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J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/ja403626g • Publication Date (Web): 15 May 2013

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Synthesis of Telechelic Olefin Polymers via Catalyzed Chain Growth on Multinuclear Alkylene Zinc Compounds

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Supporting Information Placeholder

ABSTRACT: Multinuclear alkylene zinc compounds (MAZ) of the type EtZn-(R"-Zn)$_n$-Et (R": ethyl and propyl branched alkylene groups) were synthesized by a simple one-step procedure in non-polar hydrocarbon solvents from α,ω-dienes (e.g., 1,7-octadiene or 1,9-decadiene) and diethylzinc (DEZ) using a bis(salicylaldiminato)Zr(IV) complex, [(2-methylcyclohexyl)N=CH(2-O-C_6H_3-3,5-*ditert*-butyl)]$_2$ZrCl$_2$ (**1**), as a catalyst. The MAZ serve as a divalent reversible chain transfer agent for olefin polymerization, resulting in telechelic Zn-metalated polyolefins whose molecular weights are controllable over a wide range. The Zn-terminated telechelics serve as a polymer precursor for further reactions and can be converted into a variety of telechelic functionalized polyolefins in high yield.

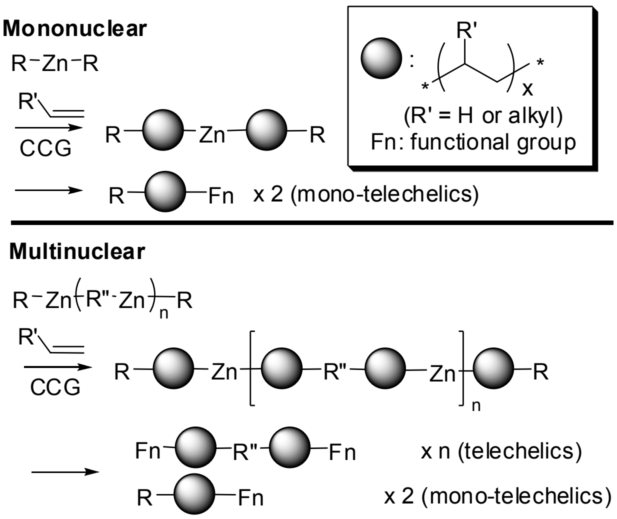
Telechelic polymers refer to macromolecules possessing two well-defined reactive functional groups situated at the chain termini.[1] Progress in single-site transition metal catalyzed polymerization of non-polar olefins such as ethylene and propylene has allowed the synthesis of polyolefins having unprecedented structural features such as monodisperse molecular weight polyolefins, olefin block copolymers, ethylene copolymers with vinyl functionalized monomers, and hyper-branched polyolefins.[2] Nevertheless, research on telechelic polyolefins with well-defined structures has been rather limited, for example, (a) The pyrolysis of high molecular weight polypropylene,[3] (b) The metathesis degradation of polybutadienes followed by functionalization and hydrogenation, resulting in a telechelic polyethylene (PE),[4] (c) ROMP in the presence of an acyclic internal olefin as a chain transfer agent (ROMP-CT)[1,5] which also requires subsequent hydrogenation to form a telechelic PE, and (d) Living polymerization using functionalized initiators followed by chain-end capping.[6] In our own research efforts, we have developed a series of robust living polymerization catalysts with bis(salicylaldiminato)Ti complexes (Ti-FI catalysts) bearing fluorinated *N*-aryl groups.[7] The active species derived from the fluorinated Ti-FI catalysts are well-defined and thermally so robust that functional initiators can be quantitatively prepared *in situ* via single insertion of functionalized α-olefins to the living Ti-Me species and also living chain ends can be quantitatively functionalized after polymerization.[6b] However, the living polymerization protocol inherently imposes some restrictions, namely 1) One catalyst molecule forms only one polymer chain; and 2) It is difficult to apply to an industrially relevant continuous processes. These drawbacks result in significant cost disadvantages for large scale manufacturing. Likewise, all the approaches raised above have some shortcomings in terms of reachable molecular weights, applicable main chain structures, and the variety of chain-end functional groups.

