ACS Catalysis

Research Article

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Analysis of Polymeryl Chain Transfer Between Group 10 Metals and Main Group Alkyls during Ethylene Polymerization

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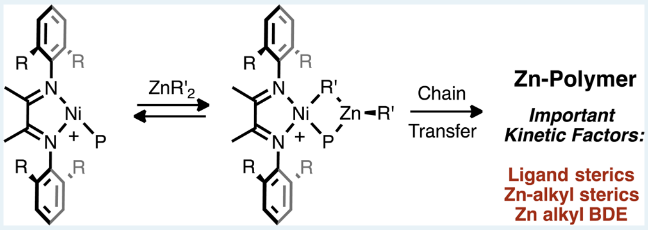
Supporting Information



ABSTRACT: The ability of various group 10 α-diimine and salicylaldimine polymerization catalysts to undergo chain transfer with main group metal alkyls during ethylene polymerization has been investigated in depth. The catalyst systems with the most efficient chain transfer were found to be cationic (α-diimine)Ni catalysts paired with dialkyl zinc chain-transfer reagents, in which all growing polymeryl chains were transferred to Zn on the basis of ^{13}C NMR analysis. In these systems, chain transfer was found to be dependent on the sterics of both the catalyst and the chain-transfer reagent (CTR). When less sterically encumbered catalysts or CTRs were utilized, the relative rate of bimetallic chain transfer to chain propagation was increased; however, in cases where chain termination via β-H elimination was extremely rapid, chain transfer to Zn was kinetically not viable. Importantly, chain transfer from (α-diimine)Ni catalysts to Zn alkyls is also very sensitive to the strength of the Zn−C bond: $ZnMe_2$ (186 kJ/mol) is a significantly poorer chain-transfer reagent than $ZnEt_2$ (157 kJ/mol), despite being less sterically encumbered. Finally, the nature of the catalyst counteranion (MAO or $B(ArF)_4^-$ ArF = 3,5-$(CF_3)_2C_6H_3$) does not have a significant impact on the rate of chain transfer to ZnR_2 relative to propagation, indicating that the same factors that determine propagation rates also determine bimetallic chain-transfer rates.

KEYWORDS: *polymerization catalysis, chain transfer, polyethylene, group 10, metal alkyls, kinetics*

INTRODUCTION

The advent of single-site catalysts for the production of polyolefins has led to significant advances in the ability to tune molecular weight, polydispersity, and polymer microstructure.[1−3] More recently, chain-transfer and chain-shuttling polymerizations, in which a growing polymer chain is transferred off the polymerization catalyst and onto a second metal (or catalyst), has established a new paradigm of precision control over olefin polymerizations.[4−6] For example, chain shuttling polymerizations have been used to change the molecular weight and molecular weight distribution of polyolefins,[7] to catalyze Aufbau-like alkyl chain growth on main group metals,[8] and for the synthesis of block copolymers through multicatalyst systems.[9,10]

Polymeryl chain-transfer-to-metal processes have been observed across the transition metal and lanthanide series, most commonly with early transition metals (Hf, Zr) and alkylzinc or alkylaluminum reagents.[5,7,8,11−16] In many of these early transition metal or lanthanide cases, chain transfer is fast, efficient, and reversible. Importantly, chain transfer/shuttling is not limited to early transition metals, but has been observed in mid-to-late transition metals (e.g., Cr, Fe, Co, and Ni) with group 2 and 12 metal alkyls.[4,7,17−19] In many of these systems, it is speculated that two main factors are necessary for efficient chain transfer: a good match of M−C bond dissociation energies for the polymerization catalyst and chain-transfer reagent, and an appropriate steric environment to promote facile bimolecular formation/breakage of alkyl-bridged bimetallic intermediates.

Comparatively little is known about the propensity of group 10 (Ni, Pd) olefin polymerization catalysts to participate in chain-transfer-to-metal events.[20,21] Utilizing late transition metal catalysts in chain-transfer polymerizations would potentially open up new types of block copolymer syntheses: Ni- and Pd-based catalysts are often capable of incorporating polar monomers and other functional groups that irreversibly deactivate oxophilic early transition metals and lanthanides.[22−29]

Gibson studied the rate of chain transfer between $[(\alpha\text{-diimine})Ni(polymeryl)]^+[MAO]^-$ and $ZnEt_2$ and found that the rate of chain transfer to Zn was approximately 200−300 times slower than propagation.[7] Given that Brookhart-type α-diimine catalysts were *specifically designed* to retard intermolecular reactivity (in particular, chain termination via β-H transfer to ethylene), it is no surprise that intermolecular chain transfer with $ZnEt_2$ would also be slow.[30−32] However, alkyl/aryl group transfer equilibria *have* been observed in some Negishi coupling reactions with group 10 metals, indicating that

Received: September 23, 2014
Revised: October 15, 2014
Published: October 17, 2014

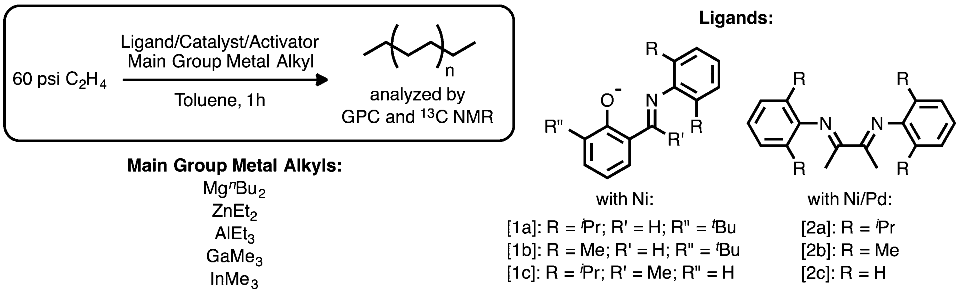


Figure 1. Initial screening of group 10 polymerization catalysts with main group alkyls.

chain transfer during polymerizations may, in some cases, be kinetically competent and synthetically useful.[33−37] Thus, we are interested in studying in depth the effects of varying sterics and electronics on the rates of chain transfer versus propagation and termination in various group 10 ethylene polymerization catalysts. Herein, we report on a survey of bimetallic chain transfer in salicylaldimine- and α-diimine-based catalyst systems with various main group metal alkyls, as well as an in-depth study of the steric and electronic effects in the most successful catalyst pair, (α-diimine)NiR^+ with ZnR_2.

