

Quantification of the Steric Influence of Alkylphosphine–Sulfonate Ligands on Polymerization, Leading to High-Molecular-Weight Copolymers of Ethylene and Polar Monomers

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S Supporting Information

ABSTRACT: A series of palladium/alkylphosphine–sulfonate catalysts were synthesized and examined in the homopolymerization of ethylene and the copolymerization of ethylene and polar monomers. Catalysts with alkylphosphine–sulfonate ligands containing sterically demanding alkyl substituents afforded (co)polymers whose molecular weight was increased by up to 2 orders of magnitude relative to polymers obtained from previously reported catalyst systems. The polymer molecular weight was found to be closely correlated to the Sterimol B5 parameter of the alkyl substituents in the alkylphosphine–sulfonate ligands. Thus, the use of bulky alkylphosphine–sulfonate ligands represents an effective and versatile method to prepare high-molecular-weight copolymers of ethylene and various polar monomers, which are difficult to obtain by previously reported methods.

Molecular weight (MW) is one of the most important factors in determining the macroscopic physical and chemical properties of a polymer. Thus, an important objective in polymer synthesis is the development of chain-growth polymerization methods, which afford high-molecular-weight polymers with low polydispersities. The generation of polyethylenes and polypropylenes with high MWs from the coordination/insertion polymerization of ethylene and propylene is usually accomplished with early-transition-metal catalysts. Unfortunately, the technique cannot be applied to the copolymerization of olefins and polar monomers, as those catalysts are easily poisoned by polar functional groups in the comonomer. Attention has thus been shifted to late-transition-metal catalysts, which have been established as powerful tools to synthesize functional polyethylenes with a defined structure.¹ The most successful catalysts for these copolymerizations are so far Ni and Pd complexes ligated by a phosphine–sulfonate;^{1d–f,2} they polymerize a variety of polar monomers such as acrylates³ and related monomers,⁴ as well as vinyl⁵ or allyl monomers.^{6,7} From an application-orientated perspective, one serious drawback remains: even though these catalysts produce polyethylenes with desirably high number-average molecular weights ($M_n > 10^6$ g/mol),⁸ almost all the reported copolymers containing polar monomers suffer from low molecular weights ($M_n < 10^4$ g/mol).^{9,10} To overcome this obstacle, the steric and electronic parameters of arylphosphine–

sulfonate ligands and their influence on the MW of the resulting copolymers have been intensively studied.^{3b,f,8d,10–12} According to these studies, it is predominantly the steric influence of the aryl substituents on the P-atom that determines the MW of the copolymers. Whereas the replacement of the standard *o*-anisyl groups^{1d–f} with naphthalen-1-yl or anthracen-9-yl groups leads to a decrease of the MW,^{3f,8d} the introduction of at least one 1,1'-biphenyl-2-yl group increases the MW of the resulting copolymers remarkably.^{3b,8c,12b} Although the correlation has not yet been quantified, the increase of the MW can be interpreted as a result of the steric congestion around the axial positions of the *xz*-plane containing the metal center (Figure 1). The electronic effects of arylphosphine–sulfonate ligands were also thoroughly investigated by Mecking et al., who reported that electron-donating substituents increase the MW of the copolymers.¹²

We recently focused our attention on Pd catalysts with alkylphosphine–sulfonate ligands, as they show higher catalytic activity compared to the corresponding arylphosphine–sulfonate ligands in the copolymerization of ethylene and vinyl^{5c} or allyl acetate,⁶ which allows the incorporation of protected hydroxy groups into the polyethylene main chains. The steric and electronic effects of alkylphosphine–sulfonate ligands on the catalytic performance remain less explored relative to those of their aryl counterparts. Here we report the synthesis of a series of alkylphosphine–sulfonate ligands for the Pd-catalyzed copolymerization of ethylene and various polar monomers (Scheme 1). Moreover, we present a systematic investigation into the steric influence of the ligands on the MW of the resulting copolymers, which was evaluated quantitatively on the basis of the Taft,¹³ Sterimol,¹⁴ and % V_{bur} ¹⁵ parameters. A close examination of these parameters revealed that the Sterimol parameter of the alkyl substituents in the ligands correlates most accurately with the MWs of the obtained polymers. When a Pd catalyst bearing a very bulky menthylphosphine–sulfonate ligand (**1f**) was employed, exceptionally high MWs were obtained for the copolymers.

