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Communications to the Editor

exo-Methylene-Functionalized Polyethylenes via Ring-Opening Ziegler Polymerization. Product Control in Organolanthanide-Catalyzed Methylenecyclopropane Polymerization/Copolymerization

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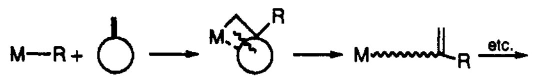
The introduction of polar and/or reactive functional groups into polyolefins via Ziegler–Natta processes is an attractive yet, with the recent exception of "masked"[1] or borane[2] comonomers, presently unrealized goal. A possible new approach to this problem, yielding *exo*-methylene-functionalized polyethylenes, would involve harnessing β-alkyl shift processes[3] at electrophilic d^0 metallocene centers to effect the polymerization of methylenecycloalkanes by coupling strained monomer ring-opening to olefin insertion (eq 1).[4] In the case of cationic zirconocene catalysts and methylenecyclobutane, we recently demonstrated facile, homogeneous copolymerization with ethylene as well as homopolymerization, to afford *exo*-methylene-functionalized polyethylenes.[4] These observations raise questions about generality, and we report here on efforts to broaden the scope of such processes using highly reactive, efficiently prepared (accessible in one step from methallyl chloride)[5] methylenecyclopropane and organolanthanide catalysts of the type $(Cp'_2LnH)_2$ ($Cp' = \eta^5\text{-}Me_5C_5$; Ln = lanthanide),[3a,6] the activities of which can be significantly varied with the Ln^{3+} ionic radius.[6b,7]



(1)

Copolymerization reactions with ethylene were carried out by rapidly stirring dilute toluene solutions of the catalyst and methylenecyclopropane under 1 atm of ethylene using rigorously anhydrous/anaerobic procedures. After measured time intervals, reactions were quenched with methanol and the polymeric products collected by filtration, washed with acetone, and dried in vacuo. Polymer characterization was by ^{1}H/^{13}C NMR and GPC. The results (Table 1) indicate that both the Ln = Sm and Lu hydrides are highly active copolymerization catalysts and that sizable (unoptimized) molecular weights can be achieved with unexceptional polydispersities for these types of catalysts and reaction conditions.[7a,b]

The incorporation of *exo*-methylene units in the copolymers (Scheme 1) is confirmed by a sharp signal at δ 4.8 in the ^{1}H NMR (Figure 1), while the absence of upfield features in the δ 0.1–0.5 region argues that ring-unopened (cyclopropane) units have not been incorporated (also confirmed by ^{13}C NMR). Since the polymer sample in Figure 1 was derived from reaction at a relatively high methylenecyclopropane concentration (Table 1, entry 4), NMR spectral features assignable to adjacent ring-opened monomer subunits are also evident (Figure 1, signal b). This feature is not evident (or is diminished) in samples prepared at lower methylenecyclopropane concentrations and can also be correlated with an analogous reasonance in the ^{1}H NMR of the homopolymers (vide infra).

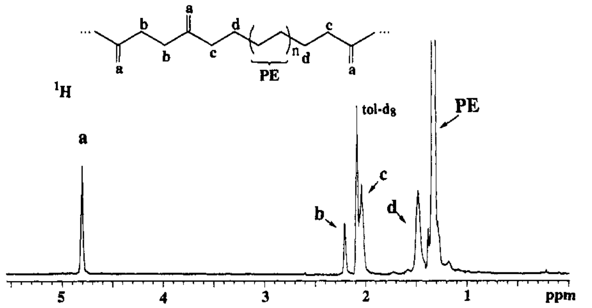


Figure 1. ^{1}H NMR spectrum (400 MHz, toluene-d_8, 130 °C) of the ethylene–methylenecyclopropane copolymer from Table 1, entry 4.

