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2-Phosphinophenolate Nickel Catalysts: Formation of Ethylene Copolymers with Isolated *sec*-Alkyl, Aryl, and Functionally Substituted Alkyl Groups†

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ABSTRACT: The 2-phosphinophenolate nickel catalyzed oligo- or polymerization of ethylene in the presence of olefins usually leads to improved conversion or copolymerization. The outcome depends strongly on the nature of the P-substituents and olefins. The diphenylphosphinophenolate ligand (PPHH) favors improved yields of waxy linear ethylene oligomers, whereas the more P-basic dicyclohexylphosphinophenolate (CCHH) induces incorporation of alkyl-, aryl-, and ester-substituted α-olefins into a growing ethylene polymer chain and larger molar masses of the polymers. Depending on the nature of the olefin, the reaction rate and the conversion are lowered by olefin incorporation. Ester groups are tolerated if distant to the C=C bond but block the catalyst if close to the olefinic group. A remarkable increase of activity accompanied by small branching was observed in the copolymerization with ethyl undecenoate by the nickel diphenylphosphinophenolate catalyst. ^{13}C and ^{1}H NMR spectra give evidence that ethylene copolymers with isolated side groups, imbedded into linear polyethylene blocks with vinyl end groups, are formed.

Introduction

The first P⌒O⁻-nickel chelate catalysts for oligo- and polymerization of ethylene were discovered three decades ago by Keim and co-workers[1] and received considerable industrial importance as part of the Shell higher olefin process.[2] This inspired extensive studies on various types of nickel catalysts with O-functional phosphine ligands[2,3] such as phosphinoalkanoates and 2-phosphinoenolates,[4,5] -phenolates,[6,7] -benzoates,[8] and -benzenesulfonates,[9] but also various other chelate ligands.[10] These catalysts are more or less moisture tolerant, and the sulfonated species are even applicable in suspension polymerization.[5] This raises the question for the applicability in copolymerizations of ethylene with a variety of functionally substituted comonomers. Early examples for P⌒O⁻ nickel catalyzed copolymerizations of ethylene with some α-olefins and functionalized olefins were recorded for 2-diphenylphosphinoenolate[11] and triphenylphosphonioenolate P-ylide ligands.[3c] A more bulky disubstituted 2-diphenylphosphinoenolate nickel complex[12] and cationic diimine nickel polymerization catalysts[13] allowed even the incorporation of methyl methacrylate as an end group of polyethylene.

During our studies on tuning of 2-phosphinophenolate nickel catalysts for oligo- or polymerization of ethylene, we observed improved catalyst stability and ethylene conversion if olefins were added.[7] A closer study showed slight to substantial incorporation of linear α-olefins if these were added as comonomers. The amount of incorporation depends on the size of the α-olefin, the molar ratio of the α-olefins to ethylene and the P-basicity of the ligand.[14] While olefin incorporation is much lower than that with conventional transition metal/organoaluminum catalysts, the products might be of interest due to their particular microstructure. Because the P⌒O⁻ nickel catalysts are unable to homopolymerize α-olefins, the products are not usual random copolymers with compositions governed by the reactivity ratios and monomer concentrations but are copolymers with isolated side chains, separated by polyethylene blocks. Here we investigate the question whether polyethylenes with isolated branched alkyl, aryl or functional groups can be obtained by incorporation of branched 1-alkenes, internal alkenes, aryl-, ester-, and OH-functionally substituted olefins into the growing polyethylene chains.

Results and Discussion

Catalyst System and General Remarks. Equimolar amounts of 2-diphenylphosphinophenol (**PPHH**) (Chart 1) and Ni(COD)$_2$ form ethylene polymerization catalysts at temperatures ranging from 70 to 100 °C, whereas dicyclohexylphosphinophenol (**CCHH**) requires 100−120 °C, as reported for the respective methylallylnickel phosphinophenolate precursor complexes.[7b] The average temperature (100 °C) was selected as the usual working temperature to compare the results with the two catalysts. The tests were performed as batch reactions with catalyst formation during heating up the precatalyst solution in the presence of ethylene. The ethylene consumption was monitored by observing the pressure decrease versus the time. With both catalysts, **PPHH/Ni** and **CCHH/Ni**, in the absence of stabilizing additives the reaction slows or ceases after some time without complete conversion of ethylene (Table 1, entries 1 and 2). A slight excess of the P,O ligand relative to nickel stabilizes the catalyst and improves the conversion while the molecular weights of the product are lowered. The same effect is observed if DMF or THF are used

†Dedicated to Prof. Dr. mult. h.c. Wilhelm Keim on the occasion of his 75th birthday.

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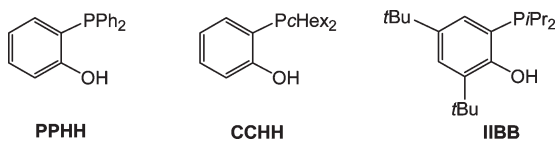
Chart 1. 2-Phosphinophenols Used as Ligands



as solvent.[7b] The presence of THF and 1-hexene blocked the catalyst (entry 3) so that toluene olefin mixtures or neat olefins were used as solvents in this study.

Table 1 compiles the results of ethylene polymerization in the presence of various olefins induced by the nickel 2-phosphinophenolate catalysts. The olefins were found to play a dual role—they may behave simply as π-bases and also as reactants. The behavior ranges from mere stabilization of the catalyst in ethylene oligo- or polymerization, usually combined with decreased reaction rates and molar masses, to inclusion of the comonomer into linear polymers.

