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Copolymerization of Ethylene with Norbornene by Neutral Aryl Phosphine Sulfonate Palladium Catalyst

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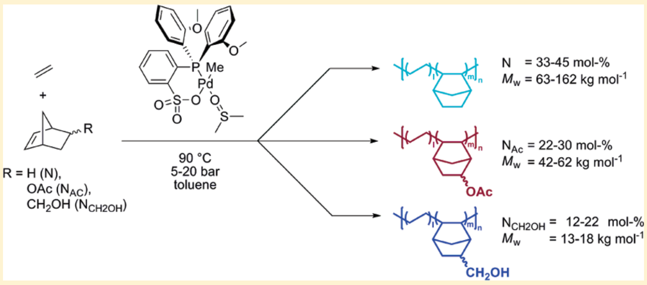
S *Supporting Information*

ABSTRACT: Complex [Pd(κ^2-*P*,*O*-{2-(2-MeOC$_6$H$_4$)$_2$P}-C$_6$H$_4$SO$_3$)Me(dmso)] (**1**) was investigated as a single component catalyst for the copolymerization of ethylene with norbornene affording P(E-*co*-N) in excellent yields and molar masses significantly higher than those of polyethylene. Copolymer molar masses increased with N concentration. Determination of microstructure and reactivity ratios revealed a strong inherent tendency to form alternating copolymers. The ability of palladium complex **1** to effectively copolymerize ethylene with functionalized norbornene derivatives was also demonstrated.



INTRODUCTION

Transition-metal-catalyzed polymerization of olefins, applied today on a vast industrial scale, provides superior control of polymer composition, structures, and properties with respect to radical processes.[1] The introduction of low amounts of polar groups into polyolefins is consequently desirable because they would greatly impact upon polyolefin properties such as toughness, flexibility, crack resistance, gas permeability, miscibility, adhesion, and paintability.[2] However, even the acclaimed α-diimine Ni- and Pd-based catalysts[3] can efficiently copolymerize only a limited number of polar vinyl monomers such as alkyl acrylates[4] and vinyl ethers.[5] Hence, neutral nickel and palladium catalysts with monoanionic mixed chelating ligands (NO, PO, etc.) have been developed. Drent first reported that the *in situ* generated neutral Pd(II) catalyst, bearing a phosphonium-sulfonate ligand, effectively copolymerizes ethylene with acrylates to linear copolymers.[6] Since then, several research groups reported on olefin (co)polymerization using *in situ*-generated phosphine-sulfonate Pd catalysts.[7] The development of well-defined neutral alkyl phosphine sulfonate Pd(II) species allows one to have deep insights into polymerization mechanisms and to extend the copolymerization of ethylene with a variety of functionalized monomers such as methyl acrylate (MA), acrylonitrile (AN), vinyl acetate (VA), vinyl halides, vinyl ethers, and others.[2] Most of these well-defined systems have the general formula [(κ^2-PO)PdR(L)] and include N- and P-based stabilizing ligands (L) such as pyridine, 2,6-lutidine, PPh$_3$, and amines.[8] Catalyst activation depends on the relative binding strength of L to the metal center. The relatively strong σ-donors compete with the monomer for coordination at the metal center, resulting in a large portion of active centers in a dormant inactive state. Dimethyl sulfoxide (dmso) was therefore selected as a more labile candidate and dmso-containing complexes were found to be highly active single component catalysts for the polymerization of ethylene, copolymerization of ethylene with MA,[9] and opened the way for the first time to the synthesis of new polymers such as ethylene-*co*-vinyl sulfone and ethylene-*co*-acrylic acid copolymers.[10,11]

In recent years, there has also been great interest concerning cyclic olefin copolymers (COC), owing to their unique properties. Among the family of COC the most versatile and interesting ones are the copolymers of ethylene with norbornene (N). E-*co*-N copolymers are amorphous with a glass transition temperature (T_g) varying up to more than 200 °C, depending on the N content and the copolymer microstructure. Glass-like clarity as well as good solvent resistance and high thermal stability made such copolymers attractive as high-tech engineering materials.[12−14] The use of appropriately functionalized norbornene derivatives would further expand the range of properties of these copolymers.

Only few examples of E-*co*-N copolymerization with a neutral alkyl phosphine sulfonate Pd(II) species have been reported so far. Claverie reported on E-*co*-N copolymerization in aqueous emulsion.[7b] Latexes of such polymers should present the unique properties of E-*co*-N copolymers, such as high durability and UV and chemical resistance. Nevertheless, the emulsion copolymers, by *in situ* generation of the catalyst from Pd$_2$(dba)$_3$ (dba = dibenzilideneacetone) and {2-(2-MeOC$_6$H$_4$)$_2$P}C$_6$H$_4$SO$_3$H ligand in the presence of sodium dodecyl sulfate (SDS) as surfactant, resulted as being very heterogeneous in composition, since they contain a fraction rich in N and a fraction rich in E.[7b] At about the same time Sen reported on the copolymerization of ethylene with functionalized norbornene derivatives from palladium species generated in situ.[7c] Preliminary results on E-*co*-N copolymerization with a well-defined neutral alkyl phosphine

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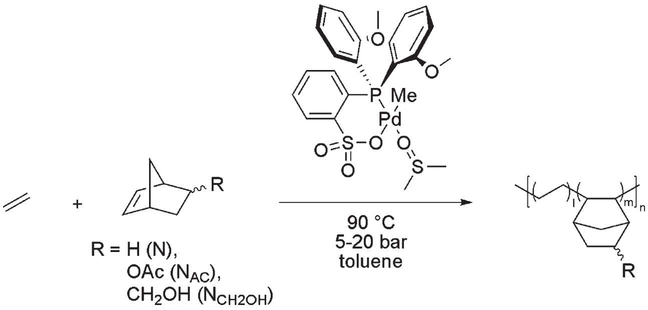
Scheme 1. Copolymerization of Ethylene with Norbornene, 5-Norbornene-2-yl Acetate, and 5-Norbornene-2-methanol by Catalyst 1



sulfonate Pd(II) with pyridine ligand were also reported by Claverie.[8c]