Palladium/alkylphosphine–sulfonate complexes **1a–f** were either prepared according to literature procedures (**1a**¹⁶ and **1c**^{6a}) or synthesized from the corresponding phosphonium–sulfonates (**1b**^{3f,17} and **1d–f**²). The molecular structures of **1a–f**

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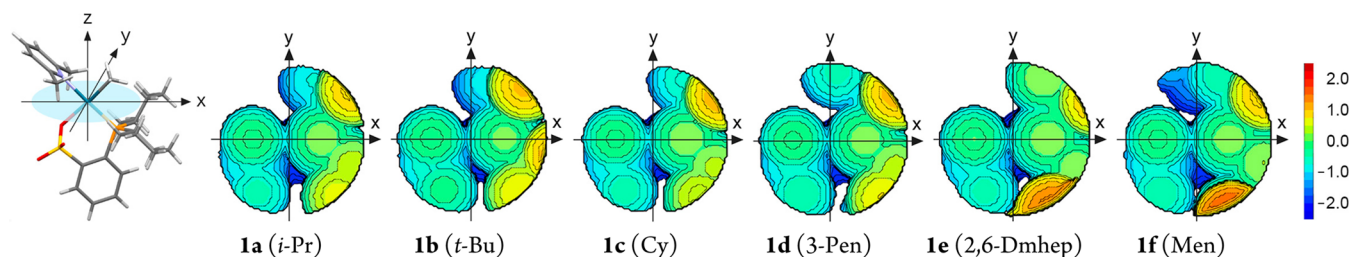
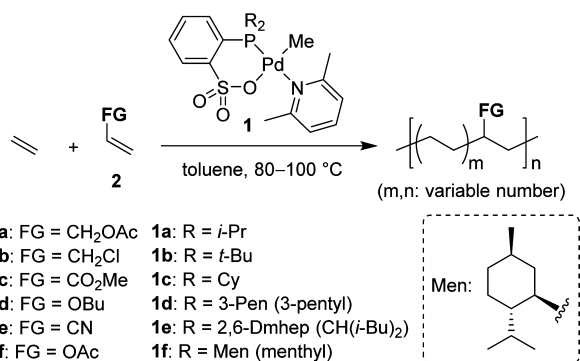


Figure 1. Steric maps of palladium/alkylphosphine-sulfonate complexes **1a–f**. The Pd-atom is placed at the center of the xyz coordinate system (left). The P–Pd–O plane is placed in the xz -plane with the z -axis bisecting the P–Pd–O angle. The y -axis represents the axial position of the xz -plane containing the Pd center. The methyl and 2,6-lutidine groups were omitted for the analysis of the steric maps.

Scheme 1. Copolymerization of Ethylene and Polar Monomers **2a–f** with Palladium/Alkylphosphine-Sulfonate Catalysts **1a–f**



were confirmed unambiguously by single-crystal X-ray diffraction analyses, which also allowed the elaboration of the steric maps (Figure 1) and a determination of various other metric parameters, including the Sterimol parameter. As complexes **1a–f** contain two alkyl substituents each, the Sterimol parameters were calculated for each substituent individually and then averaged.⁹ The calculated Sterimol values for most of the alkyl substituents were in good agreement with previously reported values.¹³

Initially, we investigated the homopolymerization of ethylene using Pd catalysts **1a–f** (Table 1). ¹³C NMR analyses of the obtained polyethylenes revealed that **1a–f** produced exclusively linear polymers containing less than one branch per 1000 C-atoms in their polyethylene backbone. Although **1a** (*i*-Pr), **1b** (*t*-Bu), and **1c** (Cy) exhibited high catalytic activities, the M_n of the