Ethylene/Alkene Systems. Our earlier attempts at copolymerization of ethylene with linear α-olefins by **PPHH/Ni** and **CCHH/Ni** catalysts had shown that **PPHH/Ni** in almost all cases led to improved ethylene conversion but low olefin inclusion, whereas the **CCHH/Ni** catalyst allowed incorporation of linear α-olefins with amounts depending on the concentration and size of the olefin at lower reaction rate.[14] Whether the more bulky branched 1-olefins can also be incorporated has not yet been explored. Because ethylene/4-methyl-1-pentene copolymers are important materials with better mechanical properties and processability than ethylene/1-butylene copolymers[15] the copolymerization of ethylene and 4-methyl-1-pentene (4M1P) was tested with the two model phosphinophenolate nickel catalysts. The pressure time curves of the batch conversions with the **PPHH/Ni** catalyst indicate a similar fast initial reaction as in the absence of the comonomer (Figure 1, c vs a) and a moderate improvement of the catalyst lifetime and ethylene conversion. However, the product displays a very low molar mass and low 4M1P incorporation of ca. 1 mol %, indicated by proton NMR signals of isobutyl groups (Table 1, entry 4). The catalyst **CCHH/Ni** behaves quite differently with respect to the reaction rate and amount of comonomer incorporation. The large decrease of the ethylene consumption rate in the presence of 4M1P (Figure 2, d vs b) suggests that the increased P-basicity strengthens the coordination of this comonomer relative to ethylene, accompanied by slow insertion into the polymer chain. The molecular weight decreased relative to the homopolymer but is with M_w = 29200 g/mol still much higher than that for polymers obtained with **PPHH**-based nickel catalysts. The molecular weight distribution remains unchanged and is still narrow (M_w/M_n=2.3). The density is similar to the respective LLDPE prepared with traditional Ziegler−Natta or metallocene/MAO catalysts despite the fact that the latter incorporated much more 4-methyl-1-pentene and possess a different microstructure with higher molecular weights.[15] The polymers obtained with the phosphinophenolate nickel catalysts show in the ^{1}H NMR spectra isobutyl side group signals at 1.10 (d, Me), 1.36 (t, CH_2), and 1.82 ppm (m, CH), partly superimposing signals of PE, and integration reveals for **CCHH/Ni** a branching degree of about 13 side chains per main chain, corresponding to ca. 4 wt % or 1.3 mol % (Table 1, entry 5). Compared to the incorporation of the linear isomer 1-hexene (ca. 15 wt %[14]) in the copolymer with the same catalyst, conditions and the olefin as solvent, the uptake of the branched α-olefin is much smaller. The ^{1}H NMR spectra show further that the dominant end groups

Table 1. Nickel 2-Phosphinophenolate Catalyzed Polymerization of Ethylene in the Presence of Substituted Olefins

entry	ethylene (g, mmol); comonomer (g, mmol); solvent (mL)	ligand, Ni (μmol); P_{start} (bar), T (°C), t (h)	product (g); C_2H_4 conversion (%); TON (mol/mol)	Mp (°C); D (g/cm^3)	M_w, M_n (g/mol), M_w/M_n; M_{NMR} (g/mol)	α/internal olefins (mol/mol)	Me/C=C; comonomer incorp. (mol %)
1[7b]	12.6, 448; no; toluene 20	PPHH 100; 43, 100, 15	8.3; 66; 2960	124−126; 0.960	n.d.; 2000	93:7	1.3; 0
2[7b]	15.3, 544; no; toluene 20	CCHH 100; 50, 100, 15;	11.0; 72; 3920	134−136; 0.950	59000, 26500, 2.2;	87:13	1.4−2; 0
3	15.7, 560; 1-hexene 6.7, 80; THF 10	CCHH 100; 50, 100, 15	0.7; 4.5; 300	125−127;			
4	11.1, 395; 4-methyl-1-pentene 6.7, 80; toluene 10	PPHH 100; 58, 100, 15	8.0; 71; 2816	116−118; 0.945	1100, 400, 2.8;	82:18	2.2; 1.0
5	12.9, 459; 4-methyl-1-pentene 6.7, 80; toluene 10	CCHH 110; 41, 100, 15	11.1; 83; 3520	128−130; 0.91	29200, 12890, 2.3;	78:22	13.9; 1.3
6	10.7, 381; *trans*-2-hexene 6.7, 80; toluene 10	PPHH 100; 40, 100, 15	9.5; 88; 3380	116−118; 0.935	1700, 600, 2.8;	84:16	2.0; <0.5
7	10.9, 388; *trans*-2-hexene 6.7, 80; toluene 15	CCHH 105; 32, 100, 15	6.4; 58; 2160	129−131; 0.940	30900, 11000, 2.8;	91:9	3; 0.2
8	11.7, 416; cyclohexene 16.2, 198; no solvent	PPHH 105; 42; 100; 16	7.1, 59; 2390	124−126, 0.955	6900, 4000, 1.7;	93:7	1.4; ca. 0
9	13.4, 477; cyclohexene 16.2, 198; no solvent	CCHH 100; 42, 100, 16	5.5; 41; 1770	130−133, 0.951	20900, 4400, 4.8;	89:11	1.5; 0.08
10	11.7, 417; 1,5-COD 0.88, 8.2; toluene 19	PPHH 100; 40; 110; 14	10.9; 93; 4180	120−123, 0.955	n.d.; 2030	88:12	1.5; ca. 0
11	9.5, 338; styrene 9.1, 87.3; toluene 10	PPHH 100; 38, 100, 15	11.3; 99; 3770	106−108; 0.965	1200, 500, 2.4;	94:6	1.4; 3.4
12	8.2, 292; styrene 9.1, 87.3; toluene 10	CCHH 110; 31, 100, 15	7.5; 66; 1990	124−126; 0.945	7700, 3500, 2.2;		1.3; 2.6
13	9.9, 352; allylbenzene 4.5, 37.7; toluene 15	PPHH 100; 40, 100, 15	6.8; 67; 2390	116−119 0.930	n.d.; 1100	91:9	1.5; 0.9
14	9.5, 338; allylbenzene 4.5, 37.7; toluene 15	CCHH 120; 40, 100, 16	4.8; 48; 1640	124−126; 0.925	24900, 10600, 2.3;	88:12	1.3; 0.8
15[7b]	12.7, 453; ethyl oleate 4.4, 14.0; toluene 15	PPHH 100; 45, 100, 15	11.0; 87; 3960	117−119; n.d.	3840, 1900, 2.0;		
16	9.3, 331; ethyl undecenoate 17.6, 83; no solvent	PPHH 120; 41, 100, 15	9.2; 88; 2430	121−123; 0.952	3000, 1200, 2.5;	84:16	5.5; 1.5
17	9.7, 345; ethyl undecenoate 17.6, 83; no solvent	CCHH 100; 43, 100, 17	4.6; 46; 1590	123−125; 0.954	26100, 6950, 3.8;	71:29	n.d.; 2.9
18	11.4, 407; 9-decen-1-ol 4.4, 28.1; toluene 15	PPHH 110; 45; 100; 15	9.8; 86; 2900	111−114, 0.950	1300, 700, 1.9;	88:12	1.3; 0.9
19	9.3; 332; 9-decen-1-ol 8.8, 56.2; toluene 10	CCHH 100; 43; 100; 15	4.0; 93; 1890	124−127, 0.925	16200, 4300, 3.8;	94:6	1.4; 0.8
20	10.7; 382; 9-decen-1-ol 4.4, 28.1; toluene 15	IIBB 100; 43; 100; 15	5.1; 48; 1630	126−129, 0.920	n.d.; 9600	80:20	1.4; 0.9

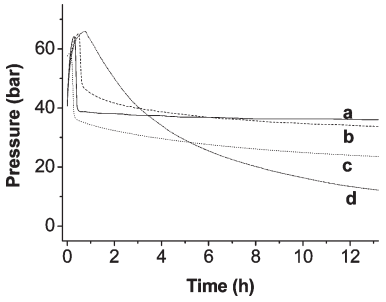


Figure 1. Pressure−time plots of the batch-(co)polymerization: (a) ethylene by **PPHH**/**Ni**; (b) ethylene by **CCHH**/**Ni**; (c) ethylene/4-methyl-1-pentene by **PPHH**/**Ni**; (d) ethylene/4-methyl-1-pentene by **CCHH**/**Ni**; each at 100 °C, solvent toluene.