Herein, we report a detailed study of the E-*co*-N copolymerization reaction with the single component catalyst precursor $[Pd(\kappa^2\text{-}P,O\text{-}\{2\text{-}(2\text{-}MeOC_6H_4)_2P\}C_6H_4SO_3)Me(dmso)]$ (**1**) (Scheme 1). Excellent activity as well as a strong inherent tendency to form alternating copolymers is demonstrated. The microstructural and chain end group analysis and the molecular and thermal characterization of the copolymers are presented. On the basis of the ascertained copolymer microstructure, the copolymerization kinetics could be expressed by reactivity ratios r_i and r_{ij}. All results are discussed to have insights into polymerization mechanisms operating in this system. In addition, in order to explore the functionalized comonomers that can be incorporated, experiments and results for the copolymerization of ethylene with norbornene derivatives 5-norbornene-2-yl acetate (N_{AC}) and 5-norbornene-2-methanol (N_{CH_2OH}) are included.

RESULTS AND DISCUSSION

Synthesis and Characterization of P(E-*co*-N). Series of copolymerization reactions of ethylene with norbornene were performed by **1** in toluene at 90 °C at 5 and 20 bar pressure of ethylene. These conditions were found optimal for balancing the displacement of the labile dmso for generating the active species and preventing catalyst deactivation.[9] A range of [N]/[E] feed ratios as wide as possible was investigated. The polymerization tests were designed to study the copolymer microstructure; low comonomer conversion and low polymer concentration in the polymerization medium were imposed. Norbornene conversion was kept ideally below 10%. Norbornene content and copolymer microstructure were determined from analysis of ^{13}C NMR spectra. Glass transition temperatures and molar masses were estimated by DSC and size exclusion chromatography (SEC) measurements, respectively. The results concerning the synthesis and the characterization of selected copolymers are summarized in Table 1. Runs 1 and 9 confirm that **1** is a highly active single component catalyst for ethylene polymerization. Activity and molar masses are in line with previous data.[9] By raising the ethylene pressure from 5 to 20 bar, the activity doubles. Polyethylene is linear, the number of methyl branches is in the order of 7 per 1000 carbon atoms in the polymer prepared at 5 bar and decreases to 2 per 1000 in the polymer prepared at 20 bar. This catalyst shows unique characteristics, such as extremely high activity for E−N copolymerization at high temperature. To our knowledge, this is the highest activity reported for copolymerization of ethylene and norbornene with late transition metal catalysts (e.g., the activity of run 5 exceeds 1500 kg polymer mol Pd^{-1} h^{-1}). There is a dependence of the activity of the catalyst on the norbornene concentration: as in almost all N copolymerizations the increase in N concentration in the polymerization feed results in a decrease in catalytic activity, most likely due to the facile N coordination to the active sites.

Incorporation of norbornene in copolymers increased with increasing [N]/[E] feed ratio up to a plateau under 50 mol %. It is worth emphasizing that high norbornene content in the copolymers (higher than 40 mol %) is already reached at [N]/[E] = 1, which is an indication that this copolymerization approaches the features of a truly alternating one. Moreover, ^{13}C NMR analysis excludes the presence of methyl branches in the copolymers, which is related to the high N content. Indeed, the constrained geometry catalyst $[Ti(\eta^5\text{-}C_5Me_4SiMe_2N^tBu)Cl_2]$/MAO, which typically is able to incorporate long chain branches in polyethylene, gave E-*co*-N copolymers with decreasing degree of branching with an increasing norbornene molar fraction in the feed.[12p]

Molar-mass distributions (M_w/M_n) are consistent with single-site catalytic systems. Molar masses were greater at higher pressure, though the effect was not so strong as on activity (see run 1 and run 9). This reveals that propagation rate increases more than chain transfer reaction rate with pressure and is an indication that β hydrogen elimination is more important than chain transfer to the monomer, in line with other experimental and theoretical mechanistic studies on the formation of linear polyethylene by analogous palladium complexes.[16] Interestingly, the molar mass values of copolymers are significantly higher than polyethylene (PE) molar masses. The plot of molar masses (M_n) versus the ratio [N]/[E] in feed, displayed in Figure 1, shows that the higher the [N]/[E] in feed the higher the molar masses. It is worth noting that copolymers prepared at [N]/[E] feed ratios of 1, 1.5, 2, and 3, having similar norbornene content, have completely different molar masses. This indicates that the coordination of norbornene which slows down the propagation rate also slows down the chain transfer reactions.

Analysis of thermal properties revealed no melting events indicating the homogeneous composition of copolymers. The evolution of T_g values versus norbornene content in the copolymers is plotted in Figure 2. Inspection of the graph reveals that the differences in T_g values arise mainly from the different amount of norbornene incorporated in the copolymer.

Copolymerization of Ethylene with Functionalized Norbornene Derivatives. The ability of catalyst **1** to incorporate functionalized norbornene derivatives was tested by using 5-norbornene-2-yl acetate (N_{AC}) and the protic, thus more challenging, 5-norbornene-2-methanol (N_{CH_2OH}). Both the monomers were of commercial grade, therefore mixtures of *endo* and *exo* isomers. Selected results of these experiments are reported in Table 2.