EXPERIMENTAL SECTION

General Considerations and Materials. All air- and moisture-sensitive compounds were manipulated in a glovebox under a nitrogen atmosphere. Toluene was dried on a vacuum atmospheres solvent purification system, filtered through activated basic alumina in a nitrogen glovebox, and titrated with a stock solution of Na/benzophenone to ensure <1 ppm of H_2O. Ultrahigh-purity ethylene (99.9%) was purchased from Airgas and was further purified using a Matheson PUR-Gas in-line purifier system to remove oxygen and water. Methylaluminoxane (MAO) was purchased from Albemarle as a 30% solution in toluene and used as received. $ZnMe_2$, $ZnEt_2$, $ZnPh_2$, $AlEt_3$, $GaMe_3$, and $InMe_3$ were purchased from Strem and used as received. Nickel and palladium α-diimines,[30,38−41] salicylaldimines,[42−45] $[H(OEt_2)_2]^+[(3,5\text{-}(CF_3)_2C_6H_3))_4B]^-$ (HBArF),[46,47] Zn^nBu_2,[48] and Zn^sBu_2[49] were prepared according to literature procedures.

Instrumentation. ^1H, ^{13}C, and ^{31}P spectra of ligands and catalysts were recorded on Varian INOVA 300 or 500 MHz spectrometers. ^{13}C spectra of polymers and oligomers were recorded on an Agilent/Varian 600 MHz spectrometer at 130 °C in $C_2D_2Cl_4$ and referenced to the solvent carbon (73.78 ppm). Polymer branching was assigned according to the literature.[50−52] GPC analyses were carried out on an Agilent PL-GPC 220 high temperature GPC/SEC system at 135 °C in 1,2,4 trichlorobenzene using polystyrene standards.

General Polymerization Reactions. All polymerization reactions were carried out in a Biotage Endeavor parallel pressure reactor with overhead stirring housed in an N_2 atmosphere glovebox. A solution of chain-transfer reagent (0.00600−0.200 mmol) in toluene was added to the reactor, and the reactor was sealed and pressurized with C_2H_4 (15−225 psi). Then, a toluene stock solution of catalyst was injected into the reactor at pressure, and the reactions were run for 1 h. Typical reactions were run with 3 mL total reaction volume at catalyst concentrations of 3.33×10^{-5} M. Reactions were monitored via gas uptake measurements taken by the Endeavor software. After 1 h, the reactions were depressurized, removed from the glovebox and quenched by the addition of 5% HCl in methanol prior to GPC and NMR analysis. All polymerizations were run in triplicate. Full tables of all polymerizations and their analyses are available in the Supporting Information (SI).

RESULTS AND DISCUSSION

Initial Screening of Group 10 Polymerization Catalysts with Main Group Alkyls. Cationic (α-diimine), neutral salicylaldimine and salicylketimine Ni or Pd ethylene polymerization catalysts were examined for their competency for ethylene polymerization in the presence of excess molar equivalents (150 and 600 equiv) of main group metal alkyls (Figure 1). The reactions were monitored via gas uptake measurements to determine the rate and extent of polymerization and catalyst lifetime, and the molecular weights of the resultant polymers were determined via gel permeation chromatography (GPC). In the cases where polymerization was successful, catalyst systems that underwent chain transfer were identified by a reduction of M_n as the concentration of main group metal alkyl increased. The amount of chain transfer was quantified in two ways: first, as a percentage of main group metal alkyl groups extended (eq 1) and, second, by examining the number of chains initiated per total molar amount of polymerization catalyst (eq 2).

$$(\text{M-R})_{\text{extended}} = \frac{\text{yield}_{\text{polymer}}}{M_n} \tag{1}$$

$$\text{chains}_{\text{initiated}} = \frac{(\text{M}-\text{R})_{\text{extended}}}{\text{moles}_{\text{catalyst}}} \tag{2}$$

The results of the initial catalyst combination screen are presented in Table 1. In Table 1, catalyst combinations where addition of a main group alkyl resulted in no polymer formation are signified by a dash (−); combinations that resulted in polymer formation but no observable chain transfer are highlighted in gray; and systems that successfully yielded polymer and chain transfer are highlighted in black. The percentages in the table indicate the increase in the number of chains initiated in the presence of the main group alkyl.

Neither Ni salicylaldimine-based complexes ([**1a**−**c**]NiLX) nor Pd α-diimine-based complexes ([**2a**]PdX_2) were competent for ethylene polymerization in the presence of any of the tested main group metal alkyls. To determine why these catalyst systems failed, several stoichiometric and catalytic experiments were performed. Initially, it was speculated that the main group metal alkyl may be reacting with $Ni(COD)_2$, which was used as a phosphine scavenger for [**1a**]$NiPh(PPh_3)$. Polymerizations were attempted with [**1a**]NiPh(py); however, the activator-free catalyst system also generated no polymer in the presence of main group metal alkyls. ^1H NMR spectra of

Table 1. Initial Screening of Group 10 Polymerization Catalysts with Main Group Alkyls[e]

Catalyst/Activator	None	Mg^{n}Bu$_2$	ZnEt$_2$	AlEt$_3$	GaMe$_3$	InMe$_3$
[1a]NiPh(PPh$_3$)/Ni(COD)$_2$ [a]	▨	–	–	–	–	–
[1a]NiPh(py) [b]	▨	–	–	–	–	–
[1b]NiPh(PPh$_3$)/Ni(COD)$_2$ [a]	▨	–	–	–	–	–
[1c]NiPh(py) [b]	–	–	–	–	–	–
[2a]NiBr$_2$/MAO [c]	▨	–	+ 640%	+ 1%	+ 10%	+ 30%
[2a]NiMe$_2$/HBArF [d]	▨	–	+ 640%	+ 1%	+ 70%	+ 25%
[2a]PdCl$_2$/MAO [c]	▨	–	–	–	–	–
[2a]PdMe$_2$/HBArF [d]	▨	–	–	–	–	–

