

Supplementary Information

Selective Ethylene Oligomerization in the Presence of ZnR_2 : Synthesis of Terminally-Functionalized Ethylene Oligomers

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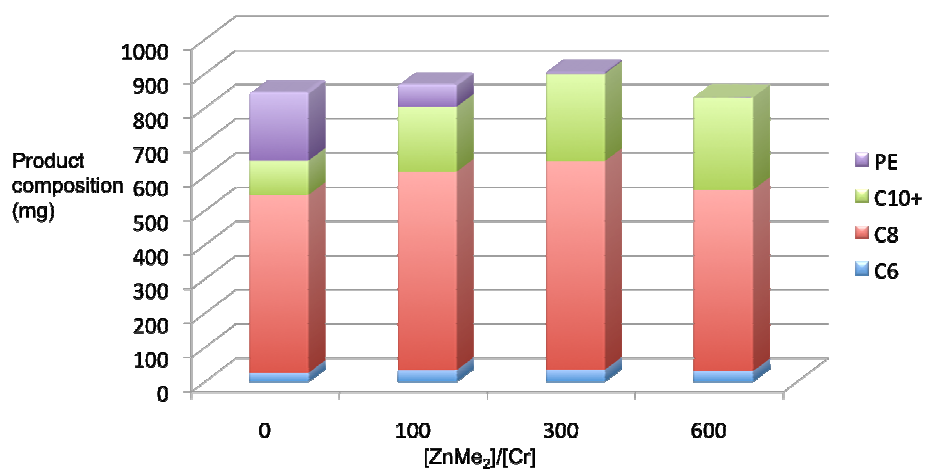
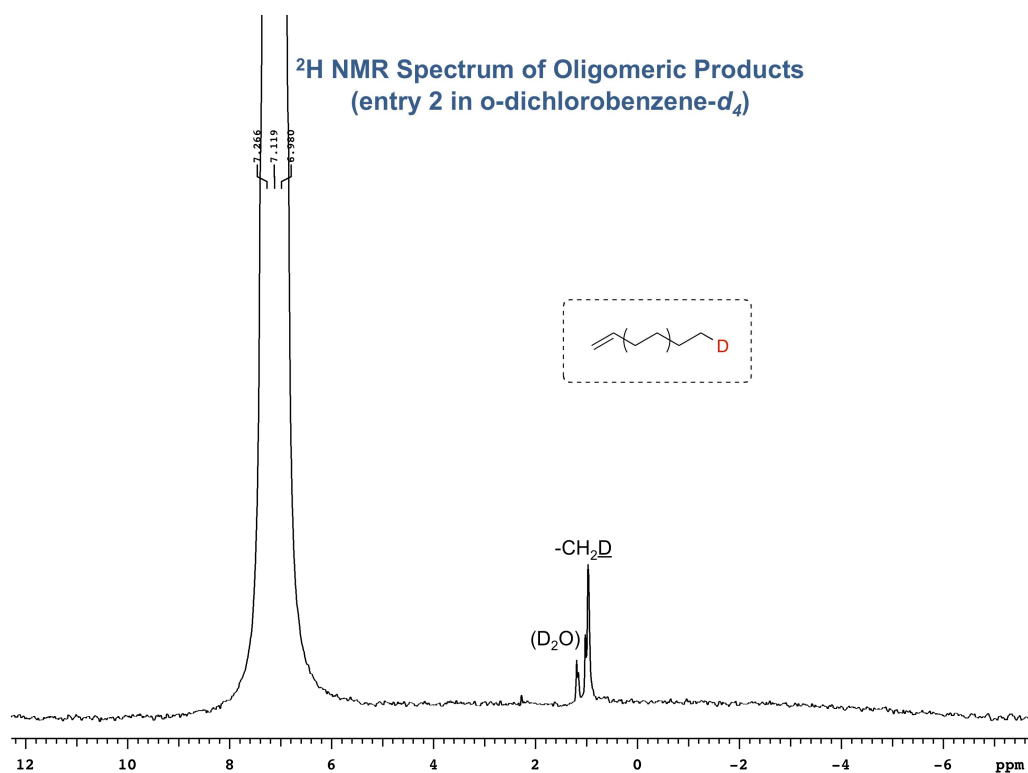


Figure S1. Product composition depending upon $[\text{ZnMe}_2]/[\text{Cr}]$ ratio (entries 5-8, Table 1)