Remarkably, E-*co*-N_{AC} copolymerization by **1** occurred with excellent activity, which was even higher than in E-*co*-N copolymerization. As in N copolymerization, a slight decrease in activity, was observed with increasing concentration of N_{AC} (see entries 14 and 15). Additionally, analogous behavior to N copolymerization was also observed regarding incorporation and molar mass. The higher the $[N_{AC}]/[E]$ feed ratio the higher the incorporation and M_w. N_{AC} was readily incorporated as a result of the propensity of **1** to afford alternating copolymers. Indeed, N_{AC} content reached 30.2 mol % already for $[N_{AC}]/[E] = 1$, as determined by ^1H and

Table 1. Selected Results and Conditions for Copolymerization of Ethylene with Norbornene Catalyst 1[a]

run[a]	p(E), bar	t, min	amt of N, mmol	[N]/[E]	yield, g	A[b]	T_m,[c] °C	T_g,[c] °C	amt of N,[d] mol %	% N_{conv}[d]	M_w, kg mol^{-1}	M_w/M_n
1	5	30	-	-	2.7	1543	127	-	-	-	17[e]	2.09[e]
2	5	30	15.3	0.5	1.15	656	-	68	33.6	50.1	63[f]	2.06[f]
3	5	5	15.3	0.5	0.60	2071	-	73	34.7	26.8	68.3	2.08
4	5	30	30.7	1	1.08	619	-	100	40.6	26.1	84.6[f]	2.06[f]
5	5	5	30.7	1	0.45	1550	-	102	41.5	11.0	91.4[f]	2.07[f]
6	5	30	46	1.5	0.63	359	-	110	42	10.3	99.6[f]	2.03[f]
7	5	30	61.3	2	0.9	514	-	117	45.1	11.1	121.6[f]	2.16[f]
8	5	30	92	3	0.41	231	-	121	45.4	3.4	126.3[f]	1.96[f]
9	20	30	-	-	5.1	2914	134	-	-	-	25.3[e]	2.06[e]
10	20	5	61.5	0.5	1.62	5554	-	74	41.7	19.8	79[f]	2.31[f]
11	20	30	123	1	7.4	4229	-	86	39.7	44	108.2[f]	1.96[f]
12	20	5	123	1	1.69	5794	-	94	36.6	9.3	109.9[f]	2.23[f]
13	20	30	245.3	2	0.65	371	-	120	44.8	2.1	162.5[f]	2.11[f]

[a] [Pd($\hat{P}$O)Me(dmso)] = 3.5 μmol in CH_2Cl_2 (2 mL); $V_{toluene}$ = 100 mL; T = 90 °C. [b] Activity in kg polymer * mol Pd^{1-} * h^{-1} [c] Determined by DSC. [d] Determined by ^{13}C NMR in $C_2D_2Cl_4$ at 103 °C with HMDS as reference. [e] Determined by SEC in o-$C_6H_4Cl_2$ with universal calibration. [f] Determined by SEC in o-$C_6H_4Cl_2$ with standard PS calibration.

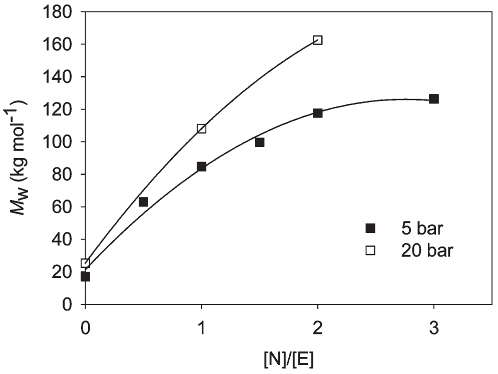


Figure 1. Plot of M_w of P(E-*co*-N) copolymers vs the [N]/[E] feed ratio in copolymerization at 5 and 20 bar.

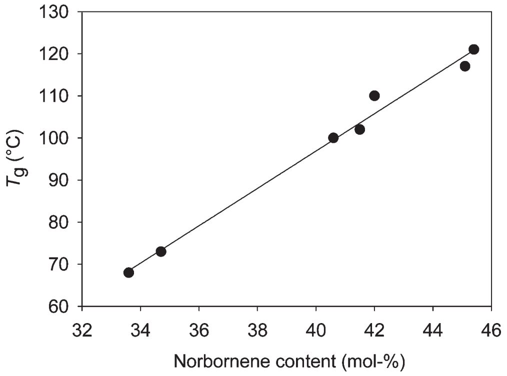


Figure 2. Plot of T_g vs the norbornene content for of P(E-*co*-N) copolymers prepared at 5 bar.

^{13}C NMR spectroscopy. The *endo*/*exo* ratio of incorporated N_{AC} reflected that of starting material.[17] This is in contrast to the marked preference for the *exo*-N_{AC} observed with other catalytic systems, attributed to both coordinating ability and steric encumbrance of endo isomers of functionalized norbornene derivatives.[18] Interestingly, molar masses were fairly high and M_w/M_n narrower than those of P(E-*co*-N) counterparts, suggesting that also coordination of carbonyl moiety of N_{AC} prevents to some extent chain transfer reaction. Surprisingly, despite the high N_{AC} content in copolymers, T_g values were not detected.

Conversely, catalyst tolerance toward N_{CH_2OH} was significantly reduced and activity for E-*co*-N_{CH_2OH} copolymerization drastically dropped. This suggests that Pd-R (R = growing chain) probably undergoes alcoholysis when exposed to the comonomer N_{CH_2OH}. Molar masses of P(E-*co*-N_{CH_2OH})s were lower than those of P(E-*co*-N_{AC})s. Nevertheless, incorporation resembles that of acetate counterpart (see entries 14 and 17), but exo isomer insertion is preferred.[17]

NMR Investigation and Determination of Reactivity Ratios of P(E-*co*-N). Assignments of ^{13}C NMR spectra of copolymers were made on the basis of our previous investigation of the microstructure of norbornene copolymers by ^{13}C NMR.[13a] The spectra show the typical pattern of alternating stereoirregular copolymers from an addition type copolymerization of N with cis *exo*—*exo* enchainment (see details in Supporting Information). Such a situation is frequently encountered with a variety of catalysts such as group III and IV half-sandwich catalysts.[14a−c] The dominant signals are those of alternating NENE sequences and of isolated N units present in ENEE sequences, with traces of NN diads. The relative peak intensities also revealed similar content of syndiotactic and isotactic NENE sequences that indicates atacticity.