Catalyzed chain growth (CCG) on main group metals is a process in which a reversible transmetallation takes place between transition metal alkyl species responsible for chain propagation and main group metal alkyls.[8] Polymer chains carried by main group metals are inactive for polymerization and subject to chain growth only when transferred back to a catalytically active transition metal species through transmetallation. The transmetallation occurs at a statistically equal probability at a comparable rate to chain propagation for all main group metal alkyls, and thus CCG affords polymers with a Poisson distribution that are quantitatively capped with the main group metals. Unlike living polymerization, CCG requires a much less stoichiometric amount of transition metal catalyst to polymer chains and can also operate in a continuous process. Hence, a catalyzed chain growth on zinc has been successfully applied to the manufacturing of olefin block copolymers on an industrial scale.[9] Recently, Boisson and D'Agosto reported that telechelic PE was successfully prepared using CCG with bis(10-undecenyl)magnesium and a neodymium catalyst.[10] Although it works well, the obtained telechelic polymers were limited to PE as the Nd catalyst could polymerize only ethylene, and the PE molecular weights remained at M_n~1,500, presumably, I believe, to avoid precipitation of high molecular weight PE (polymerization was carried out at 75 °C).

In this article, we would like to present a new process enabling a catalytic synthesis of high molecular weight telechelic polyolefins via CCG in the presence of multinuclear alkylene zinc compounds (MAZ) to provide a solution for the problems described above. We believe that our method displays advantages over that of Boisson and D'Agosto because we can obtain a higher molecular weight range, a more versatile main chain structure, and a higher polymerization activity.

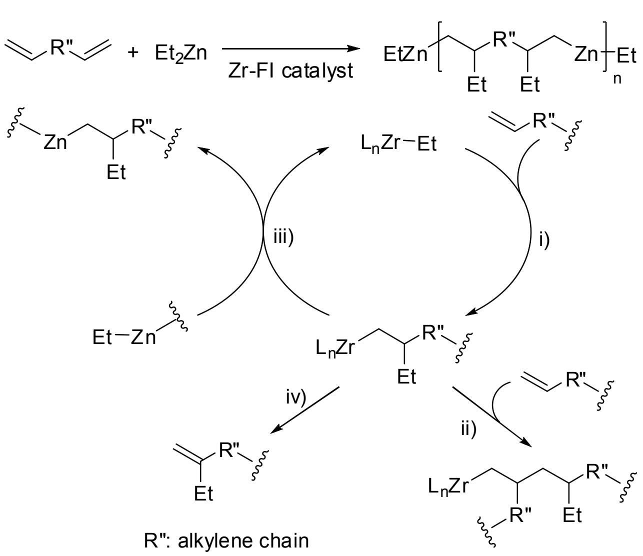
In CCG with dialkylzinc, the divalent zinc metal carries two polymer chains and these polymers are considered to be end functionalized with zinc albeit only at one chain end (mono-telechelic, Scheme 1). If the alkyl groups on zinc in this polymerization are substituted with divalent alkylene groups (-R"-) having two Zn-C bonds in one molecule, telechelic polyolefins should result, in theory (Scheme 1). However, synthesis of such divalent alkylene multinuclear metal compounds is not straightforward. If one tries to apply common practices for the synthesis of alkylzinc compounds (alkylation of zinc halides, transmetallation of alkylboranes and Et_2Zn, etc.) to divalent alkylene zinc compounds, the challenges to be involved are: 1) Commercial unavailability of divalent alkylene metal agents (M-R"-M, M: main group metal); 2) Multistep reactions including purification; 3) Low atom economy (formation of metal halide salts or BEt_3); 4) Possible use of oxygen-containing polar solvents which cause adverse impacts in subsequent polymerization steps even if only a minute amount is carried over.

Scheme 1. CCG with mono- and multinuclear zinc compounds



Since olefin insertion to an M'-C bond is a facile and atom-economic reaction to form C-C and C-M' bonds simultaneously (M': transition metal), we envisioned the following reactions to prepare multinuclear alkylene zinc compounds (MAZ) to address all the challenges discussed above (Scheme 2).

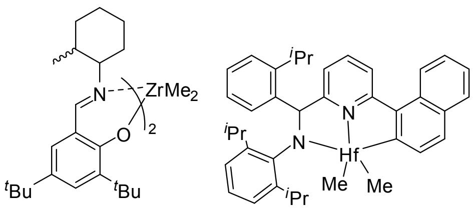
Scheme 2. Synthesis of multinuclear alkylene zinc via polyaddition reaction



The overall reaction is a polyaddition reaction between two bifunctional monomers, i.e., α,ω-dienes (e.g., 1,7-octadiene or 1,9-decadiene) and diethylzinc ($ZnEt_2$). The reaction is catalyzed by an olefin polymerization catalyst through repetitive olefin insertion and transmetallation until all vinyl groups or Zn-Et groups are consumed. The degree of polymerization, "*n*", can be determined by molar ratios of diene and $ZnEt_2$ (DEZ) and high molecular weight products will result when DEZ/diene is close to one (DEZ/diene = 1.0). When DEZ/diene > 1, the polymer chain ends will be exclusively $Zn-CH_2CH_3$. In the opposite cases (DEZ/diene < 1), the vinyl groups will remain at the chain ends, which can be engaged in olefin polymerization in the next step when used as a chain transfer agent (CTA), resulting in long chain branching.