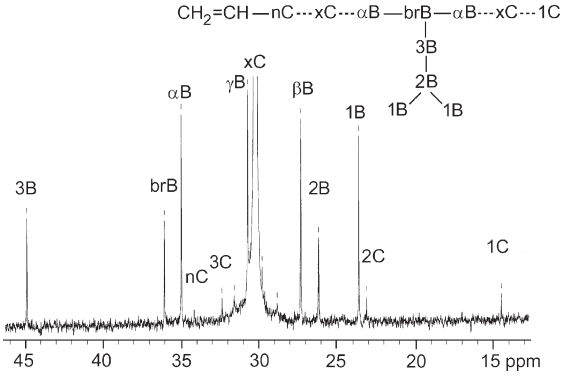


Figure 2. ^{13}C NMR (C_6D_5Br) spectrum of ethylene/4-methyl-1-pentene copolymer, prepared with catalyst **CCHH**/**Ni** (nomenclature of Usami and Takayama used for isolated branches[16]).

of the ethylene-4M1P copolymers obtained with **PPHH/Ni** or **CCHH/Ni** catalysts are methyl and vinyl groups. Trace signals at 2.40 (m) and 2.08 (t) ppm, respectively, by integration compatible with the content of internal olefins, are assigned to minor $Me_2CHCH{=}CH{-}CH_2{-}$ and $Me_2CHCH_2CH{=}CH{-}$ end groups (ca. 1:1). They indicate slightly favored chain termination after insertion of 4M1P by β-hydride elimination at either of the two β-CH_2 groups of the nickel bound polymer ($Ni{-}CH(CH_2CHMe_2)CH_2{-}$ chain) and cause the decreased ratio of α/internal olefins in the presence of 4M1P compared to polyethylenes prepared with the same catalysts (cf. Table 1, entries 4, 5 vs 1, 2), likewise decreased molecular weights. Terminal $C_q{=}CH_2$ signals at 4.92 and 4.99 ppm were also detected, but with extremely low intensity (almost noise level). Further evidence of the microstructure is given by the ^{13}C NMR spectra. The ethylene-4M1P copolymer prepared with **CCHH/Ni** exhibits distant side chains, isolated by polyethylene segments (Figure 2). This is the same microstructure as observed for copolymerization with the unbranched α-olefins.[14] The signals for the major end groups are small, those of the minor end groups not visible (noise level). Hints for $Me_2CH{-}CH_2CH(Me){-}$ end groups, expected in the case of initial addition of 4M1P at NiH groups and in the ^1H NMR spectra possibly superimposed, could also not be detected. In contrast to phosphinophenolate nickel catalysts the Ziegler−Natta or metallocene-MAO catalysts are able to homopolymerize α-olefins. In copolymerizations the incorporation of the two comonomers into the polymer backbone is thus governed by the reactivity ratios and monomer concentrations.[15] Hence adjacent side chains can be detected by NMR,[15c] which is not the case with the above nickel catalysts.

Introduction of an isomer of 4-methyl-1-pentene, *trans*-hex-2-ene as the comonomer (50 vol % in toluene), changed

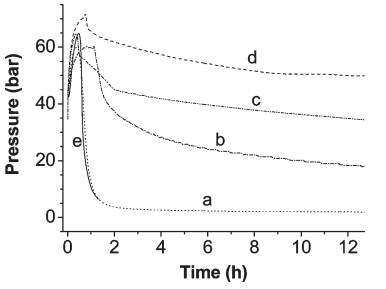


Figure 3. Pressure−time plots of the batch-polymerization of ethylene in the presence of (a) *trans*-2-hexene by **PPHH**/**Ni**, (b) *trans*-2-hexene by **CCHH**/**Ni**, (c) cyclohexene by **PPHH**/**Ni**, (d) cyclohexene by **CCHH**/**Ni**, and (e) 1,5-COD by **PPHH/Ni**.

the behavior dramatically. The internal olefin with *trans*-configuration stabilized the **PPHH/Ni** catalyst and led to rapid reaction after the initial period and complete consumption of ethylene within less than 2 h and without clearly detectable incorporation of the comonomer into the polymer chain. The molecular weight (Table 1, entry 6) was not markedly changed compared to that of entry 1, but the selectivity for vinyl end groups was somewhat lower in favor of internal CH=CH bonds and a trace of $RR'C{=}CH_2$ end groups. In the case of the **CCHH/Ni** catalyst the ethylene consumption rate was strongly decreased by *trans*-hex-2-ene, though less than by 4-methyl-1-pentene, whereas the total conversion of ethylene was lower and the incorporation of the comonomer much lower. Only about 0.9 comonomer per olefin chain, i.e. 0.2 mol % of *trans*-hex-2-ene per polymer chain was incorporated on the basis of the methyl to olefinic group ratio, and a small multiplet at 2.3−2.5 ppm was detected which hints at $CH_2{-}CH{=}CMe{-}CH_2$ and/or $CH_2{-}CH{=}CH{-}CHMe{-}CH_2$ substructures, possibly as parts of *trans*-2-hexene derived end groups. The molecular weight (Table 1, entry 7) relative to the homopolymer synthesized in the absence of an olefin (entry 2) was smaller.