A methodology to completely quantify tetrad and pentad sequence distributions from copolymer microstructure was achieved by our group.[15] Such analysis of copolymer microstructure can give insight into the copolymerization mechanism. It is known that when the insertion of a comonomer is influenced by the last inserted unit (ultimate effect) or by the penultimate unit, a first order or a second Markovian statistical model is adopted to determine the reactivity ratios.[15,19−22] In our studies on E-*co*-N copolymerization we have found that when hindered monomers such as norbornene are involved, second order models are often needed to describe the copolymerization.

Table 2. Conditions and Results for the Copolymerization of Ethylene with Functionalized Norbornene Derivatives[a]

run[a]	p(E), bar	t, min	N_X, mmol		$[N_X]/[E]$	yield, g	A[b]	T_m,[c] °C	T_g,[c] °C	amt of N_X,[d] mol %	% N_{conv}[d]	M_w[e] kg mol^{-1}	M_w/M_n[e]
14	5	30	N_{AC}	15.33	0.5	2.44	1394	n.o.	n.o.	22.2	63.6	42.2	1.61
15	5	30	N_{AC}	30.67	1	1.83	1046	n.o.	n.o.	30.2	27.5	62.1	1.68
16	5	30	N_{CH_2OH}	3.07	0.1	0.25	143	112	-	12.3[f]	25.2[f]	13.8	1.42
17	5	60	N_{CH_2OH}	15.33	0.5	0.10	29	-	80	22.4[f]	3.0[f]	18.5	2.50

[a] $[Pd(\hat{P}O)Me(dmso)] = 3.5\ \mu$mol in CH_2Cl_2 (2 mL); $V_{toluene} = 100$ mL; $T = 90$ °C. [b] Activity in kg polymer * mol Pd^{1-} * h^{-1} [c] Determined by DSC; n.o. stands for not observed. [d] Determined by ^{1}H NMR in $C_2D_2Cl_4$ at 103 °C with HMDS as reference. [e] Determined by SEC in $CHCl_3$ with standard PS calibration. [f] Determined by ^{13}C NMR in $C_2D_2Cl_4$ at 103 °C with HMDS as reference.

Table 3. Reactivity Ratios of E-N Copolymerizations with Catalyst 1 Calculated Using First and Second Order Markovian Models from Tetrad Distribution

run	P_E	[N]/[E]	amt of N, mol %[a]	r_1	r_2	r_{11}	r_{12}	r_{21}	r_{22}
5	5	1	42.4	0.39	0.03	0.26	0.03	0.41	0.00
7	5	2	43.8	0.65	0.05	1.40	0.05	0.59	0.00
13	20	2	44.3	0.56	0.02	0.80	0.02	0.55	0.00

[a] Determined from tetrads.

From the first Markovian model, the r_1 ($=k_{11}/k_{12}$) and r_2 ($=k_{22}/k_{21}$) reactivity ratios are derived, where k_{ij} is the rate constant of the reaction for the addition of the monomer j to a growing chain bearing the comonomer i as the last inserted unit. Here, 1 and 2 indicate ethylene and norbornene, respectively.

When the second-order Markov statistical model is needed to describe the copolymerization, four reactivity ratios are defined:

$$r_{11} = k_{111}/k_{112} = k_{EEE}/k_{EEN} \quad \text{and} \quad r_{22} = k_{222}/k_{221} = k_{NNN}/k_{NNE}$$

$$r_{21} = k_{211}/k_{212} = k_{NEE}/k_{NEN} \quad \text{and} \quad r_{12} = k_{122}/k_{121} = k_{ENN}/k_{ENE}$$

where k_{lmn} represents the rate constant for the insertion of monomer n into an lm-Metal ended chain.

Both first and second statistical models were applied to fit the experimental tetrad distributions of copolymers synthesized by **1**. The reactivity ratios regarding three representative samples are summarized in Table 3. Sample 5 was produced at [N]/[E] = 1, while samples 7 and 13 were produced at [N]/[E] = 2 at 5 and 20 bar, respectively.

The effect of pressure on norbornene content is reflected by the copolymerization parameters, though reactivity ratios and r_1r_2 for this catalytic system are quite similar at different conditions. It is worth noting that r_1 values are well below 1, to our knowledge the lowest observed so far, and thus, r_2 values around 0 are not much lower than r_1, as it was in the case of other E−N copolymerizations. The small differences in r_1, r_2 and r_{11}, r_{21} values are significant. These data confirm that norbornene insertions are not much less favored than ethylene insertions and that E-N copolymerizations with this catalyst have a strong tendency to alternation especially at high pressure. The similarity between r_1 and r_{21} and r_2 and r_{12} values is already indicative of validity of first order Markov statistics for these copolymerizations.

We used the tetrad description of the microstructure of these alternating copolymers to understand and visualize differences. The main features of the copolymers prepared at two pressures are evident in Figure 3, where the NMR-measured tetrad distributions obtained by the complete analysis of the spectra with our methodology[15] were compared with those calculated according to first- and second-order Markovian models. One representative copolymer sample produced at p(E) of 5 bar and one produced at p(E) of 20 bar, at [N]/[E] = 2, were selected for such a comparison. Samples 7 and 13 contained 43.8 mol % and 44.3 mol % of norbornene incorporated, respectively. The copolymer prepared at 20 bar is more alternating than the one prepared at 5 bar: the greatest difference was in NENE molar fractions, NENE being 0.65 and 0.56 at 20 and 5 bar, respectively. Another significant difference is in the lower NNEN and ENNE molar fraction in copolymer obtained at higher pressure. The second order Markov fitting was slightly better, however the first order Markov statistics seemed to be sufficient to describe these copolymerizations.