There are several key criteria to select an appropriate catalyst for this reaction: 1) High efficiency for olefin insertion (path i); 2) Prohibitive second olefin insertion (path ii); 3) Rapid transmetallation (path iii); 4) Negligible β-H transfer reaction (path iv). Complex **1** [(2-methylcyclohexyl)N=CH(2-O-C_6H_3-3,5-*ditert*-butyl)]$_2$$ZrMe_2$ (Chart) and MAO/borate cocatalysts are highly active toward ethylene polymerization and yet very sensitive to steric environments and thus two consecutive insertions of higher α-olefins are practically impossible.[11] In addition, this catalyst is also capable of CCG on Zn, meaning that transmetallation with alkylzinc is much more facile than the second monomer insertion. Lastly, the catalyst affords very high molecular weight PE,[12] which fulfills requirement 4).

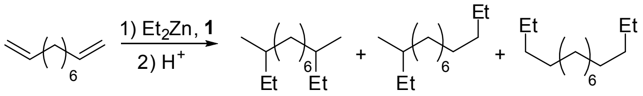
CHART. Catalyst precursors capable of CCG on zinc alkyls



1 **5**

The reactions using 1,9-decadiene and DEZ were carried out in hexane in the presence of **1** and MMAO/$Ph_3CB(C_6F_5)_4$. The products were hydrolyzed and the organic layer was analyzed by gas chromatography (Table 1).

TABLE 1. Synthesis of multinuclear alkylene zinc[a]



2 **3** **4**

entry	complex **1** mmol/L	1,9-decadiene mol/L	DEZ equiv.[b]	2 %[c]	3 %[c]	4 %[c]
1	2.0	0.2	2.1	74	24	2
2	2.0	0.2	1.5	74	24	2
3	1.2	0.12	1.5	76	22	2
4[d]	1.2	0.12	1.5	92	8	0
5[e]	2.5	0.50	1.1	79	20	1

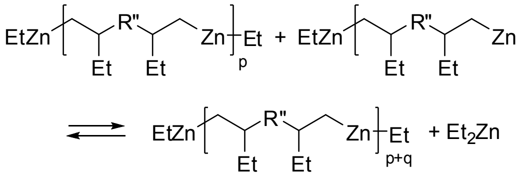
[a]Reactions were carried out at 20 °C for 30 min in hexane using MMAO and $Ph_3CB(C_6F_5)_4$ as cocatalysts (Zr/Al/B=1/14− 20/2 molar ratio). [b]To 1,9-decadiene. [c]GC area ratios. [d]Reaction at 0 °C. [e]dMAO instead of MMAO.

Within 30 min, 1,9-decadiene was completely consumed. Upon hydrolysis, three products were identified with a different regiochemistry regarding Zn-C bond addition over two double bonds in the diene, namely, 1,2-1,2 adduct (**2**), 1,2-2,1 adduct (**3**), and 2,1-2,1 adduct (**4**). The selectivity for 1,2-addition is about 87% (0.87×0.87=0.75) at 20 °C, which increases to 96% at 0 °C (entry 4). The products derived from multiple diene insertions (path ii), cyclization, insertion only at one vinyl group of diene (the other one is left untouched), and β-H elimination resulting in a vinylidene group (path iv), were not detected.[13]

A portion of the products (entry 4) was taken and the solvents were distilled off to take NMR spectra. The broad signals that appeared in ^{1}H NMR spectrum support the polymeric nature of the products. Neither the signals for DEZ nor any unsaturated bonds are discernible.[14] The ^{13}C NMR spectrum was complicated due to the mixed isomeric units but the signals for the main isomeric unit can be assigned.

The ^{13}C signals for Zn-CH_2CH_3 appear at δ 10.4 (C_β) and 7.4 (C_α), which are similar but clearly distinguishable from the ones for DEZ (δ 10.3, 6.7) that are not observed in the product.[14] However, the peak intensity of Zn-Et is clearly smaller than the one expected from the molar ratio of the reactants. Furthermore, when fresh DEZ was added to this NMR sample, the signals for DEZ did not appear. These observations suggest that there is a rapid equilibrium between each MAZ molecule as shown in Scheme 3. Therefore, upon removal or addition of DEZ the degrees of polymerization ("*n*" in Scheme 2) are controllable. In fact, the degree of polymerization can reach as high as *n* = 40 or higher after excessive removal of DEZ under a high vacuum by shifting the equilibrium in Scheme 3 to the right.