In the presence of cyclohexene (CHE), an internal olefin with intrinsic *cis*-configuration and sterically easily accessible six-membered ring, the ethylene consumption was particularly strongly retarded, even more in combination with the more P-basic **CCHH** ligand at nickel than with **PPHH/Ni**. Therefore, the conversion was rather low when the reaction was stopped after 15 h, but the catalyst was not completely blocked as seen by the steady slow decrease of the ethylene pressure (Figure 3, curves c and d). Like as for the aforementioned inner olefin nearly no incorporation into the polymer chain was observed for the **CCHH/Ni** catalyst. The ^{13}C NMR signals displayed about 0.2 CHE/chain (0.08 mol %) by signals characteristic for isolated CHE units (24.0, 30.5, 38.5, and 28.0 for αCH_2 ppm)[17] along with ca. 0.3 Me branches/chain and the same amount of another branching type (44.0 ppm). The almost linear nature of the polymers is reflected by high melting points and densities of these polymers (Table 1, entries 8, 9), which are very close to the values of polyethylenes in entries 1 and 2, respectively. The molecular weight of the polyethylene formed with **CCHH/Ni** became lower compared to that of the sample prepared in the presence of *trans*-hex-2-ene whereas the opposite was observed for the polymer obtained with **PPHH/Ni**. The strong retardation of the reaction rates in the presence of cyclohexene (Figure 3, curves c and d) is consistent with reversible blockage of the free coordination site at nickel by inner olefins, which is more effective by *cis*- than by *trans*-configuration. The lower molecular weights observed with **CCHH/Ni** suggest that the retardation of the chain

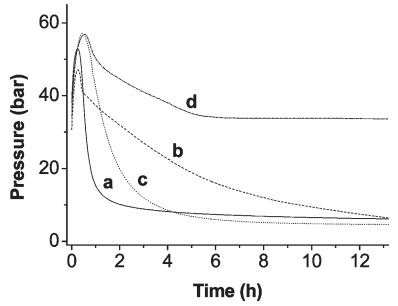


Figure 4. Pressure-time plots of the polymerization of (a) ethylene/styrene by **PPHH**/Ni(COD)$_2$, (b) ethylene/styrene by **CCHH**/Ni(COD)$_2$, (c) ethylene/allylbenzene by **PPHH**/Ni(COD)$_2$, and (d) ethylene/allylbenzene by **CCHH**/Ni(COD)$_2$.

growth, requiring coordination of ethylene (intermolecular process), is stronger for the bulky **CCHH** ligand than of the chain termination, which may be induced by intramolecular interactions between a β-hydrogen atom of the polymer chain with the free coordination site at nickel.

Addition of the cyclic diene 1,5-COD (1 mL) to the **PPHH/Ni** catalyst (molar ratio 88:1) displayed a completely different behavior. There was no retardation of the ethylene consumption but efficient catalyst stabilization and formation of polyethylene without noticeable incorporation of COD (Table 1, entry 10). 1,5-COD is thus a suitable auxiliary to improve the activity in the ethylene oligomerization by phosphinophenolate nickel catalysts. The similarity of the effects to those of *trans*-2-hexene may be due to labile Ni−olefin π-bonds, in the latter case possibly labile *cis*-chelate complexes with pentacoordinated nickel, which disfavor deactivation of (POO$^-$)Ni−R catalyst species (*R* = chain or H) while easy dissociation does not retard coordination of ethylene and its subsequent incorporation into the chain.

Ethylene Copolymerizations with Aryl- and Polar-Substituted Monomers. 2-Diphenylphosphinoenolate nickel catalysts were already shown to be able to copolymerize ethylene with styrene and with some functionally substituted α-olefins R(CH$_2$)$_n$CH=CH$_2$ (*R* = COOMe, C(O)Me, Si(OMe$_3$)), provided that the polar group and C=C bond are remote or separated by at least two methylene spacer groups.[11] Also triphenylphosphonium enolate/P-ylide nickel catalysts are reported to copolymerize ethylene and styrene to give styrene-terminated copolymers with various types of end groups such as *E*/*Z*-styryl, *E*/*Z*-benzylethenyl, 2-phenyl-alkenyl or -vinylidene, and benzyl groups, based on GC/IR and GC/MS analysis. These P-ylide nickel catalysts are even able to polymerize a variety of acrylates.[3c] Copolymers of ethylene with aryl-[18,19] or ester-functional olefins,[20,21] in particular with styrene[18] and short polar vinyl monomers,[20] are of current interest. Therefore, we studied our 2-phosphinophenolate nickel catalysts with respect to their behavior in the polymerization of ethylene in the presence of phenyl-, ester-, and OH-functional olefins.

PPHH/Ni rapidly converted most of the ethylene added to a solution of styrene in toluene and produced an ethylene/styrene copolymer with low melting point and high density (Figure 4a,b). The molar mass of the resultant copolymer is low. Proton NMR analysis reveals about 0.62 *E*-PhCH=CH and 0.23 PhMeCH groups per total olefins (sum of C=C groups), formed in competition with the vinyl and methyl end groups. Including the phenyl side groups this corresponds to incorporation of 11 wt % or 3.4 mol % styrene and is comparable to the 10 wt % reported for the phosphinoenolate nickel catalyst.[11] In the case of using **CCHH/Ni** the molar mass and number of phenyl side groups per copolymer

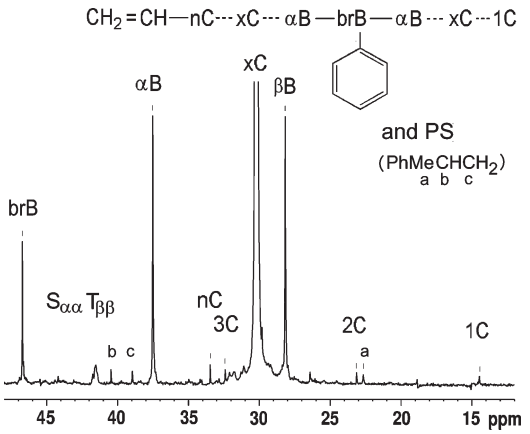


Figure 5. ^{13}C NMR (C_6D_5Br) spectrum of ethylene/styrene copolymer (catalyst **CCHH**/**Ni**).