Chain Termination Analysis of PE and P(E-*co*-N). Investigation of the olefinic region in ^{1}H NMR spectra allows to determine preferred termination pathways in (co)polymerization.[23−26] Figure 4 displays the olefinic region of ^{1}H NMR spectra of PE prepared at 5 bar and at 20 bar (Figure 4a and 4b, respectively), and of P(E-*co*-N) prepared at 5 bar and [N]/[E] = 1 and 3 (Figure 4c and 4d, respectively).

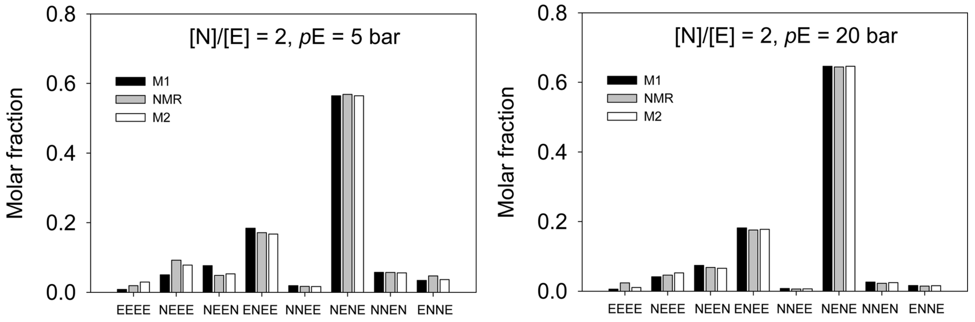


Figure 3. Experimental and calculated tetrad distribution for E−N copolymer samples prepared with catalyst **1** at feed ratio 2 and at p(E) of 5 bar (run 7) and at p(E) of 20 bar (run 13). Key: gray, experimental data obtained from NMR; black, according to model M1; white, according to model M2.

As far as ethylene homopolymerization is concerned (Figure 4, parts a and b) either resonances of terminal and internal double bonds appear. Vinyl end groups generate the typical pattern constituted by a tdd (J_{trans} = 17.1 Hz, J_{cis} = 10.3 Hz, J = 6.9 Hz) centered at 5.97 ppm and two different doublets centered at 5.18 ppm (J_{trans} = 17.1 Hz) and 5.12 ppm (J_{cis} = 10.3 Hz), respectively. Trans and cis internal olefins generate a broad multiplet centered at 5.61 ppm. The intensity of this signal decreases with increasing polymerization pressure in line with results recently reported by Jordan et al.[8a] Specifically, the ratio of internal/terminal olefin decreases from 0.5 to 0.07 for $p(C_2H_4)$ = 5 and 20 bar, respectively. This reflects the experimental evidence that increasing pressure results in decreasing methyl branch formation. In any case, β-H elimination appears to be the dominant termination pathway for both linear or branched Pd−polymeryl bonds.

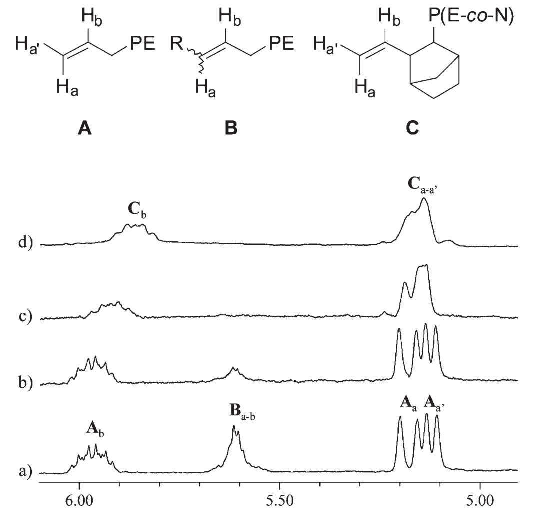


Figure 4. Olefinic region of ^{1}H NMR spectra recorded in toluene-d_8 at 103 °C: PE prepared at 5 bar (a), PE prepared at 20 bar (b), P(E-*co*-N) prepared at 5 bar and [N]/[E] = 1 (c), and P(E-*co*-N) prepared at 5 bar and [N]/[E] = 3 (d).

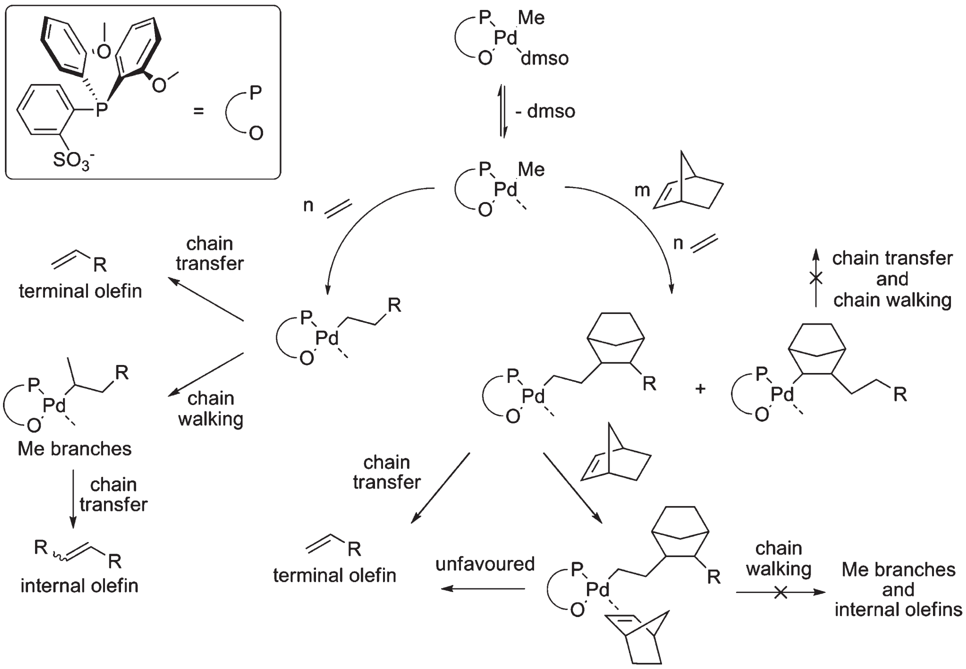
In contrast, the proton spectra of E-*co*-N copolymers reveal a simpler situation even when copolymers are synthesized at low pressure (Figure 4, parts c and d). Only a ddd centered at 5.91 ppm (J_{trans} = 13.8 Hz, J_{cis} = 10.2 Hz, J = 5.8 Hz) assigned to the hydrogen in α to norbornene and a broad signal for the other two *gem*-hydrogens centered at 5.21 ppm are visible. Thus, end groups appear to be essentially terminal vinyl groups bonded to the inserted norbornene unit. This results from the strong tendency of the catalyst to afford alternating copolymers and confirms the suppression of branch formation.