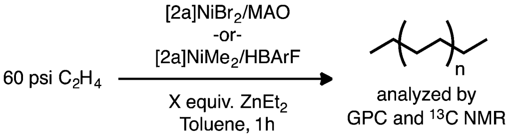
[a]Conditions: 6×10^{-7} mol of catalyst, 2 equiv of Ni(COD)$_2$, 105 psi ethylene, room temperature, 1 h, toluene solvent (3.0 mL). [b]Conditions: 6×10^{-7} mol of catalyst, 105 psi ethylene, room temperature, 1 h, toluene solvent (3.0 mL). [c]Conditions: 1×10^{-7} mol of catalyst, 500 equiv of MAO, 60 psi ethylene, room temperature, 1 h, toluene solvent (3.0 mL). [d]Conditions: 2×10^{-7} mol of catalyst, stoichiometric activation with HBArF, 60 psi ethylene, room temperature, 1 h, toluene solvent (3.0 mL). [e]Percentages indicate successful transfer reactions, giving the percent increase in the number of chains initiated in the presence of 600 equiv of the main group alkyl as determined by GPC. Gray boxes indicate polymerization without transfer; dashes indicate no polymerization activity.

reaction mixtures containing [**1a**]NiPh(py) and 15 equiv of ZnEt$_2$ revealed decomposition to an intractable mixture of products, some of which contained alkylated imine arms (SI, Figure S11). Thus, it is likely that catalyst decomposition results at least partially from reduction of the Ni metal center initially through ligand alkylation. Polymerization attempts with the ketimine-ligated [**1c**]NiPh(py), which should be more resistant to alkylation, were too slow to generate analyzable quantities of polymer. Similarly, stoichiometric reactions between [**2a**]PdCl$_2$ activated with MAO and ZnEt$_2$ resulted in rapid precipitation of Pd^0, presumably through alkylation at the diimine ligand framework or at Pd followed by reductive elimination.

The initial screen indicated that only (α-diimine)Ni-based catalysts were competent for ethylene polymerization in the presence of some main group metal alkyls. When precatalyst [**2a**]NiBr$_2$ was activated with 500 equiv of MAO and polymerized with GaMe$_3$, InMe$_3$, or ZnEt$_2$, significant reductions in the molecular weight of the resultant polymer were observed, consistent with polymeryl chain transfer to the main group metal alkyl. ^{13}C NMR analysis (SI, Figures S5–S10) of the chain-transferred polymers showed that the polymers had the same microstructure as those generated without chain-transfer reagent, indicating that addition of main group metal alkyls does not change catalyst speciation. Similarly, catalyst activity remained relatively constant upon addition of CTRs. No vinyl end groups were observed by ^{13}C NMR, consistent with chain termination by bimetallic chain transfer instead of β-H elimination. The polymeryl chain-transfer events are likely irreversible on the time scale of catalysis because the resultant molecular weight dispersity does not narrow and the molar number of chains extended is substoichiometric with respect to the main group metal alkyl (e.g., 2.72×10^{-6} mol chains extended vs 6.00×10^{-5} mol ZnEt$_2$; see the SI, Table S1). This irreversibility could be a function of the inherent kinetics of chain transfer or due to physical factors such as precipitation of long-chain metal alkyls from solution.[53]

Of the examined main group alkyls, ZnEt$_2$ was most effective at chain transfer, giving significant reduction in polymer molecular weight and also a significant increase in the number of chains initiated per mol of Ni catalyst (SITable S1, entry 7), whereas both GaMe$_3$ and InMe$_3$ were only marginally effective (SI Table S1, entries 5 and 9). Conversely, the addition of

Table 2. Counteranion Effects on Ethylene Polymerization with (α-Diimine)-nickel and ZnEt$_2$[a]



entry	catalyst	equiv ZnEt$_2$[d]	yield (g)	activity (g mol^{-1} hr^{-1} × 10^{-5})	M_n (× 10^{-5})[e]	Đ	Mol (Zn-R)$_{ext}$ (× 10^7)[f]	chains/Ni[g]
1	[**2a**]NiMe$_2$/HBArF[b]	0	0.0867	4.34	3.87	2.01	–	1.12
2		60	0.0512	2.56	2.19	2.01	2.34	1.17
3		120	0.180	8.97	1.55	2.18	11.6	5.78
4		180	0.108	5.38	1.22	2.29	8.80	4.40
5		300	0.0755	3.78	1.07	2.48	7.06	3.53
6		500	0.111	5.54	0.654	2.25	16.9	8.47
7		720	0.0952	4.76	0.541	2.26	17.6	8.81
8		1020	0.132	6.58	0.385	2.19	34.2	17.1
9	[**2a**]NiBr$_2$/MAO[c]	0	0.112	11.2	7.17	2.31	–	1.61
10		60	0.128	12.8	4.29	2.64	3.03	3.03
11		120	0.130	13.0	3.35	2.25	3.92	3.92
12		180	0.121	12.1	2.65	2.22	4.64	4.64
13		300	0.124	12.4	1.94	2.20	6.40	6.40
14		500	0.182	18.2	1.33	2.13	13.8	13.8
15		720	0.164	16.4	0.975	2.14	16.9	16.9
16		1020	0.120	12.0	0.687	2.13	17.0	17.0

[a]All values are the average of at least 3 runs. [b]Conditions: 2×10^{-7} mol catalyst, stoichiometric activation with HBArF, 60 psi ethylene, room temperature, 1 h, toluene solvent (3.0 mL). [c]Conditions: 1×10^{-7} mol of catalyst, 500 equiv of MAO, 60 psi ethylene, room temperature, 1 h, toluene solvent (3.0 mL). [d]Equivalents of ZnEt$_2$ based on the amount of catalyst. [e]Determined by GPC. [f]Defined as the number of ethyl groups that has been extended with ethylene, determined by GPC. [g]The number of chains initiated per total molar amount of polymerization catalyst.

