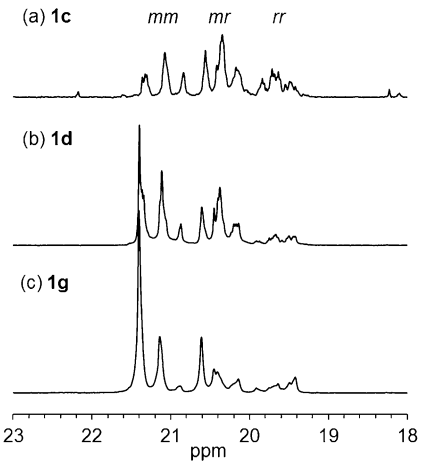

Figure 1. ^{13}C NMR spectra (δ = 18–23 ppm; -(CH(CH$_3$)CH$_2$)$_n$-) of polypropylenes obtained with a) **1c** (entry 3; Table 1), b) **1d** (entry 4; Table 1), and c) **1g** (entry 7; Table 1).

We carried out further optimizations on the phosphine-sulfonate ligand to increase the molecular weight as well as the stereoregularity of the resultant polypropylene. Previous studies on the substituent effects on the phenylene linker in phosphine-sulfonate ligands have shown that the substituent at the *ortho*-position of the sulfonate group has a strong influence on the catalytic activity and the molecular weight of the polymer.[21] Encouraged by these reports, we synthesized **1e**–**1h**[22] bearing various substituents at the *ortho*-position relative to the sulfonate group (Table 1, entries 5–8). When catalysts **1e** and **1f**, which contain a trimethylsilyl (entry 5) or a diphenylmethylsilyl (entry 6) group, were used, the molecular weight and *mm* triad ratio increased relative to that with **1d** (entry 4). The highest triad ratio (*mm* = 0.59) was observed with **1g** bearing a phenyl group (entry 7, Figure 1c), even though the molecular weight and the catalytic activity was lower compared to that with **1e** (entry 5). Replacing the phenyl group with a 1,2,3,4,5-pentafluorophenyl group (**1h**) resulted in a significant decrease in the molecular weight and *mm* triad ratio (entry 8). The favorable effects of the substituent at the *ortho*-position relative to the sulfonate group could be explained by control over the orientation of the -SO$_2$- moiety.[23,24]

As the triad ratios were affected by the substituent at the *ortho*-position of the sulfonate group (Table 1), we wanted to ascertain if the tacticity was determined by chain end control or by enantiomorphic site control. A common method to do

this is the Bernoullian test: if the value of 4[*mm*][*rr*]/[*mr*]^2 approaches 1, the stereoregularity is determined by chain end control.[25] In addition, another complementary triad test was performed: If the stereoregularity is determined by enantiomorphic site control, the value for 2[*rr*]/[*mr*] should approach 1.[26] In the case of catalysts **1e**–**1h** (entries 5–8), 4[*mm*]-[*rr*]/[*mr*]^2 values of 1.79–3.37 were calculated, and these are substantially larger than that obtained with **1d** (entry 4; 1.35). Conversely, the corresponding 2[*rr*]/[*mr*] values (0.65–0.83) were much closer to 1, compared to that with **1d** (0.55). These results suggest that the introduction of substituents at the *ortho*-position relative to the sulfonate group enhances enantiomorphic site control rather than chain end control.[27]

We also carried out copolymerizations of propylene and various polar monomers to synthesize iPPP (Table 2). For these copolymerizations, **1e** was used as the catalyst, as it showed the highest catalytic activity for the homopolymerization of propylene and furnished polypropylene with the highest molecular weight. The quantities of polar monomers in the feed were adjusted according to their copolymerizability to achieve approximately 1% incorporation of the polar monomers (entries 1, 4, 7, and 8). For example, allyl acetate (**2a**) was successfully incorporated into polypropylene (entries 1–3) with molecular weights of the copolymers (M_n = 7.2–8.9 × 10^3 g mol^{-1}; entries 1 and 2) comparable to that obtained using the Pd/IzQO catalyst system (M_n = 11 × 10^3 g mol^{-1}).[9] Increasing the amount of allyl acetate twofold resulted in the incorporation ratio also increasing by a factor of about 2, although the molecular weight and catalytic activity decreased (cf. entries 1 and 3). Copolymerization with allyl cyanide (**2b**) furnished the corresponding copolymers containing cyano groups (entries 4–6). The catalytic activity was similar to that of allyl acetate, while the molecular weight of the copolymer slightly decreased (cf. entries 1 and 4). Copolymerization with allyl chloride (**2c**) provided the corresponding halogenated polypropylene (entry 7). In the presence of methyl acrylate, a propylene/methyl acrylate copolymer was obtained (entry 8). When the amount of methyl acrylate was increased twofold (entry 9), the incorporation ratio was again increased by a factor of about 2 (cf. with entry 8).