Scheme 3. Equilibrium between MAZ species



The MAZ prepared by this method was then applied for ethylene polymerization. We selected complex **1** as an ethylene polymerization catalyst because it is capable of performing well-controlled CCG with DEZ. The polymerization results are compiled in Table 2. Complex **1** yielded high molecular weight PE having reasonable molecular weight distribution at high activity in the absence of any CTA (entry 6). In the presence of DEZ under otherwise the same conditions, the molecular weight of PE dropped dramatically and molecular weight distribution narrowed without significant changes in activity (entry 7), which is in line with the efficient CCG. When MAZ was employed instead of DEZ (entry 8), the polymerization afforded PE with similar molecular weight distribution at comparable activity but the molecular weight became higher than the PE derived from DEZ. This would be in accordance with our hypothesis, where polymers that are linked by alkylene groups in MAZ should have a molecular weight about twice as high as those generated from Zn-Et bonds (Scheme 1).

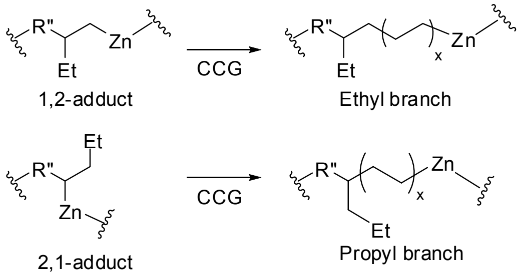
TABLE 2. Ethylene polymerization with complex 1 in the presence of zinc-based CTA[a]

entry	CTA	[Zn], mM	activity[b]	M_n[c]	M_w/M_n[c]
6	none	0	12.0	19940	1.70
7	DEZ	0.12	10.7	5770	1.46
8	MAZ[d]	0.12	11.2	7950	1.46
9	MAZ[e]	0.48	8.6	1990	1.78

[a] Reactions were carried out at 120 °C for 10 min under 0.7 MPa of ethylene pressure in hexane (5 mL as total volume) using MMAO and $Ph_3CB(C_6F_5)_4$ as cocatalysts (Zr/Al/B=0.0002/0.020/0.0008 mmol). [b] In kg-PE/mmol-Zr h. [c] Detemined by GPC (PE calibration). [d] The product from entry 2. [e] The product from entry 5.

In order to examine whether MAZ units are incorporated into polymer chains, low molecular weight PE was prepared by increasing the concentration of MAZ (entry 9). After hydrolysis, microstructures of the PE were investigated by ^{13}C NMR,[14] which revealed ethyl and propyl branches at 89/11 molar ratio aside from major *n*-butyl chain ends. No *sec*-butyl branches were observed. The regio-selectivity of the Zn-Et addition at 20 °C was about 87/13 for 1,2- and the 2,1- addition as discussed above. Since each regiochemistry results in ethyl and propyl branches upon multiple insertions of ethylene monomers between Zn-C bonds (Scheme 4), the observed branch composition demonstrates that CCG from primary Zn-C bonds (1,2-adduct) and secondary Zn-C bonds (2,1-adduct) is equally facile under the conditions and that Zn-bound alkylene groups in MAZ serve as an efficient divalent chain transfer agent.

Scheme 4. Branch formation derived from MAZ



To further confirm the formation of telechelic PE capped with Zn and to obtain telechelic end-functionalized PE, chemical conversion of the Zn-C bonds were attempted using a highly reactive acyl chloride. When ethyl succinyl chloride (ESC) was added at 6 equivalents to Zn at 120 °C after the polymerization, the Zn-CH_2- bonds were converted to $EtOCOCH_2CH_2COCH_2$- at 89-96% estimated by ^{1}H NMR. A typical example is shown in Figure 1. For this particular example, the functionality (F_n(%)/100: functionalized chain ends/all chain ends) can be estimated at F_n= 82% from the ^{1}H NMR integral ratios of all the methyl groups appearing around δ 0.8-0.95 ppm (chain ends that are not functionalized and branches derived from alkylene groups of MAZ) and the 4-ethoxy-4-oxobutanoyl group of ESC. The DEZ/diene ratio of MAZ used in this polymerization is 1.098 (determined by ^{1}H NMR as a mixture of reactants), from which theoretical values, *n*=10.2 and F_n=83.6% are elucidated. The observed F_n (82%) is slightly lower than the theoretical value possibly because the minor chain transfer to MAO (or trimethylaluminum) is included therein.