In conclusion, the polymerization mechanism depicted in Scheme 2 is consistent with our observations. The coordination of norbornene, a π donor stronger than ethylene, limits β-H elimination and thus both chain walking and chain termination in accord with experimental evidence of higher molar masses at higher N concentration.

■ CONCLUSIONS

In summary, copolymerization of ethylene with norbornene by the well-defined neutral aryl phosphine sulfonate palladium catalyst **1**, having dmso as labile ligand, is reported. Excellent activity as well as strong intrinsic tendency to afford alternating copolymerization is demonstrated on the basis of microstructural analysis and reactivity ratios. With respect to previous reports on copolymerization of ethylene with norbornene with similar catalysts based on P∼SO_3/Pd scaffold reported by Drent,[6] the use of the well-defined catalyst rather than the in situ generated one[7] leads to higher activity and a better control of copolymerization in terms of norbornene incorporation. This allowed us to have a detailed and accurate characterization of the copolymers and understanding of these copolymerizations. The more labile dmso with respect to the pyridine in Claverie catalyst,[8c] due the

Scheme 2. Mechanism for (Co)polymerization and Branch Formation with 1



more facile activation, leads to higher activities in E-*co*-N copolymerization, in line with results in ethylene and acrylate polymerization.[9]

Effect of pressure and feed ratio on microstructure and molar masses has been discussed. Interestingly, the molar mass values of copolymers are significantly higher than PE molar masses. They increase with N concentration and reach values that are interesting for industrial applications. Such an increase along with the presence of only terminal vinyl groups in ^{1}H NMR spectra of copolymers reveal that norbornene limits β-H elimination and thus both chain walking and chain termination, due to a relatively strong coordination to the active sites. In addition, copolymers with high content of functionalized norbornene derivatives and with high molar masses were prepared and characterized. In the case of 5-norbornene-2-yl acetate, activity resembles that of ethylene-*co*-norbornene copolymerization.

EXPERIMENTAL SECTION

Materials. All experiments were performed under nitrogen by glovebox or standard Schlenk techniques. Complex $[Pd(\kappa^2\text{-}P,O\text{-}\{2\text{-}(2\text{-}MeOC_6H_4)_2P\}C_6H_4SO_3)Me(dmso)]$ (**1**) was kindly donated by Prof. Mecking of Konstanz University. Ethylene was purified by passage over columns of $CaCl_2$, molecular sieves, and BTS catalysts. Toluene was distilled from sodium. Norbornene was distilled from sodium and used as stock solution in toluene. 5-norbornene-2-methanol (N_{CH_2OH}) and 5-Norbornen-2-yl-acetate (N_{AC}) were purchased from Aldrich and distilled over molecular sieves. The *endo*/*exo* isomer composition of monomers N_{CH_2OH} and N_{AC} determined by ^{13}C NMR was in both cases *endo*/*exo* = 4/1. Toluene-d_8 and $C_2D_2Cl_4$ were purchased from Cambridge Isotope Laboratories and used as received.

General Polymerization Procedure. Polymerizations were carried out in a stainless steel 250 mL pressure reactor, mechanically stirred and equipped with a heating/cooling jacket, a pressure transducer, and a mass flow meter to monitor ethylene consumption. Prior to starting polymerization, the reactor was heated to 90 °C under vacuum for 1 h and backfilled with nitrogen. In glovebox a Schlenk tube was charged with complex **1** dissolved in CH_2Cl_2 and stored at −20 °C. The reactor was charged at room temperature with toluene and the opportune amount of comonomer (N, N_{AC}, or N_{CH_2OH}). After thermal equilibration at 90 °C, ethylene was added until saturation. Catalyst solution was charged in the injector via syringe. The injector was overpressurized by nitrogen and the solution was injected into the reactor. The reaction was quenched by addition of MeOH and the polymer was precipitated in MeOH, collected by filtration, and dried in a vacuum overnight.

Polymer Characterization. NMR spectra were recorded on a Bruker NMR advance 400 Spectrometer operating at 400 MHz (^{1}H) and 100.58 MHz (^{13}C) working in the PFT mode at 103 °C. ^{13}C experiments were performed with 10 mm probe in $C_2D_2Cl_4$ and referred to hexamethyldisiloxane (HMDS). ^{1}H experiments were performed with 5 mm probe in toluene-d_8 and referred to internal solvent resonances.