The structure of the propylene/polar monomer copolymers was examined by NMR analysis. All the obtained copolymers consisted of regioregular polypropylene backbones with approximately 1% 1,2-/2,1-regiodefects, and with the polar monomers incorporated into the polymer main chain. The stereoregularity was characterized by triad values of *mm* = 0.55–0.57,[28] when **1e** and **1g** were used as catalysts (Table 2). The *mm* values are almost identical to those of the corresponding propylene homopolymers (Table 1). All the propylene/allyl monomer copolymers exhibited a polymer structure that is consistent with the insertion of allyl monomers **2a**–**2c** with the same regioselectivity as that of propylene (Figure 2), which suggests that **2a**–**2c** underwent exclusive 1,2-insertion. Conversely, the NMR spectra of the propylene/methyl acrylate copolymer indicated that methyl acrylate underwent a 2,1-insertion.[29]

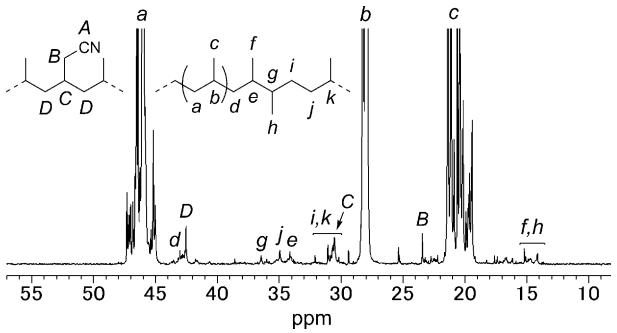

Figure 2. ^{13}C NMR spectrum of the propylene/allyl cyanide copolymer.

Table 2: Copolymerization of propylene and polar vinyl or allyl monomers using **1e** and **1g**.[a]

Entry	Co-monomer	Time [h]	Monomer [mL]	Yield [g][b]	Activity [g mmol^{-1} h^{-1}]	M_n [kg mol^{-1}][c]	M_w/M_n[c]	Incorp. [%][d]	[*mm*][e]	Regiodefects [%][f]	T_g[g] [°C]	T_m[h] [°C]	ΔH[i] [J g^{-1}]
1	**2a** (CH_2OAc)	12	0.5	0.18	0.75	8.9	2.7	1.7	0.55	1.0	−11.7	43.4, 60.4	6.7
2	**2a**	48	0.5	0.22	0.22	7.2	3.4	1.7	0.56	1.1	nd	nd	nd
3	**2a**	12	1.0	0.09	0.38	5.8	2.6	2.9	0.55	1.3	nd	nd	nd
4	**2b** (CH_2CN)	12	1.0	0.19	0.79	7.5	1.9	1.6	0.55	1.1	nd	nd	nd
5	**2b**	48	1.0	0.49	0.51	10	2.4	1.3	0.57	1.0	−10.0	45.4, 61.8	10.1
6[j]	**2b**	48	1.0	0.19	0.20	6.3	2.3	1.4	0.57	1.0	−12.0	43.1, 62.1	15.5
7	**2c** (CH_2Cl)	12	0.25	0.14	0.58	11	2.2	1.7	0.56	1.1	−10.0	42.9, 61.7	11.0
8	**2d** (CO_2Me)	12	0.25	0.20	0.83	4.6	2.2	1.6	0.56	0.9	−14.3	43.3, 61.8	11.4
9	**2d**	12	0.5	0.14	0.58	2.9	1.9	3.3	0.55	1.3	nd	nd	nd