chain is considerably higher (Table 1, entries 11,12). Along with the PhCH=CH and PhMeCH groups (ca. 0.6 and ca. 0.2/total olefins) this corresponds to a similar content of styrene (9 wt % or 2.6 mol %). The *E*-PhC*H*=C*H*CH$_2$ end groups are indicated by conclusive proton signals at 6.57 (d, 15.9 Hz) and 6.36 ppm (dt, 15.9, 7.3 Hz), the C*H*Ph branches by a quintet at 2.73 ppm, and the PhMeCHCH$_2$ group by a doublet at 1.39 (d, 7.6 Hz) and multiplet at 3.85 ppm. The ^{13}C NMR spectrum (Figure 5) gives evidence that the phenyl side groups are mainly isolated, characterized by only one strong signal for the branching methine carbon and two double intensity signals for the methylene carbon nuclei in α- and β-position. Alternative ethylene−styrene blocks (SES or SSES) were not formed as seen by the absence of the CH−CH$_2$−*C*H$_2$−CH$_2$−CH signal (S$_{\beta\beta}$ 25 ppm) and lack of line broadening of the αC signal by CH-*C*H$_2$−CH$_2$−*C*H$_2$−CH carbon nuclei (S$_{\alpha\gamma}$ 37 ppm).[f8] Likewise, signals characteristic for copolymers formed from ethylene and ethylene/styrene cooligomers[22] could not be detected. Small signals, similar to those of PhCH=CHMe and attributable to the PhCH$_a$=CH$_b$ end group were observed at 130.7 (CH$_a$), 126.1 (sh), 127.4, 128.5, 128.9, and 138.8 ppm (CH$_b$ and phenyl). Head-to-tail polystyrene SSS blocks were also detected by small signals in the region of the respective CH (T$_{\beta\beta}$ 41.5 ppm) and CH$_2$ signals, the latter broad by heterotactic splitting (S$_{\alpha\alpha}$ 43−45 ppm[23]) but easily to recognize by integration. In addition, trace signals for PhMeCH are indicated by small signals at 22.7, 38.9, 40.5, and 148.3 ppm (Me, CH, CH$_2$, *i*C; assignment *cf.* 2-phenylhexane,[24] relative intensity by one-third higher than that of C1). Considering the usual preference of phosphinophenolate nickel catalysts for generation of isolated branches, the occurrence of SSS blocks and both end group signals suggests competing formation of linear polystyrene, by integration comprising ca. one-third of the styrene content, rather than formation of block copolymers. The terminal methyl and vinyl groups (14.5, 114.7, 139.4 ppm) of the copolymers appear as trace signals. Few further ^{13}C trace signals in the range of alkyl and *ipso*-phenyl carbon absorptions may derive from CH$_2$CH-phenyl segments close to the vinyl end of the polymer chain differing in their molecular environment from the respective internal chain segments. This is suggested by an additional very weak vinyl-CH multiplet detected at 5.85 ppm, 0.15 ppm upfield from the stronger usual vinyl signal of linear polyethylenes. Terminal *Z*-PhCH=CH and H$_2$*C*=CPh groups, detected besides the aforementioned end groups in copolymers obtained with phosphonium-enolate/P-ylide nickel catalysts,[3c] could not be observed in our ethylene/styrene copolymers.

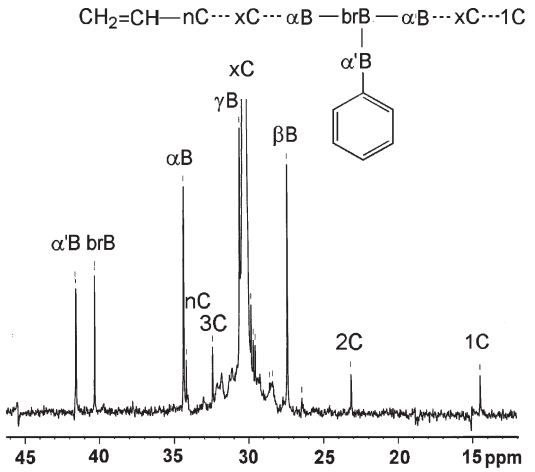


Figure 6. ^{13}C NMR (C_6D_5Br) spectrum of ethylene/allylbenzene copolymer (catalyst **CCHH**/**Ni**).

Allylbenzene is less usual in copolymerization studies and was found to produce smaller copolymers with ethylene by chain transfer reactions to aluminum using various zirconocene catalysts and MAO.[19] Using allylbenzene as the comonomer, both catalysts, **PPHH/Ni** and **CCHH/Ni**, exhibited lower reaction rates (Figure 4c,d) and ethylene conversion (Table 1, entries 13 and 14) than in the presence of styrene. The molar mass of the resulting copolymers is unchanged by use of the **PPHH/Ni** catalyst but increased by **CCHH/Ni** catalysis whereas the comonomer incorporation was low in both cases (ca. 4 and 2.5 wt % or 0.9 and 0.8 mol %, respectively) compared to the ethylene-styrene copolymers. Like as for the other copolymers obtained with the **CCHH/Ni** catalyst, distant side groups isolated by polyethylene segments were detected, here by a rather sharp doublet at 2.75 ppm (^3J = 6.9 Hz) in the proton NMR spectra and a single set of strong side group signals in the ^{13}C NMR spectrum (Figure 6). Benzyl or CH_2=CBz end groups or $HOCH_2CHR$ (R = H, Bz) groups formed in copolymers obtained with zirconocene/MAO catalysts by Al transfer of the allylbenzene unit[19] were not observed.

A comparison of the ethylene/allylbenzene with the above ethylene/4-methyl-1-pentene copolymerization reveals strong similarities with respect to the molar masses as well as to branching. This indicates that the reactivity of allylbenzene, due to the electronic isolation of the phenyl and olefinic π-system by the CH_2 group, is not much affected by the phenyl group and resembles the usual behavior of substituted 1-alkenes whereas the reactivity of styrene with a conjugated π-system is different. The latter slightly facilitates the insertion of styrene into the polymer chain, and the presence of a phenyl group bound to the α-carbon of the chain also favors the chain transfer by β-elimination.

Ester functionalized low-density ethylene copolymers are of industrial interest as polyolefins with modified surface properties or as compatibilizers for polyolefins and functionalized polymers. Considerable progress was recently achieved by use of more functional group tolerant palladium $P^{\frown}O^{-}$-chelate catalysts using 2-phosphinobenzene sulfonate ligands.[20] Since triphenylphosphonium enolate/P-ylide nickel catalysts are able to polymerize a variety of acrylates,[3c] 2-diphenylphosphinoenolate nickel catalysts with strong steric hindrance on the O-side allowed copolymerization of ethylene with methyl methacrylate,[12] and 2-phosphino-enolate nickel catalyst have proven useful in the copolymerization of ethylene with methyl undecenoate,[11] we performed tests with phosphinophenolate nickel catalysts. All attempts to copolymerize ethylene with

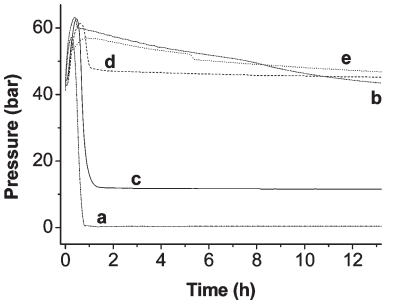


Figure 7. Pressure−time plots of the polymerization of (a) ethylene/ethyl 1-undecenoate by **PPHH**/Ni(COD)$_2$, (b) ethylene/ethyl 1-undecenoate by **CCHH**/Ni(COD)$_2$, (c) ethylene/1-decenol by **PPHH**/Ni(COD)$_2$, (d) ethylene/1-decenol by **CCHH**/Ni(COD)$_2$, and (e) ethylene/1-decenol by **IIBB**/Ni(COD)$_2$.