Table 1. Homopolymerization of Ethylene with Palladium/Alkylphosphine-Sulfonate Complexes **1a–f^a**

entry	catalyst	B5	yield ^b (g)	activity (g/mmol-h)	M_n^c ($\times 10^3$ g/mol)	M_w/M_n^c
1	1a (<i>i</i> -Pr)	3.07	6.41	641	6.7	2.7
2	1b (<i>t</i> -Bu)	3.09	18.6	1860	6.2	4.1
3	1c (Cy)	3.38	11.5	1150	9.9	2.4
4	1d (3-Pen)	4.28	1.25	125	33	2.4
5	1e (2,6-Dmhhep)	5.22	1.97	200	72	2.4
6	1f (Men)	5.64	2.05	205	169	1.5

^aA mixture of catalyst **1** (0.010 mmol) in toluene (100 mL) was stirred under ethylene atmosphere (3.0 MPa) in a 300 mL autoclave for 1 h at 80 °C. ^bIsolated yields after precipitation with methanol. ^cMolecular weights determined by size-exclusion chromatography (SEC) using polystyrene standards, and corrected by universal calibration.

resulting polyethylenes remained relatively low ($M_n < 10 \times 10^3$ g/mol, entries 1–3 in Table 1). When bulkier ligands such as **1d** (3-Pen), **1e** (2,6-Dmhhep), and **1f** (Men) were used, the M_n of the polyethylenes increased to 33×10^3 , 72×10^3 , and 169×10^3 g/mol, respectively, albeit with lower catalytic activity than **1a–c**. The exceptionally high M_n values achieved with catalyst **1f** even exceeded those gained by bis(2,6'-dimethoxy-1,1'-biphenyl-2-yl)phosphine-sulfonate ($M_n = 57 \times 10^3$ – 96×10^3 g/mol, after universal calibration¹⁸).^{3b,f} To gain a deeper understanding, we quantified the steric effects of the substituents on the basis of various steric parameters. A close correlation was observed between the polymer MWs and the Sterimol B5 parameters of the substituents (Figure 2).¹⁹ Catalysts containing alkyl

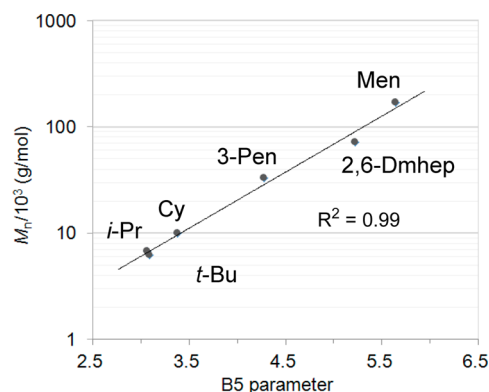


Figure 2. Correlation between the number-average molecular weight (M_n) of the obtained polyethylene homopolymers and the Sterimol B5 parameter of the alkylphosphine-sulfonate ligands.

substituents with higher B5 values, such as **1d–f**, were observed to produce polyethylene with higher MW and lower polydispersity. A plausible explanation for the increase in MW could be the steric congestion in the axial positions of the xz -plane, which contains the metal center.^{3f,8c,12b,20} This notion is supported by the X-ray crystal structures of **1e** (Figure S79) and **1f** (Figure S80), where one of the 2,6-dimethylheptyl or menthyl substituents occupies one of the axial positions of the xz -plane. To determine the steric bulk around the Pd center, steric maps were also used as shown in Figure 1,²¹ which confirmed increasing steric congestion in the axial positions of the Pd center as a result of the increased steric demand of the alkyl substituents from **1a** to **1f**.⁹

With these encouraging results in hand, we subsequently explored the copolymerization of ethylene and polar monomers by Pd complexes **1a–f**, starting with allyl acetate (**2a**)⁶ as a benchmark comonomer (Table 2). All the catalysts **1a–f** exhibited desirable activity under the applied conditions, and

Table 2. Copolymerization of Ethylene and Allyl Acetate (2a) with Palladium/Alkylphosphine–Sulfonate Complexes 1a–f^a

entry	catalyst	yield ^b (g)	activity (g/mmol·h)	M_n^c ($\times 10^3$ g/mol)	M_w/M_n^c	i.r. ^d (%)
1	1a (<i>i</i> -Pr)	0.35	12	5.2	2.4	1.9
2	1b (<i>t</i> -Bu)	0.31	10	10.3	5.1	0.6
3	1c (Cy)	0.30	10	7.8	2.0	1.8
4	1d (3-Pen)	0.36	12	17	2.4	1.5
5	1e (2,6-Dmhph)	0.35	12	29	2.8	1.1
6	1f (Men)	1.65	55	177	2.0	0.6