DSC measurements were performed on a Pyris 1 Perkin-Elmer instrument. Samples were heated from 50 to 250 at 20 °C min^{-1}, with a nitrogen flow (30 mL min^{-1}). Alternatively, low cycloolefin content samples were heated from -50 to 250 °C.

Molar masses and molar mass distributions (M_w/M_n) were determined by a GPCV2000 high temperature size exclusion chromatography (SEC) system from Waters (Millford, MA) equipped with two online detectors: a viscometer (DV) and a differential refractometer (DRI). The column set was composed of three mixed TSK-Gel GMHXL-XT columns from Tosohaas. The universal calibration was constructed from 18 narrow M_w/M_n polystyrene standards, with the molar mass ranging from 162 to 5.48×10^6 g mol^{-1}. Measurements of PE and P(E-*co*-N) samples were performed in *o*-dichlorobenzene at 145 °C, whereas P(E-*co*-N_{AC}) and P(E-*co*-N_{CH_2OH}) samples were tested in $CHCl_3$ at 35 °C.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Examples of SEC profiles, ^{13}C NMR spectra, and DSC thermograms of copolymers. This material is free of charge via the Internet at http://pubs.acs.org

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REFERENCES

(1) (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed.* **1995**, *34*, 1143–1170. (b) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223–1252. (c) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253–1346. (d) Angermund, K.; Fink, G.; Jensen, V. R.; Kleinschmidt, R. *Chem. Rev.* **2000**, *100*, 1457–1470. (e) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283–315.

(2) (a) Boffa, L. S.; Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479–1494. (b) Nakamura, A.; Ito, S.; Nozaki, K. *Chem. Rev.* **2009**, *109*, 5215–5244.

(3) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169–1204.

(4) (a) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267–268. (b) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888–899.

(5) Luo, S.; Jordan, R. F. *J. Am. Chem. Soc.* **2006**, *128*, 12072–12073.

(6) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 744.

(7) (a) Kochi, T.; Yoshimura, K.; Nozaki, K. *Dalton Trans.* **2006**, 25–27. (b) Skupov, K. M.; Marella, P. M.; Hobbs, J. L.; McIntosh, L. H.; Goodall, B. L.; Claverie, J. P. *Macromolecules* **2006**, *39*, 4279–4281. (c) Liu, S.; Borkar, S.; Newsham, D.; Yennawar, H.; Sen, A. *Organometallics* **2007**, *26*, 210–216. (d) Skupov, K. M.; Hobbs, J. L.; Claverie, J. P. *Prog. Org. Coat.* **2009**, *65*, 314–321.

(8) (a) Vela, J.; Lief, G. R.; Shen, Z.; Jordan, R. F. *Organometallics* **2007**, *26*, 6624–6635. (b) Kochi, T.; Noda, S.; Yoshimura, K.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 8948–8949. (c) Skupov, K. M.; Marella, P. R.; Sismard, M.; Yap, G. P. A.; Allen, N.; Conner, D.; Goodall, B. L.; Claverie, J. P. *Macromol. Rapid Commun.* **2007**, *28*, 2033. (d) Nowack, R. J.; Hearley, A. K.; Rieger, B. *Z. Anorg. Allg. Chem.* **2005**, *631*, 2775. Newsham, D. K.; Borkar, S.; Sen, A.; Conner, D. M.; Goodall, B. L. *Organometallics* **2007**, *26*, 3636–3638.

(9) Guironnet, D.; Roesle, P.; Rünzi, T.; Göttker-Schnetmann, I.; Mecking, S. *J. Am. Chem. Soc.* **2009**, *131*, 422–423.

(10) Bouilhac, C.; Rünzi, T.; Mecking, S. *Macromolecules* **2010**, *43*, 3589–3590.

(11) Rünzi, T.; Fröhlich, D.; Mecking, S. *J. Am. Chem. Soc.* **2010**, *132*, 17690–17691.

(12) (a) Kaminsky, W.; Bark, A.; Arndt, M. *Macromol. Chem. Macromol. Symp.* **1991**, *47*, 83–93. (b) Cherdron, H.; Brekner, M.-J.; Osan, F. *Angew. Makromol. Chem.* **1994**, *223*, 121–133. (c) Arndt, M.;

Kaminsky, W. *Macromol. Symp.* **1995**, *97*, 225–246.(d) Kaminsky, W.; Arndt-Rosenau, M. In *Metallocene-based Polyolefins*; Scheirs, J., Kaminsky, W., Eds.; Wiley: Chichester, U.K., 2000; p 89 and references therein. (e) Ruchatz, D.; Fink, G. *Macromolecules* **1998**, *31*, 4674–4680. (f) Arndt-Rosenau, M.; Beulich, I. *Macromolecules* **1999**, *32*, 7335–7343. (g) Arndt, M.; Beulich, I. *Macromol. Chem. Phys.* **1998**, *199*, 1221–1228. (h) Herfert, N.; Montag, P.; Fink, G. *Makromol. Chem.* **2001**, *94*, 3167–3182. (i) McKnight, L. A.; Waymouth, M. R. *Macromolecules* **1999**, *32*, 2816–2825. (l) Tritto, I.; Boggioni, L.; Sacchi, M. C.; Locatelli, P. *J. Mol. Catalysis A: Chem.* **1998**, *133*, 139–150. (m) Provasoli, A.; Ferro, D. R.; Tritto, I.; Boggioni, L. *Macromolecules* **1999**, *32*, 6697–6706. (n) Tritto, I.; Marestin, C.; Boggioni, L.; Zetta, L.; Provasoli, A.; Ferro, D. R. *Macromolecules* **2000**, *33*, 8931–8944. (o) Tritto, I.; Marestin, C.; Boggioni, L.; Brintzinger, H. H.; Ferro, D. R. *Macromolecules* **2001**, *34*, 5770–5777. (p) Thorshaug, K.; Mendichi, R.; Tritto, I.; Trinkle, S.; Friedrich, C.; Mülhaupt, R. *Macromolecules* **2002**, *35*, 2903–2911. (q) Tritto, I.; Boggioni, L.; Ferro, D. R. *Macromolecules* **2004**, *37*, 9681–9693. (r) Tritto, I.; Boggioni, L.; Zampa, C.; Ferro, D. R. *Macromolecules* **2005**, *38*, 9910–9919.

