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Novel Nickel(II)- and Palladium(II)-Based Catalytic Systems for the Synthesis of Hyperbranched Polymers from Ethene

Jang Sub Kim, James H. Pawlow, Louis M. Wojcinski II,
Shahid Murtuza, Smita Kacker, and Ayusman Sen*

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

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The transition-metal-catalyzed polymerization (and oligomerization) of ethene leads principally to linear polymers.[1] However, Brookhart has recently demonstrated that substantially branched polymers (methyl hydrogens/total aliphatic hydrogens up to 0.30) can be synthesized using palladium(II) and nickel(II) catalysts incorporating very bulky chelating diimine ligands.[2] Branching is thought to arise from β-hydrogen abstraction followed by readdition of the resultant coordinated vinyl-ended polymer to the metal hydride, a process that competes with polymer chain growth. Herein, we report that the presence of a bulky ligand on the metal is not a necessary criterion for the formation of branched polymers; indeed, polymers with a degree of branching higher than hitherto reported (methyl hydrogens/total aliphatic hydrogens up to 0.65) can be synthesized from ethene using relatively simple, sterically unencumbered, metal catalysts. Furthermore, it is possible to efficiently graft these hyperbranched polymer moieties on to aromatic rings in small molecules and polymers.

The catalyst system that we have uncovered consists of two components: a transition-metal complex (typically, $[Ni(\pi\text{-methallyl})(Br)]_2$[3] or Pd(1,5-cyclooctadiene)(Me)(Cl))[4] and an excess of an aluminum compound ($AlCl_3$ or $AlEt_3$).[5] The reaction rates were particularly high for the Ni(II)/$AlCl_3$ systems with the turnover frequency approaching 10 000/h for the polymers isolated. There was also an exotherm observed for the Ni(II)/$AlCl_3$ reaction with the temperature reaching 140 °C. In addition to the polymer, significant quantities of 1- and 2-butenes were formed in all of the reactions.

Our results on the synthesis of polymers are summarized in Table 1. Especially noteworthy are the low polydispersities (M_w/M_n). Because of the problem associated with comparing a highly branched polymer with a linear polymer (polystyrene) standard (due to differences in hydrodynamic volumes), the polymers corresponding to entries 3 and 4 were also examined by light scattering. The corresponding M_w and M_w/M_n values obtained were 1700, 1.4 and 1200, 1.2. The polymers formed were very highly branched with no discernible backbone; typical ^1H and ^{13}C NMR ($CDCl_3$) spectra are shown in Figure 1a and 1b, respectively. Perhaps the most remarkable feature of the ^1H NMR spectra is the resonance due to the methyl protons at 0.85 ppm which dwarfed all other resonances. A combination of ^{13}C NMR DEPT and HMQC $^1H-^{13}C$ NMR correlation experiments indicated that there were multiple ^{13}C NMR resonances between 8 and 30 ppm that corresponded to the methyl group in the ^1H NMR spectrum. While broadly similar NMR spectra were obtained in every case, there were some significant differences. For example, irrespective of the aluminum compound used, the ^1H NMR ($CDCl_3$) resonances centered at 1.3 ppm always were of higher intensity than those centered at 1.7 ppm when the nickel catalyst was employed, while the reverse was true with the palladium catalyst. Finally, an extremely regular series of fragmentation peaks separated by 14 mass units were observed in the mass spectrum of a polymer sample with M_w = 550 (GPC).