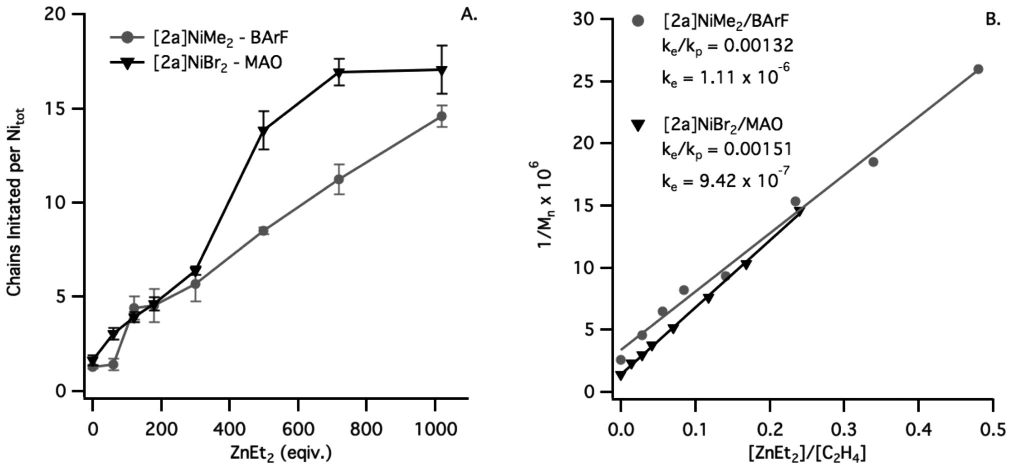
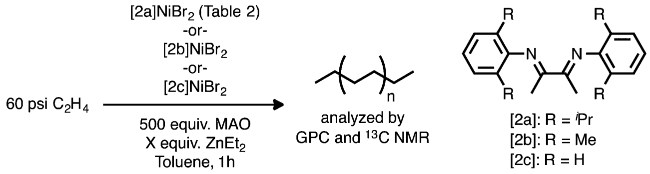


Figure 2. (A) Polymer chains initiated per nickel catalyst versus the amount of $ZnEt_2$ for [**2a**]$NiBr_2$/MAO and [**2a**]$NiMe_2$/[$H(OEt_2)_2$][BArF]. (B) Mayo plot of the counteranion effects on ethylene polymerization with (α-diimine)-nickel and $ZnEt_2$, and calculations of k_e/k_p and k_e for [**2a**]$NiBr_2$/MAO and [**2a**]$NiMe_2$/[$H(OEt_2)_2$][BArF].

Table 3. Catalyst Ligand Steric Effects on Ethylene Polymerization with (α-Diimine)-nickel Catalysts and $ZnEt_2$[a]



entry	catalyst	equiv $ZnEt_2$[b]	yield (g)	activity (g mol^{-1} hr^{-1} × 10^{-5})	M_n (× 10^{-5})[c]	Đ	Mol (Zn-R)$_{ext}$ (× 10^7)[d]	chains/Ni[e]
17	[**2b**]$NiBr_2$	0	0.199	19.9	1.52	2.37	–	13.1
18		60	0.180	18.0	1.31	2.56	13.8	13.8
19		120	0.299	29.9	1.12	2.41	26.7	26.7
20		180	0.216	21.6	0.953	2.46	22.7	22.7
21		300	0.178	17.8	0.689	2.39	25.8	25.8
22		500	0.189	18.9	0.506	2.17	37.2	37.2
23		720	0.179	17.9	0.406	2.08	44.1	44.1
24		1020	0.268	26.8	0.278	2.16	96.4	96.4
25	[**2c**]$NiBr_2$	0	0.135	13.5	0.00167	2.21	*f*	8110
26		60	0.0845	8.45	0.00166	2.32	*f*	5140
27		120	0.150	15.0	0.00174	2.23	*f*	8600
28		180	0.0940	9.40	0.00180	2.08	*f*	5280
29		300	0.0592	5.92	0.00197	1.98	*f*	3000
30		500	0.0727	7.27	0.00264	1.97	*f*	2880
31		720	0.0287	2.87	0.00245	1.88	*f*	1170
32		1020	0.0897	8.97	0.00269	2.59	*f*	3340

[a] All values are the average of at least 3 runs. Conditions: 1 × 10^{-7} mol of catalyst, 500 equiv of MAO, 60 psi ethylene, room temperature, 1 h, toluene solvent (3.0 mL). [b] Equivalents of $ZnEt_2$ based on the amount of catalyst. [c] Determined by GPC [d] Defined as the number of ethyl groups that has been extended with ethylene, determined by GPC. [e] The number of chains initiated per total molar amount of polymerization catalyst. [f] No chain transfer; only vinyl chain ends determined by ^{13}C NMR.

dialkylmagnesium reagents shut down polymerization catalysis entirely, presumably through irreversible alkylation of the Ni catalyst similar to the [**1*x***]Ni- and [**2a**]Pd-based catalyst systems. Addition of $AlEt_3$ resulted in direct reaction with the PEEK overhead stirring paddles, so no useful information was gained through these reactions (SI Table S1, entry 3). The efficacy of $ZnEt_2$ for chain transfer may be explained by examining bond dissociation energies of the main group metal alkyls: $ZnEt_2$ (155 kJ/mol) has a lower BDE compared with $AlEt_3$ (265 kJ/mol), $GaMe_3$ (259 kJ/mol), and $InMe_3$ (197 kJ/mol) and also a close energy match to a nickel−carbon bond (188 kJ/mol),[11,54−56] resulting in the potential for $ZnEt_2$ to facilely form bridging Zn−Ni heterobimetallic species.

Because $ZnEt_2$ was the most effective at chain transfer with [**2a**]NiX_2, this metal pairing was chosen for more in-depth study of the rate of chain transfer as a function of catalyst counteranion, steric bulk, ethylene pressure, and Zn−C BDE. The results of this more in-depth study are presented below.