methyl methacrylate, *n*-butyl acrylate or vinylacetate by the **PPHH/Ni** or **CCHH/Ni** catalyst failed so far by deactivation of the catalyst in toluene. Also introduction of the bulky 6-*tert*-butyl group on the O-side of the $P^{\frown}O^{-}$-Ni chelate by using the **IIBB/Ni** catalyst did not prevent blockage of the catalyst in attempts to copolymerize ethylene with vinyl acetate. Saturation of the **IIBB/Ni** solution with ethylene prior to vinyl acetate addition in the catalyst preparation led likewise to formation of a pale orange solution of inactive complexes. Acrylonitrile, vinyltrimethoxysilane, vinylpyridine, and vinyl bromide also suppressed the polymerization of ethylene by the **PPHH/Ni** catalyst. This behavior is comparable to the deactivation of phosphino-enolate nickel catalysts in the presence of MMA or vinyl acetate, attributed to the increase in π-bond strength of olefins to Ni(II) by conjugated electron withdrawing ester groups or by formation of stable chelates.[11] Introduction of methylene spacers between the C=C bond and the functional group removed the catalyst blockage. **PPHH/Ni** catalyzed the polymerization of ethylene in the presence of ethyl oleate without incorporation of the ester olefin whereas ethyl undecenoate is prone to copolymerization with ethylene by both, the **PPHH/Ni** and **CCHH/Ni** catalysts (Table 1, entries 15−17). **PPHH/Ni** behaves similarly to the diphenylphosphino-enolate catalyst of Klabunde and Ittel[11] but is less active than a recently reported bulky salicylaldiminato nickel catalyst of Grubbs and co-workers[21] and furnishes much shorter chains. Nevertheless, it converted most of the ethylene stock in less than 1 h (Figure 7a) and produced a copolymer with about four functional side chains per main chain, corresponding to 10 wt % or 1.5 mol %. This behavior is remarkable insofar as the reaction rate is much faster than with smaller olefins and the branching degree relatively high for this catalyst. However, an interesting trend becomes clear by comparison with the copolymerization of ethylene and 1-decene or lower α-olefins.[14] The ethylene consumption rate in the ethylene/α-olefin copolymerization catalyzed by **PPHH/Ni** decreases from propylene via butylene to 1-pentene (toluene as solvent) and then increases again in the order 1-hexene < 1-octene < 1-decene < ethyl undecenoate (comonomer as solvent). This order suggests that longer 1-olefins with larger mass and slower diffusion rate compete increasingly less with ethylene but still stabilize the catalyst by coordination and are able to incorporate few olefin molecules into the polyethylene chain.

The higher P-basicity and bulk in the dicyclohexylphosphinophenolate ligand strongly change the catalyst properties and cause decreasing ethylene consumption rates with increasing chain length of the α-olefin. In the copolymerization of ethylene with undecenoate (Figure 7b), like as with

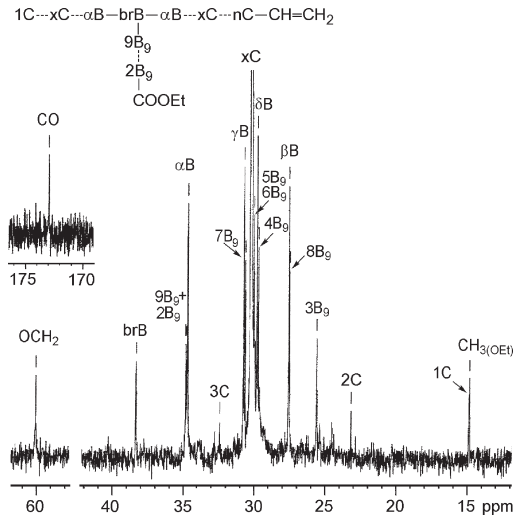


Figure 8. ^{13}C NMR (C_6D_5Br) spectrum of ethylene/ethyl undecenoate copolymer (catalyst) **CCHH/Ni**.

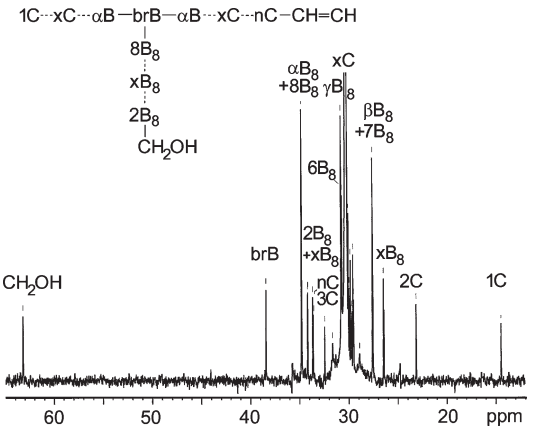


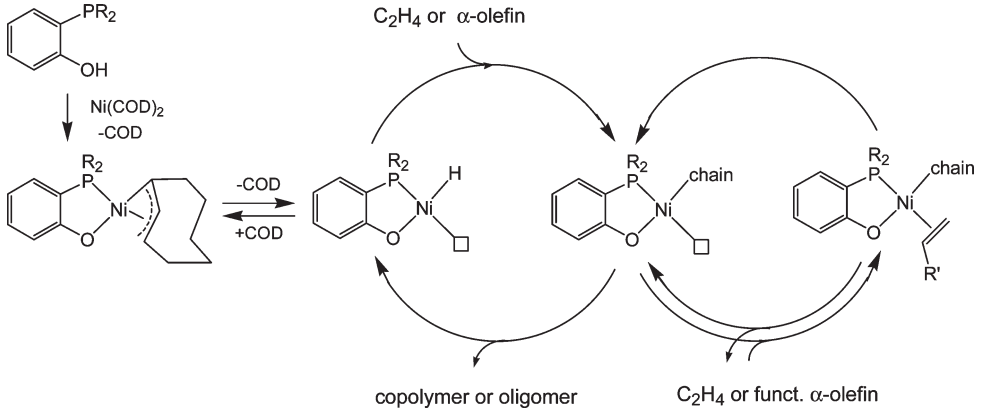
Figure 9. ^{13}C NMR (C_6D_5Br) spectrum of ethylene/9-decenol copolymer (catalyst **CCHH/Ni**).

1-decene,[14] the ethylene consumption was low (46 to 45%) due to the low reaction rate. The catalyst was stabilized and still active when the reaction was stopped (after about 15 h), and in both cases higher molar mass copolymers (M_w ca. 26100 vs 15000 g mol^{-1}) with similar branching degree (19 vs 14 side groups per main chain) were formed. The undecenoate incorporation was 18 wt %, corresponding to 2.9 mol %. The microstructure is similar as in the above copolymers and the ethylene undecenoate copolymer obtained with phosphino-enolate nickel catalysts.[11] The branches arising from incorporated ethyl undecenoate isolated from each other by polyethylene segments result in very simple ^{13}C NMR spectra, which display mainly the carbon nuclei of the side chains, the branching sites, and in double intensity those of its neighbor atoms in α- and β-postion and here even in γ- and δ-position (Figure 8). The strong retardation is thus not due to another mechanism but to strengthened coordination of the olefins at the **CCHH/Ni catalyst** and the slow insertion step. The increased molecular weights of the copolymers are caused by the same effect; ethylene or olefins are able to π-back bonding, enhanced by the strong dicyclohexylphosphino donor in *trans*-position, but hydrogen not. Thus, the β-hydride elimination is disfavored by the more basic dicyclohexylphosphino group and the ratio of chain growth to chain termination increased.