Table 1. Synthesis of Hyperbranched Polymers from Ethene

catalyst	ligand	solvent	yield (g)[h]	M_w[i]	M_w/M_n[i]	Me/total[j]
$Ni/AlCl_3$[a]		$CHCl_3$	2.9	800	1.2	0.53
$Ni/AlCl_3$[a]		C_6H_5Cl	3.6	450	1.2	0.49
$Ni/AlCl_3$[a]	dppe[d,k]	C_6H_5Cl	3.5	1010	1.3	0.43
$Ni/AlCl_3$[a]	dppp[d,k]	C_6H_5Cl	2.2	800	1.2	0.42
$Ni/AlBr_3$[a]		C_6H_5Cl	3.6	490	1.1	0.57
$Ni/AlEt_3$[b]		$CHCl_3$	3.0	580	1.2	0.52
$Ni/AlEt_3$[b]	dbu[e]	$CHCl_3$	1.3	370	1.1	0.54
$Ni/AlEt_3$[b]	dppp[f,k]	$CHCl_3$	4.7	370	1.1	0.57
$Pd/AlCl_3$[c]		$CHCl_3$	2.6	460	1.1	0.61
$Pd/AlCl_3$[c]	dppp[f,k]	$CHCl_3$	3.2	600	1.2	0.55
$Pd/AlCl_3$[c]	PPh_3[g]	$CHCl_3$	3.4	520	1.1	0.58
$Pd/AlEt_3$[c]		$CHCl_3$	1.0	410	1.1	0.62
$Pd/AlEt_3$[c]	dppp[f,k]	$CHCl_3$	2.2	550	1.1	0.60
$Pd/AlEt_3$[c]	PPh_3[g]	$CHCl_3$	2.4	580	1.1	0.64

[a] $[Ni(\pi\text{-MeC}_3H_4)(Br)]_2$, 0.013 mmol; $AlCl_3$, 0.25 mmol; 10 mL of solvent; 800 psi of ethene (constant pressure); 25 °C; 30 min; 125 mL pressure reactor equipped with glass liner. [b] $[Ni(\pi\text{-MeC}_3H_4)(Br)]_2$, 0.075 mmol; $AlEt_3$; 0.75 mmol; 10 mL of solvent, 800 psi of ethene (single charge), 55 °C, 16 h; 125 mL pressure reactor equipped with glass liner. [c] Pd(1,5-cyclooctadiene)(Me)(Cl), 0.075 mmol; $AlCl_3$ or $AlEt_3$; 0.75 mmol; 10 mL of solvent, 800 psi of ethene (single charge), 55 °C, 16 h; 125 mL pressure reactor equipped with glass liner. [d] 0.025 mmol. [e] 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU); 0.38 mmol. [f] 0.075 mmol. [g] 0.15 mmol. [h] Yield of polymer obtained after applying vacuum (1 mmHg) at 50 °C to the purified organic reaction product to remove volatiles. [i] Determined by GPC relative to linear polystyrene standards. [j] Ratio of methyl protons (at 0.85 ppm)/total alkyl protons (by ^1H NMR integration). [k] dppe = 1,2-bis(diphenylphosphino)ethane; dppp = 1,3-bis(diphenylphosphino)propane.

The reaction of ethene with Ni(II)/$AlCl_3$ at ambient temperature was monitored by ^1H NMR spectroscopy. The addition of 10 equiv (0.10 mmol) of $AlCl_3$ to a $CDCl_3$ (0.5 mL) solution of $[Ni(\pi\text{-methallyl})(Br)]_2$ (0.005 mmol = 0.01 mmol of Ni) caused a significant change in the NMR resonances of the methallyl group (from 2.85 (2H), 2.32 (3H), 1.94 (2H) ppm to 3.52 (2H), 2.50 (3H), 2.46 (2H) ppm). Upon the addition of 1 equiv of ethene, the intensity of the methallyl resonances decreased by 50% while the peaks due to the hyperbranched polymer appeared. After 5 equiv of ethene was added, the methallyl resonances were no longer observable; only those of the hyperbranched polymer remained in the spectrum. The simplest explanation for the above observations is that the methallyl group on the nickel was directly involved in the formation of the polymer but the rate of initiation was slower than the propagation rate. Control experiments indicated that neither $[Ni(\pi\text{-methallyl})(Br)]_2$ nor $AlCl_3$ alone gave rise to the polymer under the above conditions.