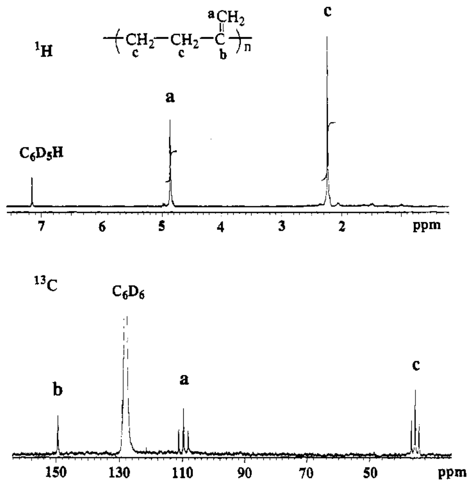
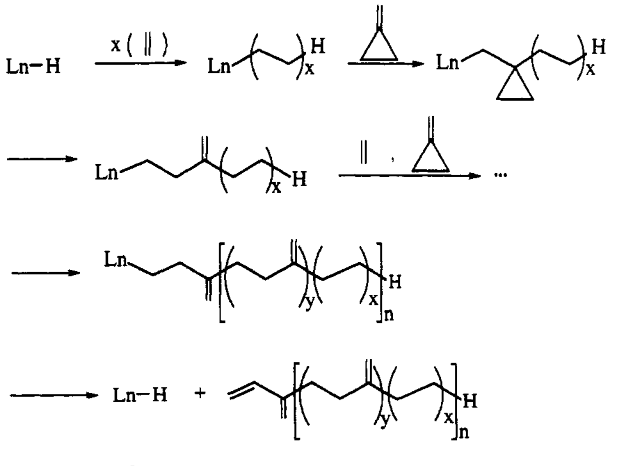


Figure 2. ^{1}H and proton-coupled ^{13}C NMR spectra (400 and 100 MHz, respectively; benzene-d_6, 20 °C) of the homopolymer from the $(Cp'_2LuH)_2$-catalyzed polymerization of methylenecyclopropane.

Scheme 1



The homopolymerization of methylenecyclopropane in the presence of $(Cp'_2LuH)_2$ proceeds cleanly to afford the

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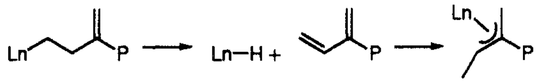
Table 1. Copolymerization of Methylenecyclopropane with Ethylene Using a $(Cp'_2LnH)_2$ (Ln = Sm, Lu) Catalysts[a]

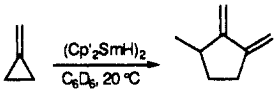
entry	catalyst amount (μmol)	methylene-cyclopropane (mL)[b]	ethylene pressure (atm)	reaction time (h)	yield of polymer (g)	activity (g of polymer/mol of Ln h)	no. of *exo*-methylenes per 1000 $-CH_2-$ units[c]	M_w (M_n)[d] (×1000)
1	21.4 (Sm)	0.25	1.0	0.10	0.42	2.0×10^5	4.2	184 (42)
2	21.4 (Sm)	0.50	1.0	0.17	0.45	1.2×10^5	10	13 (7)
3	33.6 (Lu)	0.50	1.0	0.10	0.60	1.8×10^5	33	92 (26)
4	33.6 (Lu)	2.50	1.0	0.10	0.47	1.4×10^5	65	66 (29)

[a] In 15 mL of toluene at 20 °C. [b] Measured at −78 °C. [c] Determined by ^1H NMR. [d] GPC in 1,2,4-trichlorobenzene vs polystyrene.

ring-opened, *exo*-methylene product as assessed by ^1H and ^{13}C NMR (Figure 2). However, polymer yields are low and the polymerization process ceases before monomer consumption is complete. That this loss in activity is not due to poisoning by trace impurities is confirmed by the observation that ethylene addition at this stage rapidly initiates copolymerization. We suggest that the deactivation may involve β-H elimination/readdition[7a] to afford less reactive (but not inert with respect to small olefin insertion)[3a,7a,b] η^3-allyl products via a 1,3-diene intermediate (e.g., eq 2).[7a,8] In marked contrast to this result, the larger Sm^{3+} ion cleanly effects catalytic methylenecyclopropane *dimerization* to yield known 1,2-dimethylene-3-methylcyclopentane (1),[9] identified by $^1H/^{13}C$ NMR and high-resolution MS (eq 3).[10] At 5.0 mM $(Cp_2SmH)_2$ and 1.0 M methylenecyclopropane, $N_t \approx 20$ h^{-1} at 25 °C. A plausible scenario for the formation of 1 again invokes β-H elimination and the intermediacy of a free (or coordinated) 1,3-diene fragment (Scheme 2).