Finally, it was of interest to check if OH functionally substituted olefins can be used for copolymerization with ethylene by phosphinophenolate nickel catalysts. Recently, copolymerization of ethylene with 1-decen-9-ol[25] as well as 5- and 1-undecen-9-ol[26] was studied using α-iminocarboxamide or bulky *N*,*N*′-disubstituted diimino−acenaphthene nickel complexes. In both systems, protection of the OH group by metalation with Me_3Al was required. As phosphinophenolate nickel catalysts tolerate water in toluene or THF we carried out this reaction without protecting the OH group using **PPHH/Ni**, **CCHH/Ni**, and **IIBB/Ni** catalysts (Table 1, entries 18, 19, and 20, respectively). In the first case rapid and high conversion of ethylene was realized (Figure 7c), only slightly lower than in the presence of ethyl 1-undecenoate. The more P-basic **CCHH/Ni** and **IIBB/Ni** catalysts, however, convert ethylene only slowly (Figure 7d, e). The **CCHH/Ni** catalyst is nearly blocked after short reaction time and provides a copolymer with smaller molecular weight than the **IIBB/Ni** catalysts. If the concentration of 9-decen-1-ol in toluene was lowered to the half value, as used in the experiments with **PPHH/Ni** or **IIBB/Ni**, nearly no conversion was observed. Since no colloidal nickel was observed, formation of an inactive complex is assumed. It was earlier observed that ethanol is unsuitable as solvent in the **PPHH/Ni**-catalyzed ethylene polymerization and that it promotes the formation of catalytically inactive nickel bis-(phosphinophenolates).[7] It is assumed that a slow but in principle similar complex formation is induced by the OH group of the comonomer which competes with the polymerization. In the case of the slow ethylene conversion by **CCHH/Ni** the catalyst is deactivated after conversion of only 43% of ethylene whereas in the case of the rapid conversion by **PPHH/Ni** dialkyphosphinophenolate most of the ethylene is converted (86%) before deactivation. The bulky 6-*tert*-butyl diisopropylphosphinophenolate catalyst **IIBB/Ni** after an initial short radical reaction converts ethylene only slowly, but complete deactivation is prevented by steric hindrance on the O-side (6-*tert*-butyl group), which disfavors formation of nickel *cis*-bis(phosphinophenolate) complexes.[27] The incorporation of 9-decen-1-ol into the copolymers is low, according to ^1H NMR integration of OCH_2 versus olefin groups about 5 wt % (0.9 mol %) for all three catalysts, for the short waxy polymers with PPHH/Ni ca. 0.4 side groups/main chain, for the longer polymers ca. 3.0 side groups/main chain. The microstructure of the copolymers, determined by ^{13}C NMR measurements, is the same as detected for the other copolymers, a linear polyethylene main chain with isolated side groups. The CH_2OH end of the side groups gives a strong, slightly broadened ^{13}C NMR signal at 63.2 ppm with about the same intensity as the branching carbon (C_{br}) and triple intensities of the α-, β-, and γ-CH_2 signals, each superimposed by the α-, β-, and γ-CH_2 signals ($8B_8$, $7B_8$, $6B_8$) of the long side group (Figure 9), whereas the incorporation of 1-(un)decenol into the ethylene/hydroxyolefin copolymers, obtained with Me_3Al activated α-iminocarboxamide or diimino−acenaphthene nickel complexes,[25,26] was not detected by ^{13}C NMR. The free OH group in the polymer side groups was of interest to us as it allows for the introduction of a wide variety of functional groups.

Mechanistical Aspects. Concerning the mechanism, a catalytic cycle like as shown for SHOP-type oligomerizations[2] can be discussed (Scheme 1). The methyl and vinyl, in the case of styrene also PhMeCH and *E*-PhCH=CH styryl end groups, hint at chain starts by insertion of ethylene (or styrene) units into the Ni−H bond and termination reactions by β-hydride elimination. Other olefins are less eminent or not involved into starting and termination steps.

Scheme 1. Proposed Mechanism for the Copolymerization



The olefins coordinate and dissociate in competition with ethylene which undergoes much faster insertion. As shown by the PhMeCH end group, the insertion of substituted vinyl monomers leads to α-substituted organonickel species. These may still insert ethylene but by steric reasons probably not the bulkier substituted vinyl monomers and thus explain the microstructure with isolated side groups separated by ethylene blocks. Polar vinyl monomers with a functional group close at the C=C bond block the catalyst metal nickel by complexes being too stable under the (co)polymerization conditions and thus cannot compete with the phosphinobenzenesulfonate palladium catalysts introduced by Drent et al.[28] and currently intensively studied.[20]

Conclusions

In situ generated 2-phosphinophenolate nickel catalysts from 2-phosphinophenol and $Ni(COD)_2$ initiate ethylene polymerization in the presence of olefins and afford polyethylene or copolymers with isolated side groups in most cases. Varying substituents at phosphorus has profound effects in adjusting ethylene conversion and molar mass of the copolymers obtained. M_w/M_n values of about 2 for the majority of the copolymers investigated by GPC reflect the maintenance of the single site characteristics of the phosphinophenolate catalysts after inclusion of the various comonomers. **PPHH/Ni** inclines to faster and higher ethylene conversion than **CCHH/Ni** with low incorporation of most olefin comonomers and can be interpreted as a comonomer stabilization effect on the catalyst. Additives of 1,5-COD to toluene or longer olefins as solvents may thus be used to improve the productivity of **PPHH/Ni** catalysts in the ethylene polymerization. Ethylene polymerization in the presence of long-chain α-olefins proceeds with incorporation of a few of these olefins into the polyethylene chain (minor long chain branching). **PPHH/Ni** gives rise to lower molecular weights of the polymers compared to **CCHH/Ni**. This can be attributed to the lower basicity of the Ph_2P compared to the $cHex_2P$ donor group. The usually slower ethylene consumption rate in the presence of the **CCHH/Ni** catalyst may be due to strengthened π-back bonding to olefin. If the dissociation and insertion of the olefin is slow, the ethylene consumption is strongly retarded or even blocked. The highest comonomer incorporation of the here studied hexenes (4-methyl-1-pentene, *trans*-hex-2-ene and cyclohexene) was observed for the **CCHH/Ni**-mediated ethylene/4-methyl-1-pentene copolymer. The microstructure as reflected in the ^{13}C NMR spectrum of the copolymer confirms the existence of isolated isobutyl side groups in the polyethylene main chain. The isomeric internal olefins *trans*-hex-2-ene and cyclohexene are not or only in traces incorporated into the polyethylene chain. Styrene showed slightly better inclusion into the polymer chain than methylpentene and favors chain termination, shown by the substancial amount of PhCH=CH end groups and smaller relative molar masses of the polymers. Tolerance of O-functional groups of olefins is limited for the phosphinophenolate nickel catalysts. Too short a distance between the polar group and C=C double bond inevitably blocks the coordination of ethylene to the active sites, probably by rather stable chelate coordination of these O-functional olefins to the Ni centers. A longer distance between the O-functional group and the C=C double bond such as in ethyl 1-undecenoate or 1-decen-9-ol significantly overcomes this disadvantage for 2-phosphinophenolate nickel catalysts. In this case even OH-unprotected comonomers can be incorporated to some extent, which allows for subsequent introduction of a wide variety of other residues or functional groups or for combination with inorganic materials.