When aromatic solvents susceptible to Friedel−Crafts alkylation were employed, the use of Ni(II)/$AlCl_3$/ethene system led to the formation of aryl-capped hyperbranched polymers.[6] For

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(1) For reviews, see: (a) Kaminsky, W. In *Handbook of Polymer Synthesis, Part A*; Kricheldorf, H., Ed.; Marcel Dekker: New York, 1992; p 1. (b) Odian, G. *Principles of Polymerization*; Wiley: New York, 1991; p 630. (c) Skupinska, J. *Chem. Rev.* **1991**, *91*, 613. (d) Al-Jarallah, A. M.; Anabtawi, J. A.; Siddiqui, M. A. B.; Aitani, A. M.; Al-Sadoun, A. W. *Catal. Today* **1992**, *14*, 1. (e) Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 186. (f) Jolly, P. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Permagon: Oxford, 1982; Vol. 8, p 615.

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(3) Semmelhack, M. F.; Helquist, P. M. *Org. Synth.* **1972**, *55*, 722.

(4) Ladipo, F. T.; Anderson, G. K. *Organometallics* **1994**, *13*, 303.

(5) A similar Ni(II)/$AlCl_3$ system, but with Ni/Al ratio of 1 was previously reported to catalyze the dimerization of ethene: Bogdanovic, B. *Adv. Organomet. Chem.* **1979**, *17*, 105.

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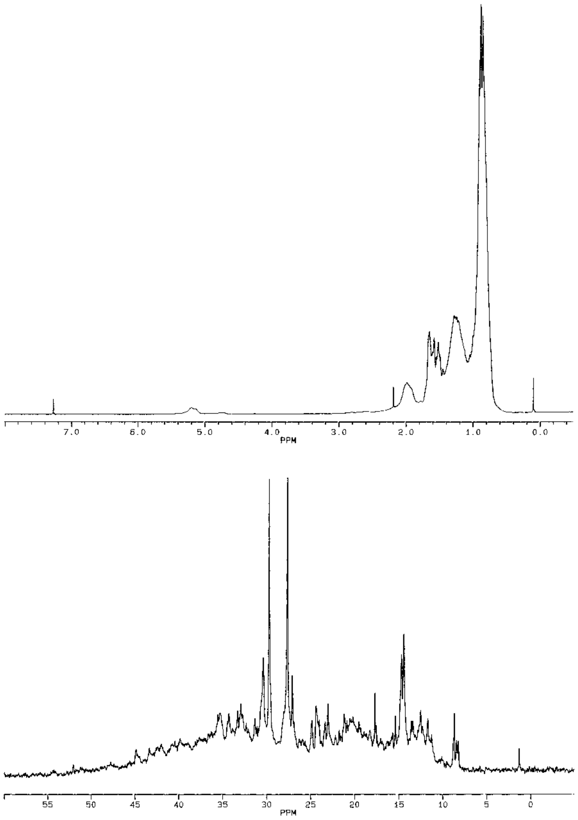

Figure 1. (a) ^{1}H NMR ($CDCl_3$) spectrum of the hyperbranched polymer and (b) $^{13}C\{^1H\}$ NMR ($CDCl_3$) spectrum of the hyperbranched polymer. Reaction conditions: $[Ni(\pi\text{-}MeC_3H_4)(Br)]_2$, 0.026 mmol; $AlEt_3$; 0.52 mmol; 10 mL of $CHCl_3$, 800 psi of ethene (single charge), 50 °C, 17.5 h; 125 mL pressure reactor equipped with glass liner.

example, under the reaction conditions shown in Table 1 (first or second entry), the use of benzene (10 mL) resulted in the formation of phenyl-capped hyperbranched polymer in which the ratio of nonaromatic to aromatic hydrogens was approximately 6. The molecular weight as determined by GPC versus polystyrene standards was 360. Thus, the ethene/phenyl ratio was approximately 10 (however, molecular weights of hyperbranched polymers that are determined versus linear polymer standards should be treated with caution). The ^{1}H NMR ($CDCl_3$) spectrum of the material was very similar to those of the noncapped hyperbranched polymers except for additional resonances at 2.60 and 3.02 ppm due to hydrogen(s) on the carbon directly bonded to the aromatic ring (i.e., benzylic hydrogens). Similar grafting of hyperbranched polymer derived from ethene was observed starting with toluene, xylene, and naphthalene.