(13) For reviews see:(a) Tritto, I.; Boggioni, L.; Ferro, D. R. *Coord. Chem. Rev.* **2006**, *250*, 212–241. (b) Li, X.; Hou, Z. *Coord. Chem. Rev.* **2008**, *252*, 1842–1869.

(14) Recent progress:(a) Li, X.; Baldamus, J.; Hou, Z. *Angew. Chem., Int. Ed.* **2005**, *44*, 962–965. (b) Ravasio, A.; Zampa, C.; Boggioni, L.; Tritto, I.; Hitzbleck, J.; Okuda, J. *Macromolecules* **2008**, *41*, 9565–9569. (c) Marconi, R.; Ravasio, A.; Boggioni, L.; Tritto, I. *Macromol. Rapid Commun.* **2009**, *30*, 39–44. (d) Terao, H.; Iwashita, A.; Ishii, S.; Tanaka, H.; Yoshida, Y.; Mitani, M.; Fujita, T. *Macromolecules* **2009**, *42*, 4359–4361. (e) He, L. P.; Liu, J. L.; Li, Y. G.; Liu, S. R.; Li, Y. S. *Macromolecules* **2009**, *42*, 8566–8570. (f) Yang, X. H.; Wang, Z.; Sun, X. L.; Tang, Y. *Dalton Trans.* **2009**, 8945–8954. (g) Wang, B.; Tang, T.; Li, Y.; Cui, D. *Dalton Trans.* **2009**, 8963–8969. (h) Lin, Y. C.; Yu, K. H.; Huang, S. L.; Liu, Y. H.; Wang, Y.; Liu, S. T.; Chen, J. T. *Dalton Trans.* **2009**, 9058–9067. (i) Ravasio, A.; Boggioni, L.; Tritto, I.; D'Arrigo, C.; Perico, A.; Hitzbleck, J.; Okuda, J. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 5709–5719. (l) Tritto, I.; Ravasio, A.; Boggioni, L.; Bertini, F.; Hitzbleck, J.; Okuda, J. *Macromol. Chem. Phys.* **2010**, *211*, 897–904. (m) Chen, Y.; Mandal, S.; Sen, A. *Organometallics* **2010**, *29*, 3160–3168.

(15) Tritto, I.; Boggioni, L.; Jansen, J. C.; Thorshaug, K.; Sacchi, M. C.; Ferro, D. R. *Macromolecules* **2002**, *35*, 616–623.

(16) Noda, S.; Nakamura, A.; Kochi, T.; Chung, L. W.; Morokuma, K.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 14088–14100.

(17) The isomer composition of monomers 5-norbornen-2-yl-acetate (N_{AC}) and 5-norbornene-2-methanol (N_{CH_2OH}), determined by ^{13}C NMR, is in both cases *endo*/*exo* = 4/1. The *endo*/*exo* copolymer composition was calculated for the E-*co*-N_{AC} copolymers from the areas of signals of the *endo*-C═O (8*n*, 168.7 ppm) and *exo*-C═O (8*x*, 168.4 ppm) and signals of *exo*-CHOAc (9*x*, 76.1 ppm) and *endo*-CHOAc (9*n*, 73.7 ppm). The average *endo*/*exo* ratio from these signals is 4.5 which reflects the starting isomer mixture composition. Similarly, E-*co*-N_{CH_2OH} copolymers *endo*/*exo* composition was evaluated from the area of signals of the carbon atom linked to OH group (8*x* and 8*n*). In this case *endo*/*exo* ratio is 1.3, lower than in starting material. See Supporting Information for details.

(18) (a) Breunig, S.; Risse, W. *Makromol. Chem. Rapid Commun.* **1992**, *13*, 455. (b) Mathew, J. P.; Reinmuth, A.; Melia, J.; Swords, N.; Risse, W. *Macromolecules* **1996**, *29*, 2755. (c) Funk, J. K.; Andes, C. E.; Sen, A. *Organometallics* **2004**, *23*, 1680–1683.

(19) (a) Hamm, G. E. In *Copolymerization*; Hamm, G. E., Ed.; Wiley Interscience: New York, 1964. (b) Odian, G. *Principles of Polymerization*, 3rd ed.; Wiley & Sons: New York, 1991; p 455—458.

(20) Karssenberg, F. G.; Piel, C.; Hopf, A.; Mathot, V. B. F.; Kaminsky, W. *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *44*, 747–755.

(21) Karssenberg, F. G.; Wang, B.; Friederichs, N.; Mathot, V. B. F. *Macromol. Chem. Phys.* **2005**, *206*, 1675–1683.

(22) Herfert, N.; Montag, P.; Fink, G. *Makromol. Chem.* **1993**, *194*, 3167–3182.

(23) Carvill, A.; Tritto, I.; Locatelli, P.; Sacchi, M. C. *Macromolecules* **1997**, *30*, 7056–7062.

(24) Resconi, L.; Camurati, I.; Sudmeijer, O. *Top. Catal.* **1999**, *7*, 145–163.

(25) Busico, V.; Cipullo, R.; Friederichs, N.; Linssen, H.; Segre, A.; Castelli, V. V. A.; van der Velden, G. *Macromolecules* **2005**, *38*, 6988–6996.

(26) Marconi, R.; Boggioni, L.; Ravasio, A.; Di Colo, F.; Tritto, I.; Stehling, U. M. *Macromolecules* **2011**, *44*, 795–804.