^aA mixture of catalyst 1 (0.010 mmol) and allyl acetate (2a, 7.5 mL) in toluene (7.5 mL) was stirred under ethylene atmosphere (3.0 MPa) in a 50 mL autoclave for 3 h at 80 °C. ^bIsolated yields after precipitation with methanol. ^cMolecular weights determined by SEC using polystyrene standards and corrected by universal calibration. ^dMolar incorporation ratios of 2a determined by ¹H NMR analysis.

similar to the homopolymerization of ethylene, catalysts containing ligands with alkyl substituents having higher BS values produced copolymers with higher MWs. Again, complex 1f, containing very bulky menthyl substituents with the largest BS value (5.64), produced a copolymer with a particularly high MW ($M_n = 177 \times 10^3$ g/mol). However, the incorporation ratio (i.r.) of 2a obtained with complex 1f decreased to 0.6%, which suggested that increased steric congestion around the Pd center due to bulky substituents disfavors the coordination of 2a (bulkier than ethylene).

To investigate the scope and versatility of complex 1f, a variety of other polar monomers were examined under various conditions (Table 3). The copolymerization of ethylene and 2a revealed that higher reaction temperatures, or decreased ethylene pressures, increased the i.r. of 2a up to 7.8% (entries 1–5). As a concomitant decrease of the MW was observed, these results indicate a trade-off relationship between the MW and the i.r. of polar monomers (Figure 3). The solid red line shows that the values for M_n and the i.r. of 2a obtained from 1f substantially exceed those of previously reported catalytic system 1c (red dotted line).^{6a} Copolymerization of ethylene and allyl chloride (2b) with 1f afforded a copolymer with high MW ($M_n = 33 \times 10^3$ g/mol, i.r. = 0.6%, entry 6), which is ~8 times higher than that

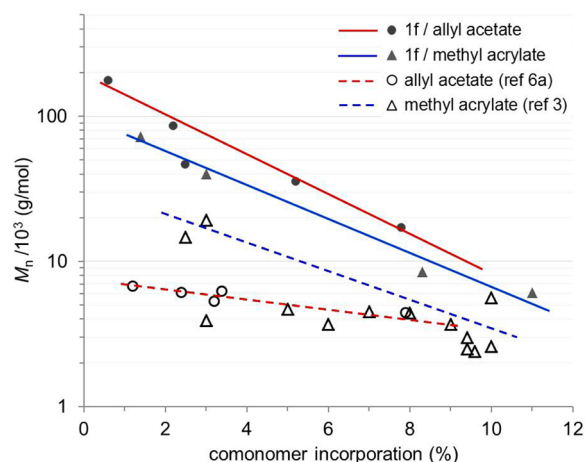


Figure 3. Comparison of M_n vs comonomer incorporation ratios obtained from 1f and other previously reported catalyst systems.^{3,6a} Solid lines represent results from the present study, whereas dotted lines represent results from previous studies.¹⁸ Red lines show allyl acetate (2a), while blue lines show methyl acrylate (2c).

obtained using 1c ($M_n = 4.2 \times 10^3$ g/mol, i.r. = 0.6%).^{6a} Catalyst 1f could also be used for the copolymerization of ethylene and other polar vinyl monomers (entries 7–14). The use of methyl acrylate (2c), which is the most common comonomer,³ afforded copolymers with high MWs ($M_n = 6.1 \times 10^3$ – 72×10^3 g/mol) and 2c i.r. = 1.4–11% (entries 7–10). The ratios between M_n and the comonomer incorporation for the ethylene/2c copolymers obtained in this study (solid blue line in Figure 3) were higher than the ratios of previously reported catalyst systems (dotted blue line).³ When vinyl ether (2d) was used as a comonomer, catalyst 1f exhibited a higher polymerization activity (54 g/mmol·h) and produced copolymers with higher MW ($M_n > 10^4$ g/mol) compared to arylphosphine–sulfonate ligands in the literature (entries 11 and 12).^{5a} Copolymerizations of ethylene with acrylonitrile (2e, entry 13) and vinyl acetate (2f, entry 14) were also accomplished, resulting in the formation of copolymers with higher MWs ($M_n = 14 \times 10^3$ and 5.6×10^3 g/mol, respectively) than previously reported catalyst systems.^{4a,5e} The incorporation and presence of the respective functional groups in