It was also possible to graft hyperbranched polymer tails derived from ethene on to the pendant phenyl groups of polystyrene.[7] For example using the Ni(II)/$AlCl_3$/ethene system and 0.5 g of polystyrene ($M_w = 360\,000$) in 5 mL of chlorobenzene, polymer-grafted polystyrene weighing approximately 18% more than the starting polymer with a ratio of nonaromatic to aromatic hydrogens of approximately 1.5 was obtained (ratio of nonaromatic to aromatic hydrogens in pure polystyrene = 0.6). As expected, the T_g of the product polymer was significantly lower than the starting polystyrene (72 versus 100 °C).

While the mechanism of branching in the present system remains to be elucidated, an obvious alternative to that suggested by Brookhart[2] involves Lewis acid promoted carbocationic rearrangements and oligomerizations. Ethene itself is unreactive toward Lewis acids under the mild conditions employed by us.[8] A more viable possibility is that the transition metal species was responsible for the dimerization of ethene to butenes which are, of course, more susceptible to Lewis acid (or H^+) promoted rearrangements and oligomerizations. *Although not conclusive*, the following observations appear to be inconsistent with the above mechanistic scenario: (a) the addition of a base, 1,8-diazabicyclo[5.4.0]undec-7-ene, (up to 50% relative to $AlEt_3$) to the Ni(II)/$AlEt_3$/ethene system resulted in somewhat reduced yields but *not* reduced branching in the polymer formed, (b) the molecular weight and the structure of the polymer obtained depended on the transition metal and its ancillary ligand (phosphine), and (c) $AlEt_3$ is a significantly *weaker* Lewis acid than is $AlCl_3$, yet the degree of branching was invariably higher when $AlCl_3$ was replaced by $AlEt_3$. The presence of quaternary carbons in the polymer formed would, of course, totally exclude the Brookhart mechanism and be consistent with carbocationic rearrangements. However, no quaternary carbons were discernible in the NMR spectrum of the hyperbranched polymer when the ^{13}C NMR DEPT technique was employed. Unfortunately, due to the complexity of the ^{13}C NMR spectra, it is possible that small resonances due to quaternary carbons escaped our detection.

In conclusion, we have achieved the synthesis of hyperbranched polymers from ethene using a novel catalyst system. The product polymers are viscous oils with a nonregular microstructure containing a high ratio of methyl group carbons to total number of carbons. The grafting of the hyperbranched polymer on to aromatic rings in small molecules and polymers was also accomplished.

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Supporting Information Available: NMR and mass spectral data for hyperbranched polymers derived from ethene (12 pages). See any current masthead page for ordering information and Web access instructions.

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[6] For reviews on Friedel−Crafts alkylation, see: (a) Roberts, R. M.; Khalaf, A. A. *Friedel−Crafts Alkylation Chemistry*; Marcel Dekker: New York, 1984. (b) Olah, G. A. *Friedel−Crafts Chemistry*; Wiley: New York, 1973.

[7] Polystyrene has been grafted by Friedel−Crafts systems, but the reports do not include the use of ethene as the alkylating agent: (a) Butler, J. M. U.S. Patent 2,569,400, 1951. (b) Welch, L. M. U.S. Patent 2,651,628, 1953.

[8] (a) Kennedy, J. P. *Cationic Polymerization of Olefins: A Critical Inventory*; Wiley: New York, 1975; p 52. (b) Odian, G. *Principles of Polymerization*; Wiley: New York, 1991; p 356.