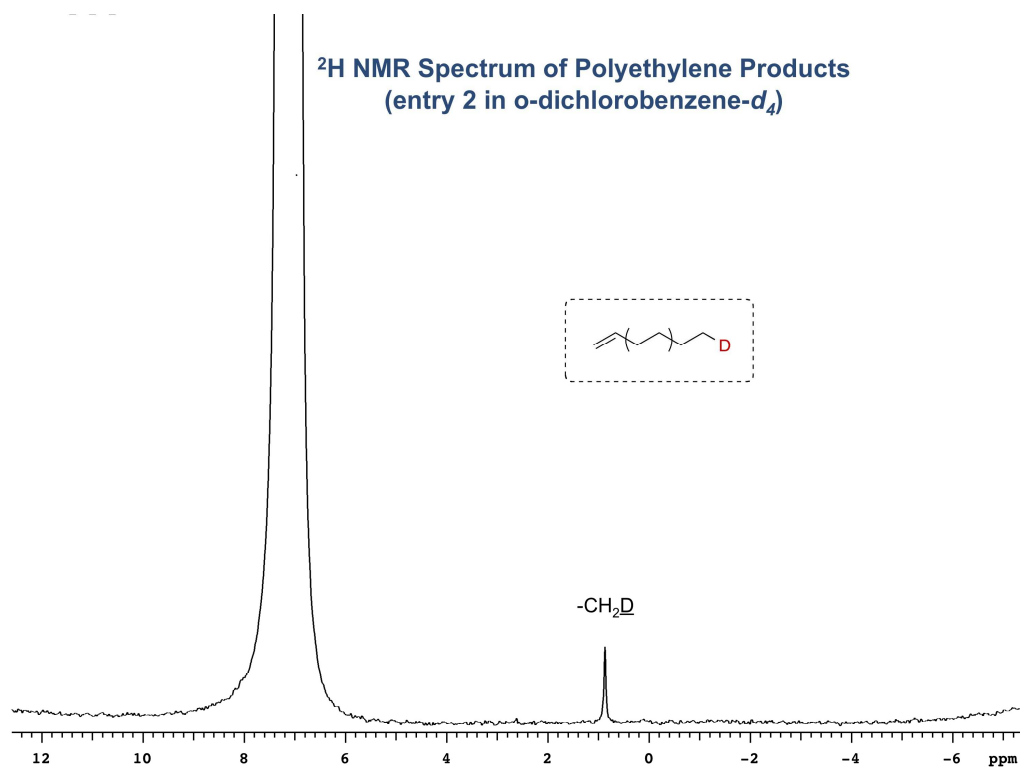


Figure S2. ^2H NMR spectra of oligomeric and polymeric products of entry 2, Table 1 (in o -dichlorobenzene- d_4 , 600 MHz)

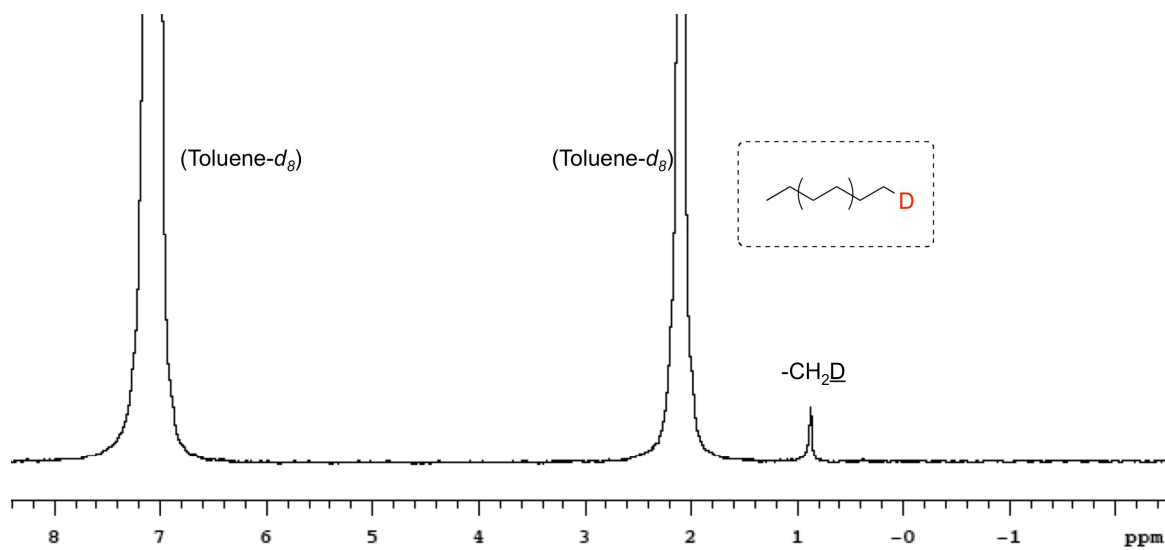


Figure S3. ^2H NMR spectrum of oligomeric products of entry 10, Table 1 (in toluene- d_8 , 600 MHz)