[a] A mixture of catalyst **1e** (0.020 mmol), propylene (6.0 g), and monomers **2a**–**d** in toluene (10 mL) were stirred at 50 °C in a 50 mL stainless-steel autoclave; nd: not determined. [b] Yields of isolated products after passing the reaction mixture through a short pad of silica gel. [c] Molecular weights determined by size-exclusion chromatography using polystyrene standards and corrected by universal calibration. [d] Molar incorporation ratios of polar monomers determined by ^{1}H NMR analysis. [e] Triad ratios determined by ^{13}C NMR analysis. [f] Regiodefects determined by quantitative ^{13}C NMR analysis. [g] Glass transition temperatures determined by DSC analysis. [h] Melting temperatures determined by DSC analysis. [i] Heats of fusion determined by DSC analysis. [j] Copolymerization performed using **1g**.

Finally, an investigation of the physical properties of the obtained (co)polymers revealed that they are crystalline. Differential scanning calorimetry (DSC) analysis of the polypropylene obtained with **1d** ($mm = 0.49$; entry 4 in Table 1) showed a glass-transition temperature (T_g) at −10 °C, but no melting endotherm. Conversely, the polypropylene obtained with **1g** ($mm = 0.59$; entry 7 in Table 1), which exhibited the highest triad ratio, revealed a T_g value of −10 °C and two melting endotherms at $T_m = 47$ and 64 °C (Figure S52). These are features that are typically observed for low-molecular-weight and/or moderately isotactic polypropylenes.[30] An X-ray diffraction analysis (Cu-K_α; $\lambda = 0.1541$ nm) was subsequently conducted to confirm the origin of the endotherms. The diffraction pattern displayed broad signals with relatively sharp peaks at $2\theta = 14.1$, 16.7, and 21.1° (Figure 3, top). These signals could be assigned to the (111), (008), and (202) + (026) reflections of the γ-crystal form.[31] The peak shape suggested that the obtained polypropylene crystallized predominantly in the γ-crystal form with low crystallinity. The degree of crystallinity was estimated to be about 12% on the basis of a comparison of the observed heat of fusion ($\Delta H = 18\ J\,g^{-1}$) with literature values (145–150 $J\,g^{-1}$).[32] The propylene/allyl cyanide copolymer (entry 6 in Table 2) showed similar T_g (−12 °C) and T_m (43/62 °C) values (Figure S109), as well as similar X-ray diffraction signals (Figure 3, bottom).[33]

In summary, we accomplished the palladium-catalyzed regio- and stereocontrolled homopolymerization of propylene and the copolymerization of propylene and polar monomers. The use of menthyl-substituted phosphine-sulfonate ligands is crucial for the formation of polypropylenes with high molecular weight. The introduction of substituents at the *ortho*-position relative to the sulfonate group increased the molecular weight of the obtained polypropylene, and favored enantiomorphic site control over chain end control in the chain propagation step. Under optimum conditions, various functional groups such as acetoxy, cyano, chloro, and alkoxycarbonyl moieties could be incorporated at 1–3 mol% into the polymer main chain to afford moderately crystalline iPPP.

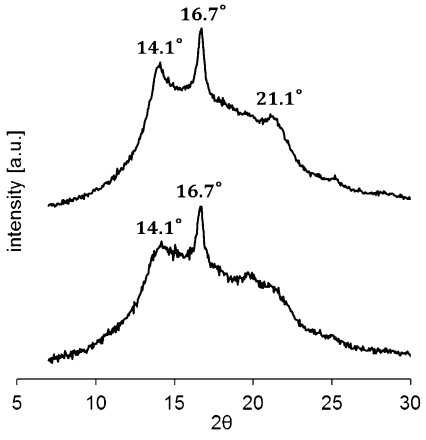

Figure 3. X-ray diffraction patterns of a) a polypropylene (entry 7 in Table 1) and b) a propylene/allyl cyanide copolymer sample (entry 6 in Table 2) obtained using **1g**.

Acknowledgements

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