Counterion Effects on Chain Transfer to $ZnEt_2$ with Ni α-Diimine Catalysts. First, the effects of the catalyst activator/counteranion on chain transfer to $ZnEt_2$ were investigated by polymerizing ethylene with either [(α-diimine)-NiMe]$^+$[MAO]$^-$ (generated from activating [**2a**]$NiBr_2$ with 500 equiv of MAO) or [(α-diimine)NiMe]$^+$[B(ArF)$_4$]$^-$ (ArF = 3,5-$(CF_3)_2C_6H_3$) (generated from activating [**2a**]$NiMe_2$ with 1 equiv of [$H(OEt_2)_2$]$^+$[B(ArF)$_4$]$^-$) and varying amounts of

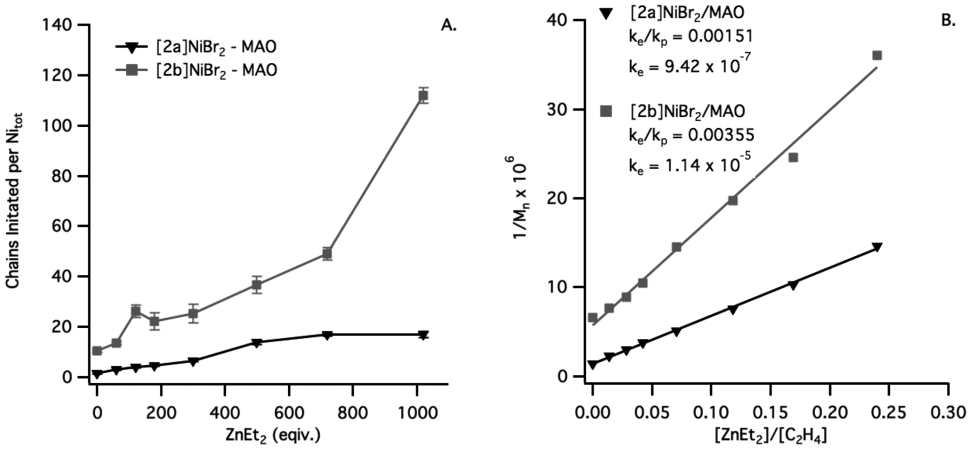


Figure 3. (A) Polymer chains initiated per nickel catalyst versus the amount of $ZnEt_2$ for [**2a**]$NiBr_2$/MAO and [**2b**]$NiBr_2$/MAO. (B) Mayo plot of the catalyst ligand steric effects on ethylene polymerization with (α-diimine)-nickel and $ZnEt_2$ and calculations of k_e/k_p, and k_e for [**2a**]$NiBr_2$/MAO and [**2b**]$NiBr_2$/MAO.

$ZnEt_2$ CTR. These similar catalyst species with different counteranions have differing rates of propagation with ethylene (as well as different polymer molecular weights and branching ratios), and thus, it was anticipated that the rate of bimolecular chain transfer with $ZnEt_2$ may also be counteranion-dependent.[57−59]

The results of the counteranion study are presented in Table 2 and Figure 2. Surprisingly, despite these two catalysts' having significantly different inherent rates of propagation as well as bimolecular chain termination, the counteranion has little to no effect on the relative rate of chain transfer to $ZnEt_2$: a Mayo plot[60] of both counteranion systems reveals the rates of chain transfer with Zn (k_e) to propagation (k_p): k_e/k_p = 0.00151 for [**2a**]$NiBr_2$/MAO and 0.00132 for [**2a**]$NiMe_2$/[$H(OEt_2)_2$]-[BArF]. By comparing these relative rates to the rate of propagation in the absence of chain-transfer agent, the absolute rate of chain transfer in each system can be determined: k_e = 1.11×10^{-6} M^{-1} s^{-1} ± 3.05×10^{-7} for [**2a**]$NiMe_2$/[$H(OEt_2)_2$][BArF] and k_e = 0.942×10^{-6} M^{-1} s^{-1} ± 1.21×10^{-7} for [**2a**]$NiBr_2$/MAO. Thus, the rate of bimetallic chain transfer from Ni to Zn is qualitatively affected by the nature of the counteranion in the same way that the rate of propagation with ethylene is affected: chain transfer is faster with the faster-propagating catalyst system [**2a**]$NiBr_2$/[$H(OEt_2)_2$][BArF], and slower with the slower-propagating [**2a**]$NiMe_2$/MAO.

Ligand Steric Effects on Chain Transfer to $ZnEt_2$ with Ni α-Diimine Catalysts. Using the (α-diimine)Ni catalysts [**2a**]$NiBr_2$, [**2b**]$NiBr_2$, and [**2c**]$NiBr_2$ activated with MAO, the influence of catalyst sterics on chain transfer to Zn was studied in the presence of 0−1020 equiv of $ZnEt_2$ (Table 3). In the case of both *ortho*-aryl disubstituted catalysts (R = *i*Pr, [**2a**]; R = Me, [**2b**]), the M_n of the produced polyethylene was reduced as a function of [$ZnEt_2$], indicating successful chain transfer from Ni to Zn. The polymerization activity, molecular weight dispersity, and polymer microstructure (^{13}C NMR) did not systematically vary across all [$ZnEt_2$] for each catalyst. Plots comparing the degree and rate of chain transfer in [**2a**]$NiBr_2$/MAO and [**2b**]$NiBr_2$/MAO are presented in Figure 3. Both catalyst systems show a linear dependence on the number of polymer chains generated per Ni and the [$ZnEt_2$]. The less sterically encumbered catalyst, [**2b**]$NiBr_2$/MAO, yields significantly more polymer chains per Ni in the presence of $ZnEt_2$ than [**2a**]$NiBr_2$/MAO (96.4 vs 17.0 with 1020 equiv of $ZnEt_2$). Although this could be a result of facile chain termination through β-H transfer, ^{13}C NMR analysis shows only polymers with saturated chain ends, indicating that the increase in the number of polymeryl chains per Ni is a result of bimetallic chain transfer to Zn.

Mayo plot analysis of the two catalyst systems also reveals a significant difference in the relative rates of chain transfer with Zn (k_e) to propagation (k_p): k_e/k_p = 0.00151 for [**2a**]$NiBr_2$/MAO and 0.00355 for [**2b**]$NiBr_2$/MAO. The absolute rates of chain transfer in these systems, calculated from k_p in the absence of $ZnEt_2$, also yield significant differences: k_e = 0.942×10^{-6} M^{-1} s^{-1} ± 1.21×10^{-7} for [**2a**]$NiBr_2$/MAO and 1.14×10^{-5} M^{-1} s^{-1} ± 4.42×10^{-7} for [**2b**]$NiBr_2$/MAO. Thus, unlike the counteranion study in which propagation and bimetallic chain transfer to Zn were similarly effected by the nature of the anion, in the case of catalyst sterics, the rate of bimetallic chain transfer to Zn (k_e) is significantly more sensitive to steric hindrance around Ni than propagation (k_p), and reducing steric hindrance from R = ^{i}Pr to R = Me results in a 10-fold increase in the absolute rate of chain transfer to Zn and 3-fold increase in the ratio of chain transfer to propagation. Presumably, this difference is a result of steric clash with $ZnEt_2$ having a significant impact on the stability of the resulting bridging bimetallic Ni−Et−Zn species compared with that of steric clashes on a simple Ni−ethylene adduct (Figure 4).