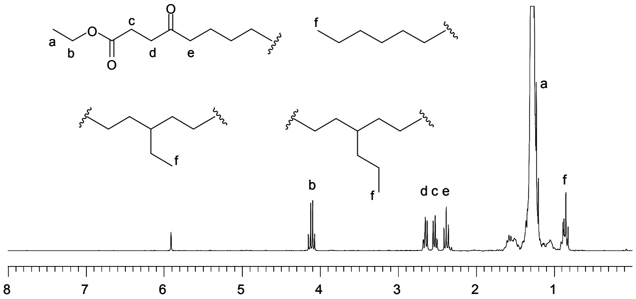


FIGURE 1. ^{1}H NMR spectrum of a telechelic PE equipped with 4-ethoxy-4-oxobutanoyl group at 82% functionality in $C_2D_2Cl_4$ at 120 °C (entry 9 in Table 2).

The MAZ we so far used for polymerization includes active complex **1** albeit in small amounts, which will irreproducibly cause unwanted polymeric byproducts when a catalyst other than **1** is used in a subsequent polymerization. Besides, the MAO remaining in MAZ may decrease the F_n values by serving as univalent CTA. Therefore, complex **1** was anchored onto SiO_2-supported MAO and the heterogenized complex **1** was used as a catalyst to prepare MAZ in the absence of additional cocatalysts such as MAO or borate. The reactions are as efficient as homogeneous catalyst **1** and after the heterogeneous catalyst was filtered off, the remaining MAZ has no color (unlike the red to orange homogeneous catalyst system, Figure 2) and contains only a minute amount of aluminum or zirconium (below 0.1% relative to Zn where [Zn] is around 0.5 M). In addition, the filtered heterogeneous catalyst can be reused for MAZ preparation several times over.

FIGURE 2. MAZ prepared with homogeneous **1**/MMAO/ $Ph_3CB(C_6F_5)_4$ (left) and with SiO_2-supported **1**/MAO (right).

The MAZ prepared with the heterogeneous catalyst was tested with hafnium pyridyl-amide complex **5**, which is known to be a good comonomer incorporator and also capable of polymerizing olefins in a well controlled CCG fashion.[9] In copolymerization of ethylene and propylene followed by reaction with ESC, telechelic elastomer terminated by ester groups was successfully synthesized (Activity: 133.4 kg-polymer (mmol-Hf h)$^{-1}$; M_w (PSt): 39,000; M_w/M_n: 2.13; Propylene content (IR): 25.1 mol%, due to the overlapping signals at 1,100-1,200 cm^{-1}, the value may not be accurate.).

In conclusion, we have developed a simple and efficient one-pot method to synthesize multinuclear alkylene zinc compounds (MAZ) from DEZ and diene using a Zr-FI catalyst. The degree of polymerization of MAZ can be controlled either by adjusting the DEZ/diene molar ratios or by adding or removing DEZ afterward to shift the equilibrium. MAZ can also be prepared by heterogenized **1**/MAO/SiO2 catalysts, where the obtained MAZ has no Al or Zr contaminations in the liquid phase. MAZ can serve as a reversible divalent chain transfer agent in CCG reactions, yielding telechelic zinc metalated polyolefins in high efficiency. Molecular weights of the telechelic Zn polymers are controllable by adjusting [olefins]/[Zn] molar ratios and reach at least M_n ~10^4. Main chain compositions can be varied from crystalline polyethylene to elastic ethylene-α-olefin copolymers, and possibly to isotactic polypropylene.[15] Unlike living polymerization, the telechelic polyolefin manufacturing technology developed in this study will be applicable to an industrial continuous solution tank reactor process just by replacing common metal alkyls with MAZ. The obtained Zn-terminated telechelic polyolefins are highly reactive and versatile polymer precursors which can be converted to end-functionalized polyolefins at high yield.

ACKNOWLEDGMENT

H.M. would like to thank Munehito Funaya, Kouji Endo, Mayumi Hiwara and Katsuyuki Harada for their technical support and helpful suggestions.

ASSOCIATED COMMENT

Supporting Information Available: NMR spectra and GPC elution curves. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) The absence of the byproducts was confirmed using GC-MS and NMR. Cyclic products for 1,7-octadiene and 1,9-decadiene were not observed while 1-ethyl-3-methylcyclopentane was detected after hydrolysis when 1,5-hexadiene was used.
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