Table 3. Copolymerization of Ethylene and Polar Vinyl or Allyl Monomers with 1f^a

entry	comonomer	ethylene (MPa)	monomer (mL)	solvent (mL)	T (°C)	t (h)	yield ^b (g)	activity (g/mmol·h)	M_n^c ($\times 10^3$ g/mol)	M_w/M_n^c	i.r. ^d (%)
1	2a (CH ₂ OAc)	3.0	7.5	7.5	80	3	1.65	55	177	2.0	0.6
2	2a	3.0	7.5	7.5	100	3	1.05	35	47	2.2	2.5
3	2a	2.1	7.5	7.5	80	3	1.10	37	86	2.1	2.2
4	2a	1.0	7.5	7.5	100	3	0.48	16	36	1.7	5.1
5	2a	1.0	12	3	100	13	0.30	2.3	17	2.0	7.8
6	2b (CH ₂ Cl)	3.0	3	12	80	16	0.35	2.2	33	2.3	0.6
7	2c (CO ₂ Me)	3.0	7.5	7.5	80	3	2.02	67	72	2.5	1.4
8	2c	2.0	7.5	7.5	80	3	0.88	29	40	2.0	3.0
9	2c	1.0	7.5	7.5	100	3	0.44	15	8.5	2.0	8.3
10	2c	1.0	12	3	100	15	0.24	1.6	6.1	1.8	11
11	2d (OBu)	3.0	7.5	7.5	80	3	1.61	54	15	4.1	1.1
12	2d	1.0	12	3	100	15	1.30	8.6	11	2.4	7.7
13	2e (CN)	3.0	7.5	7.5	80	15	0.30	2.0	14	1.9	0.7
14	2f (OAc)	3.0	12	3	80	15	0.34	2.3	4.8	2.7	1.3

^aA mixture of catalyst 1f (0.010 mmol) and monomers 2a–f in toluene was stirred under ethylene atmosphere in a 50 mL autoclave. ^bIsolated yields after precipitation with methanol. ^cMolecular weights determined by SEC using polystyrene standards and corrected by universal calibration. ^dMolar incorporation ratios of polar monomers determined by ¹H NMR analysis.

the main chain of all the obtained copolymers was confirmed on the basis of comparisons with reported spectroscopic data for the corresponding copolymers.

In summary, we synthesized a series of alkylphosphine–sulfonate ligands and quantified their steric influence on the palladium-catalyzed copolymerization of ethylene with various polar monomers. We found that the Sterimol B5 parameters of the alkyl substituents in the catalysts describe the good correlation between the steric bulk of the ligands and the molecular weight of the (co)polymers. Consequently, we designed bulky alkylphosphine–sulfonate ligands having, e.g., 2,6-dimethylheptyl and menthyl groups, and their Pd complexes afforded high-molecular-weight copolymers of ethylene and polar monomers, which were difficult to synthesize with previously reported catalyst systems.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details; characterization of ligands, Pd complexes, and polymers; crystallographic data for 1a–f. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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- (18) Determination of MWs differs depending on references, and thus the MWs were corrected by universal calibration before comparison. For details, see the SI.
- (19) For analyses using other steric parameters, see the SI.
- (20) Our preliminary calculations suggested that steric protection of axial positions suppresses two key transition states for chain transfer: (1) dissociation of ethylene from $[P-O]Pd(alkyl)(ethylene)$ and (2) associative exchange of $CH_2=CHR$ in $[P-O]PdH(CH_2=CHR)$ by ethylene. Details will be reported elsewhere.
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