On the basis of the sensitivity of bimetallic chain transfer to catalyst sterics, it was expected that further reducing the catalyst steric bulk with the ortho-unsubstituted catalyst [**2c**]$NiBr_2$/MAO would yield even faster chain transfer to Zn. However, with [**2c**]$NiBr_2$/MAO, the M_n of the produced oligomers did

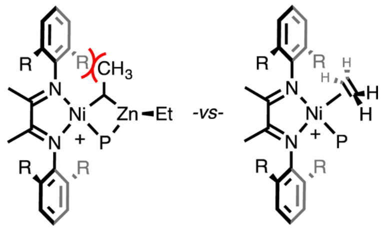
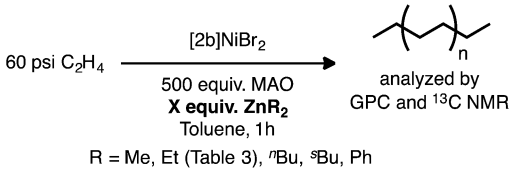


Figure 4. Diagram showing additional steric crowding around a potential Ni−Et−Zn bridged bimetallic intermediate compared with a Ni−ethylene adduct.

Table 4. Chain-Transfer Experiments with [2b]$NiBr_2$/MAO and ZnR_2[a]



entry	ZnR_2	equiv ZnR_2[b]	yield (g)	activity (g mol^{-1} hr^{-1} × 10^{-5})	M_n (× 10^{-5})[c]	*Đ*	Mol (Zn-R)$_{ext}$ (× 10^7)[d]	chains/Ni[e]
33	$ZnMe_2$	0	0.258	25.8	1.67	2.30	–	15.7
34		60	0.192	19.2	1.80	2.25	10.8	10.8
35		180	0.227	22.7	1.63	2.32	14.0	14.0
36		510	0.215	21.5	1.39	2.18	16.8	16.8
37		1020	0.170	17.0	0.783	2.11	21.8	21.8
38	Zn^nBu_2	0	0.290	29.0	1.62	2.58	–	18.1
39		60	0.329	32.9	1.62	2.51	20.5	20.5
40		180	0.307	30.7	1.39	2.47	22.3	22.3
41		510	0.356	35.6	1.00	2.15	35.5	35.5
42		1020	0.344	34.4	0.778	2.12	44.2	44.2
43	Zn^sBu_2	0	0.262	26.3	1.65	2.61	*f*	15.8
44		60	0.267	26.7	1.83	2.69	*f*	15.0
45		180	0.262	26.2	1.80	2.57	*f*	14.7
46		510	0.252	25.2	1.90	2.56	*f*	13.2
47		1020	0.214	21.4	1.97	2.31	*f*	10.9
48	$ZnPh_2$	0	0.295	29.5	1.61	2.52	*f*	18.4
49		60	0.181	18.1	2.19	2.35	*f*	8.25
50		180	0.110	11.0	2.42	2.26	*f*	4.63
51		510	0.0703	7.03	2.47	2.26	*f*	2.89
52		1020	0.0540	5.40	2.39	2.20	*f*	2.27
53	ZnMeEt[g]	0	0.194	19.4	1.80	2.59	–	10.8
54		500	0.229	22.9	1.17	2.22	19.8	19.8
55		1000	0.168	16.8	0.880	2.03	19.3	19.3
56		500[h]	0.219	21.9	0.775	1.99	28.2	28.2

[a] All values are the average of at least 3 runs. Conditions: 1 × 10^{-7} mol of catalyst, 500 equiv of MAO, 60 psi ethylene, room temperature, 1 h, toluene solvent (3.0 mL). [b] Equivalents of ZnR_2 based on the amount of catalyst. [c] Determined by GPC. [d] Defined as the number of ethyl groups that has been extended with ethylene, determined by GPC. [e] The number of chains initiated per total molar amount of polymerization catalyst. [f] No chain transfer implicated. [g] Generated in situ through the mixing of $ZnMe_2$ and $ZnEt_2$. [h] With an additional 250 equiv of $ZnEt_2$ added.

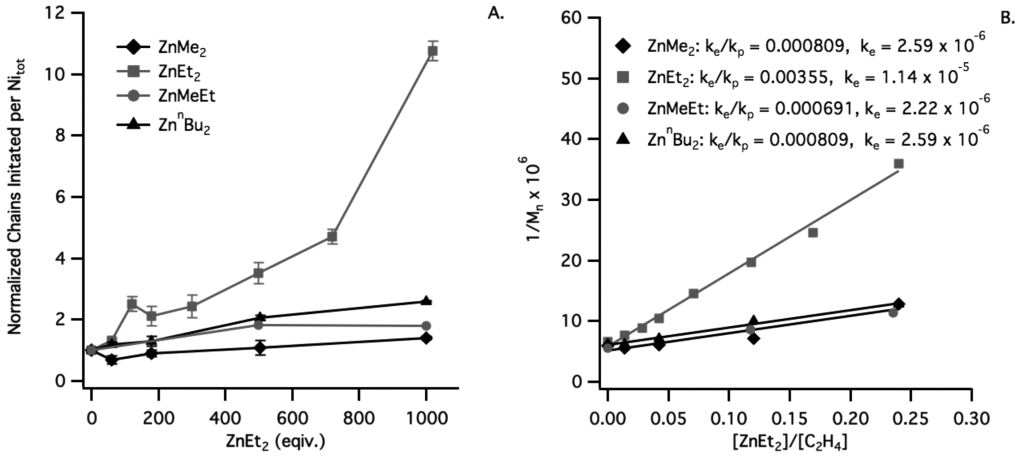
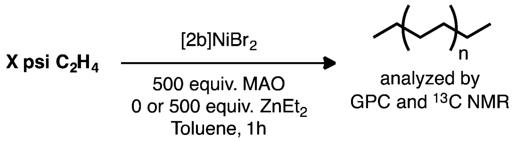