(2)



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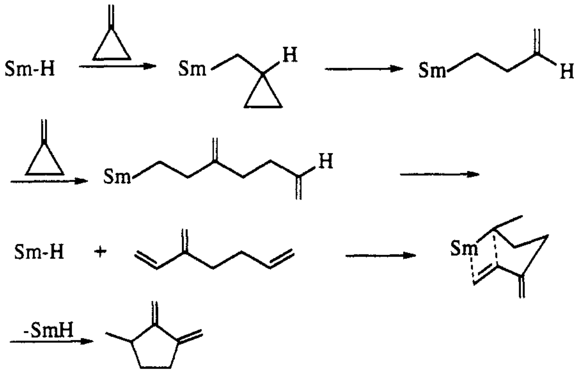
(3)

Scheme 2



In summary, these results represent an attractive elaboration of the scope of *exo*-methylenecycloalkane ring-opening Ziegler polymerization. Both a more readily available and reactive monomer as well as tunable organo-f-element catalysts are shown to be compatible with such routes to *exo*-methylene-functionalized polyolefins.

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References and Notes

(1) (a) Kesti, M. R.; Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 9679–9680 and references therein. (b) Datta, S. In *High Value Polymers*; Fawcett, A. H., Ed.; The Royal Society of Chemistry: Cambridge, U.K., 1991; pp 37–57 and references therein.

(2) (a) Chung, T. C. *Macromolecules* **1988**, *21*, 865–867. (b) Chung, T. C. *CHEMTECH* **1991**, *21*, 496–499 and references therein.

(3) (a) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51–55. (b) Bunel, E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976–978. (c) Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701–7715.

(4) Yang, X.; Jia, L.; Marks, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 3392–3393.

(5) (a) Köster, R.; Arora, S.; Binger, P. *Angew Chem., Int. Ed. Engl.* **1969**, *8*, 205–206. (b) Salaun, J. R.; Champion, J.; Conia, J. M. *Org. Synth.* **1977**, *57*, 36–40.

(6) (a) Mauermann, H.; Marks, T. J. *Organometallics* **1985**, *4*, 200–202. (b) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111–8118. (c) Heeres, H. J.; Renkema, J.; Booji, M.; Meetsma, A.; Teuben, J. H. *Organometallics* **1988**, *7*, 2495–2502. (d) Molander, G. A.; Hoberg, J. O. *J. Org. Chem.* **1992**, *57*, 3266–3268.

(7) (a) Jeske, G.; Lauke, H.; Mauermann, H.; Sweptson, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091–8103. (b) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103–8110. (c) Gagné, M. R.; Stern, C.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275–294.

(8) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 2314–2324 and references therein.

(9) Blomquist, A. T.; Wolinsky, J.; Meinwald, Y. C.; Longone, D. T. *J. Am. Chem. Soc.* **1956**, *78*, 6057–6063.

(10) ^1H NMR (toluene-d_8, 20 °C): δ 1.02 (d, ^3J = 6.4 Hz, 3H), 1.06 (m, 1H), 1.68 (m, 1H), 2.20 (m, 1H), 2.29 (m, 1H), 2.34 (m, 1H), 4.77 (s, 1H), 4.85 (s, 1H), 5.40 (m, 2H). ^{13}C NMR (toluene-d_8, 20 °C): δ 19.0 (q, $^1J_{C-H}$ = 129 Hz, CH_3), 32.2 (t, $^1J_{C-H}$ = 131 Hz, CH_2), 33.2 (t, $^1J_{C-H}$ = 130 Hz, CH_2), 40.2 (d, $^1J_{C-H}$ = 126 Hz, CH), 102.8 (t, $^1J_{C-H}$ = 159 Hz, CH_2), 103.9 (t, $^1J_{C-H}$ = 157 Hz, CH_2). High-resolution GC/MS. Calcd for C_8H_{12}: *m/e* 108.0939. Found: *m/e* 108.0941.