Experimental Section

All operations except work-up of polymers were carried out under inert atmosphere by using Schlenk techniques. The 2-phosphinophenols were synthesized as reported earlier.[7b,29] The abbreviations **PPHH**, **CCHH**, and **IIBB** denote acronyms for the two substituents at phosphorus and the substituents in 4- and 6-position of the phenol ring (**P**, phenyl; **C**, cyclohexyl; **H**, hydrogen; **I**, isopropyl; **B**, *tert*-butyl) (Chart 1). Olefins and sodium-dried toluene were freshly distilled before use. Nickel bis(1,5-cyclooctadiene) ($Ni(COD)_2$) was purchased (Strem) and, like ethylene (99.5%, Air Liquide), used without further treatment. The copolymerization reactions were performed in a stainless steel autoclave (75 mL), equipped with a mechanical manometer, pressure sensor (pressure−time registration) two valves, a safety diaphragm, Teflon-coated magnetic stirrer and a silicon heating bath. Reaction temperatures refer to the bath temperature. Further details were given earlier.[14]

Copolymerization. The phosphinophenol, **PPHH**, **CCHH**, or in few cases **IIBB**, and $Ni(COD)_2$ were dissolved each in 10 mL of toluene and/or olefin, cooled to 0 °C (10 min) and mixed. The amounts used are indicated in Table 1. The resulting yellow to orange or brown solution was stirred at room temperature for 5 min and transferred via a Teflon tube into the argon filled autoclave. After weight control the autoclave was pressurized with ethylene (30 to 50 bar, Table 1), the amount of ethylene determined by weight difference, and the autoclave set into the silicon bath and heated overnight (15 h) at 100 ± 5 °C unless indicated otherwise. After cooling to room temperature and weight control, the autoclave was connected to a cooling trap (−78 °C), and unconverted ethylene was allowed to escape. The content of the autoclave was separated by flash distillation at 80 °C/4.0 mbar. The residual polymer was stirred for 1 d with methanol/hydrochloric acid (1:1, v/v), then thoroughly washed with methanol and finally dried in vacuum.

The density of the copolymers was measured by the sinking method by using tablets obtained in an IR press (10 kbar) and addition of ethanol to water in the presence of a detergent. The molecular weight and molecular weight distribution of the copolymers were determined by gel permeation chromatography (GPC) at 150 °C with 1,2,4-trichlorobenzene as the eluent, flow rate of 1.0 mL/min, with a Waters Alliance GPC 2000 instrument equipped with a refractive index (RI) detector and a set of μ-Styragel HT columns of 10^6, 10^5, 10^4, and 10^3 pore size in series. Calibration was performed with PS of narrow molecular weight distribution as a standard. NMR spectra were measured on a Bruker ARX/Avance Spectrometer at 300.13 MHz (^{1}H) and 75.46 MHz (^{13}C) in C_6D_5Br at 100 °C after swelling at 100−110 °C for 1d (under nitrogen). Typically, 8000 scans were collected for ^{1}H (acquisition time 4.9−5.4 s, delay 1.0 s) and at least 20 000 for ^{13}C NMR measurements (acquisition time 0.6−0.9 s, delay 0.4 s), the latter in the presence of 3−5 mg Cr(acac)$_3$. Reference was *p*-CH of the solvent $\delta(^1H) = 7.23$, $\delta(^{13}C) = 126.70$ ppm. The assignment of the signals was made in accordance with literature data.[30] M_{NMR} values were calculated according to a literature method for lower MW polyethylene[31] taking into account the additional side and end groups. The 4-methyl-1-pentene/ethylene ratio in the copolymer was calculated from the ratio of methyl to olefin groups. The signals of the side chains, 1.10 (d, Me), 1.36 (t, CH_2), and 1.82 ppm (m, CH), are superimposed by those of polyethylene but the polyethylene blocks are linear (see ^{13}C NMR spectra) and allow to calculate the number of side groups via the total number of methyl groups (2 per side group) from the methyl/olefin group ratio in good approximation. The ethylene/styrene ratio in the corresponding polymers was calculated from the ratio of the CH, CH_2 and CH_3 groups belonging to the respective components, determined by integrals of vinyl doublets (CH_2= protons at 5.05−5.20 ppm), the CH═CH multiplet, PhCH═CHCH_2 (2.36 ppm) and RCH═CHCH_2 (R = H and alkyl, 2.21 ppm) quartets, and the superimposed CH and CH_2 signals at 1.2−1.9 ppm (minus protons of the styrene and additional PhMeCH groups) versus *E*-PhC*H* = C*H* signals, 6.57 (d, 15.9 Hz) and 6.36 ppm (dt, 15.9, 7.3 Hz), the PhC*H*$(CH_2)_2$ quintet at 2.73 ppm, and the PhMeC*H*CH_2 sextet at 3.85 ppm (7.2 Hz). The ethylene/allylbenzene ratio is based on the integration of the polyethylene CH, CH_2 and CH_3 signals minus CH_2CH of allylbenzene versus the PhCH_2 doublet at 2.75 ppm (^3J = 6.9 Hz). The incorporation of ethyl undecenoate and 1-decen-9-ol into the ethylene chain was determined from the integral ratio of the OCH_2 to the sum of CH, CH_2, and CH_3 groups, diminished by those derived from the comonomer. TONs were calculated from ethylene consumption and the comonomer/ethylene molar ratio within the copolymer determined by ^{1}H NMR integration.

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Supporting Information Available: Figures showing NMR spectra of selected copolymers from Table 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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