Figure 5. (A) Polymer chains initiated per nickel catalyst versus the amount of ZnR_2 for [**2b**]$NiBr_2$/MAO. (B) Mayo plot of polymerizations with catalyst [**2b**]$NiBr_2$ and various ZnR_2 (R = Me, Et, ^{n}Bu, ^{s}Bu, Ph) and calculations of k_e and k_p.

not reduce as a function of [$ZnEt_2$], and ^{13}C NMR analysis of the resulting oligomers revealed only vinyl-terminated chains. These vinyl chain ends indicate that [**2c**]$NiBr_2$/MAO does not undergo chain transfer with $ZnEt_2$ under these catalytic conditions; instead, chain-terminating via *β*-H transfer. With [**2c**]$NiBr_2$/MAO, the rates of propagation (k_p) and *β*-H transfer (k_t) are of similar magnitude; thus, even if the rate of bimetallic chain transfer in [**2c**]$NiBr_2$/MAO were an order of magnitude faster than in [**2b**]$NiBr_2$/MAO, it would still be at least 2 orders of magnitude slower than chain termination via *β*-H transfer and not kinetically relevant. [$ZnEt_2$] does appear to generally increase M_n with [**2c**]$NiBr_2$/MAO; however, the data

Table 5. Chain-Transfer Experiments with [2b]$NiBr_2$/MAO and $ZnEt_2$ at Various Ethylene Pressures[a]



entry	P_{ethylene} (psi)	equiv $ZnEt_2$[b]	yield (g)	activity (g mol^{-1} hr^{-1} × 10^{-5})	M_n (× 10^{-5})[c]	Đ	Mol (Zn-R)$_{\text{ext}}$ (× 10^7)[d]	chains/Ni[e]
57	15	0	0.184	6.13	0.836	2.17	–	7.36
58	15	500	0.143	4.76	0.0542	2.30	263	88.3
59	30	0	0.409	13.7	1.42	2.34	–	9.88
60	30	500	0.300	10.0	0.147	1.93	204	68.5
61	45	0	0.403	13.5	1.05	2.48	–	12.8
62	45	500	0.366	12.2	0.195	2.01	188	62.9
63	75	0	0.427	14.3	1.04	2.54	–	13.8
64	75	500	0.409	13.6	0.251	2.10	163	54.3
65	150	0	0.341	11.4	1.13	2.44	–	10.2
66	150	500	0.464	15.5	0.411	2.18	113	38.9
67	225	0	0.382	12.7	0.919	2.99	–	13.9
68	225	500	0.517	17.3	0.494	2.30	105	35.0

[a] All values are the average of at least 3 runs. Conditions: 3 × 10^{-7} mol of catalyst, 500 equiv of MAO, X psi ethylene, room temperature, 1 h, toluene solvent (3.0 mL). [b] Equivalents of $ZnEt_2$ based on the amount of catalyst. [c] Determined by GPC. [d] Defined as the number of ethyl groups that has been extended with ethylene, determined by GPC. [e] The number of chains initiated per total molar amount of polymerization catalyst.

are extremely noisy, and we choose not to speculate on this phenomena.

Steric and Electronic Effects of ZnR_2 on Chain Transfer with Ni α-Diimine Catalysts. Next, the effect of changing Zn alkyl sterics and electronics on the rate of chain transfer was investigated by polymerizing ethylene with [**2b**]$NiBr_2$/MAO in the presence of various ZnR_2 reagents (R = Me, Et, ^{n}Bu, ^{s}Bu, Ph).[61] The results of these polymerizations are presented in Table 4. As with earlier experiments with $ZnEt_2$, the overall polymerization activity and resultant polymer microstructure remain the same upon addition of ZnR_2, with the exception of $ZnPh_2$, which decreases activity as [$ZnPh_2$] increases, presumably because of irreversible Ni phenylation. However, $ZnEt_2$ is the *only* ZnR_2 species that results in significant chain transfer with [**2b**]$NiBr_2$/MAO, although both $ZnMe_2$ and Zn^{n}Bu$_2$ exhibit some chain-transfer capability.

Mayo plot analysis of the five ZnR_2 reagents is presented in Figure 5. Comparing k_e/k_p for $ZnEt_2$, Zn^{n}Bu$_2$, and Zn^{s}Bu$_2$ reveals that the absolute rate of chain transfer, k_e, is 4.4 times faster for $ZnEt_2$ than for the bulkier Zn^{n}Bu$_2$, whereas the bulkiest, Zn^{s}Bu$_2$, is at least 2 orders of magnitude slower and does not appear to chain-transfer on the time scale of catalysis. Thus, steric bulk of the main group alkyl plays a significant role in the rate of chain transfer with Ni catalysts. This trend could also explain why chain transfer to Zn appears irreversible: longer polymeryl chains or 2° polymeryl chains will be significantly slower to undergo subsequent chain back-transfers compared with $ZnEt_2$. Interestingly, addition of Zn^{s}Bu$_2$ results in an increase in M_n and a decrease in the number of polymer chains per Ni_{tot}. In this case, it may be that Zn^{s}Bu$_2$ inhibits β-H elimination/chain termination via reversible association to Ni without chain transfer.

Given this steric trend, it was expected that $ZnMe_2$ would chain-transfer faster than $ZnEt_2$; however, $ZnMe_2$ undergoes chain transfer with [**2b**]$NiBr_2$/MAO 4.4 times more slowly than $ZnEt_2$ ($k_e = 2.59 \times 10^{-6}$ M^{-1} s^{-1}). Calculations by Green have shown that the Zn−C bond in $ZnMe_2$ is aberrantly strong compared with other *Zn*-alkyl species;[62] thus, the likely cause for slow chain transfer with $ZnMe_2$ is that the stronger Zn−Me bond is thermodynamically disfavored to bridge to Ni, despite being more sterically accessible. This effect is further observed in chain-transfer attempts with ZnMeEt (generated in situ through mixing $ZnMe_2$ and $ZnEt_2$), which also has stronger Zn−C bonds than $ZnEt_2$: k_e is much lower for ZnMeEt (2.22 × 10^{-6} M^{-1} s^{-1}) than $ZnEt_2$. Furthermore, spiking ZnMeEt with excess $ZnEt_2$ restores chain-transfer activity (entry 56), indicating that strong Zn−C bonds do not significantly inhibit catalysis through coordination to Ni. Conversely, there is little difference in the BDE between $ZnEt_2$ and Zn^{n}Bu$_2$, leading to sterically dominated kinetics.

Compared with other polyethylene chain-transfer systems, this large stereoelectronic effect of ZnR_2 is surprising. For example, Gibson observed that there is virtually no difference in the rate of chain transfer between $ZnMe_2$ or $ZnEt_2$ and pyridyl(diimine)Fe polymerization catalysts;[7] Sita observed that the rate of transfer between Zn and Hf ethylene polymerization catalysts was similar with $ZnEt_2$ and Zn^{i}Pr$_2$;[63] and Brintzinger found negligible differences in chain transfer with early metal ethylene/norbornene chain-transfer catalysis and $ZnMe_2$ or $ZnEt_2$.[64] Clearly, (α-diimine)Ni-based catalysts are significantly more intolerant of steric and electronic mismatches than catalyst systems based on other metals, and developing efficient chain-transfer catalysis will require careful system design.

Ethylene Pressure Effects on Chain Transfer to $ZnEt_2$ with Ni α-Diimine Catalysts. Finally, using catalyst [**2b**]-$NiBr_2$/MAO the influence of pressure on chain transfer was studied in the presence of 500 equiv of $ZnEt_2$. Table 5 lists the results for polymerizations carried out under six ethylene pressures ranging from 15 to 225 psi, and Figure 6 shows a plot of the normalized chains initiated with $ZnEt_2$ versus without $ZnEt_2$ as a function of the ethylene pressure. Chain transfer is inhibited by ethylene pressure, reaching saturation kinetics near 100 psi C_2H_4. The inhibitory effect is greater than first order; however, given the large experimental errors at low pressure, this effect is best examined qualitatively. This inhibition should be expected if both ethylene and $ZnEt_2$ compete for coordination to the same 3-coordinate Ni polymeryl

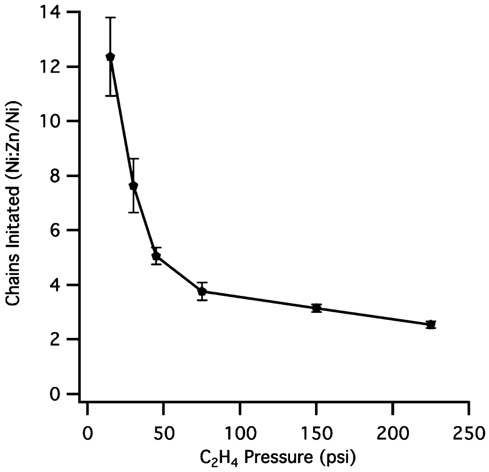


Figure 6. Number of chains initiated with $ZnEt_2$/the number of chains initiated in the control versus the pressure of ethylene using [**2b**]$NiBr_2$/MAO.

intermediate (Figure 7). Interestingly, by varying [$ZnEt_2$] and $P_{ethylene}$, the resulting polymer, M_n, can be tuned across extremely wide ranges (5400−140 000).

CONCLUSIONS

A survey of the ability of various group 10 α-diimine and salicylaldimine polymerization catalysts to undergo chain transfer with main group metal alkyls during ethylene polymerization has revealed that many of the catalysts are poor systems for chain-transfer catalysis. However, (α-diimine)Ni-based catalysts are competent for chain transfer in the presence of $ZnEt_2$, and an in-depth analysis of the electronic and steric parameters of these systems has revealed that chain transfer is highly dependent on the sterics of both the α-diimine ligand and the Zn alkyl. Unlike many other chain-transfer polymerization systems with Zn, the Zn−C bond strength also plays an important role with (α-diimine)Ni catalysts, because strong Zn−C bonds such as those in $ZnMe_2$ are extremely slow to transfer. Despite these strong stereoelectronic effects, the cocatalyst/anion plays only a small role in the relative rates of chain transfer because propagation and chain transfer are affected in similar ways. Modulation of the rate of propagation by reducing ethylene pressure results in more chain transfer, allowing for significant variation of the resulting polymer molecular weight.

Although chain transfer from Ni to Zn is slower than many previously reported systems, the surprisingly large stereoelectronic effects of both catalyst and chain-transfer agent indicate that, with prudent catalyst system design, it may be possible to finely tune and exploit chain transfer with group 10 metal complexes in much the same way as early or midtransition metal polymerization catalysts.

ASSOCIATED CONTENT

Supporting Information

Tabulated results from all of the individual polymerizations, gas uptake kinetic data, GPC traces, ^{13}C NMR spectra, ^1H NMR spectra of the reaction of [**1a**]$NiPh(PPh_3)$ with $ZnEt_2$, ^1H NMR spectra of the reaction of MAO with $ZnEt_2$, and calculations for all reported k_e and k_p values. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support was provided by the University of Minnesota (start-up funds). M.P.C. acknowledges funding from the University of Minnesota Department of Chemistry Heisig/Gleysteen Undergraduate Research Program. Equipment purchases for the Chemistry Department NMR facility were supported through a grant from the NIH (S10OD011952) with matching funds from the University of Minnesota. We acknowledge the Minnesota NMR Center for high-temperature NMR. Funding for NMR instrumentation was provided by the Office of the Vice President for Research, the Medical School, the College of Biological Science, NIH, NSF, and the Minnesota Medical Foundation. We thank John Walzer (ExxonMobil) for a gift of PEEK high-throughput stirring paddles.

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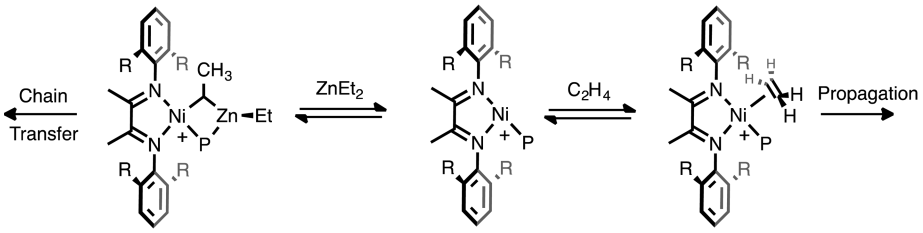

Figure 7. Schematic drawing of the competition between $ZnEt_2$ and C_2H_4, yielding C_2H_4 inhibition of chain transfer.

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