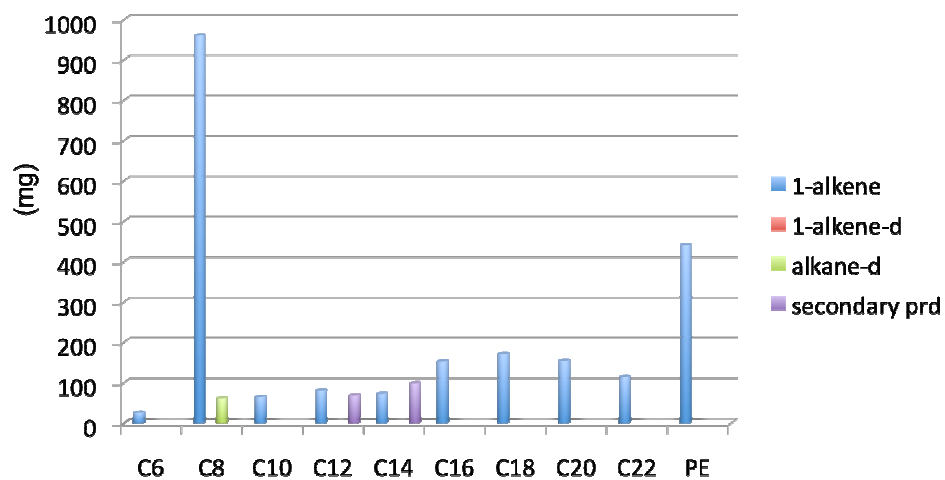


Figure S4. Product distribution in the absence of ZnR_2 at 25 °C (entry 1)

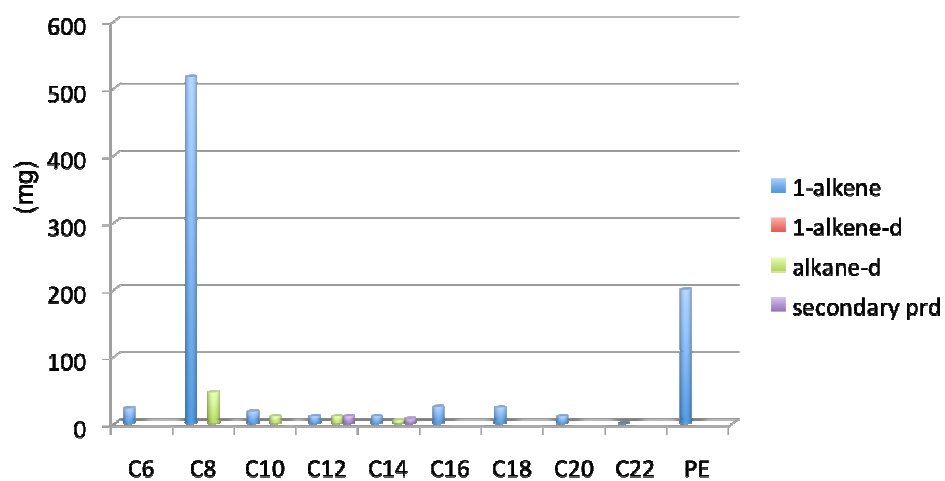


Figure S5. Product distribution in the absence of ZnR_2 at 45 °C (entry 5)

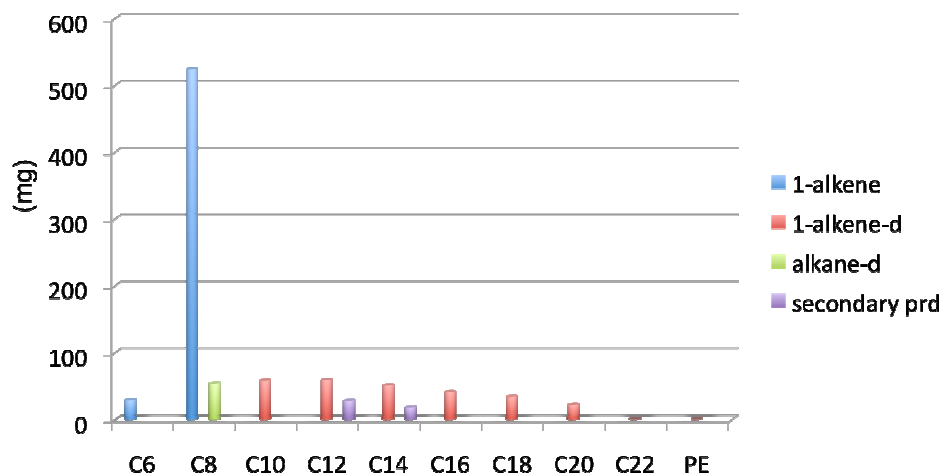


Figure S6. Product distribution in the presence of 600 eq ZnMe_2 at 45 °C (entry 8)

Thermal Properties of Polymeric Products

Polymer samples from entries 1 and 2 in Table 1 were analyzed using Differential Scanning Calorimetry (DSC) (TA Instruments Q100 differential scanning calorimeter) to compare their thermal properties. Polyethylene produced in the absence of transmetallation reagent (entry 1) exhibited a high melting point at 131 °C, heat of melting of 121 J/g, and M_n of 80500 (Figure S7), whereas one produced in the presence of 600 eq. of $ZnMe_2$ (entry 2) showed a melting point at 122 °C, heat of melting of 74 J/g, and M_n of 320 (Figure S8). This difference indicates that the chain transfer mediated by Zn alkyls decreased the average molecular weight of resulting polyethylene.

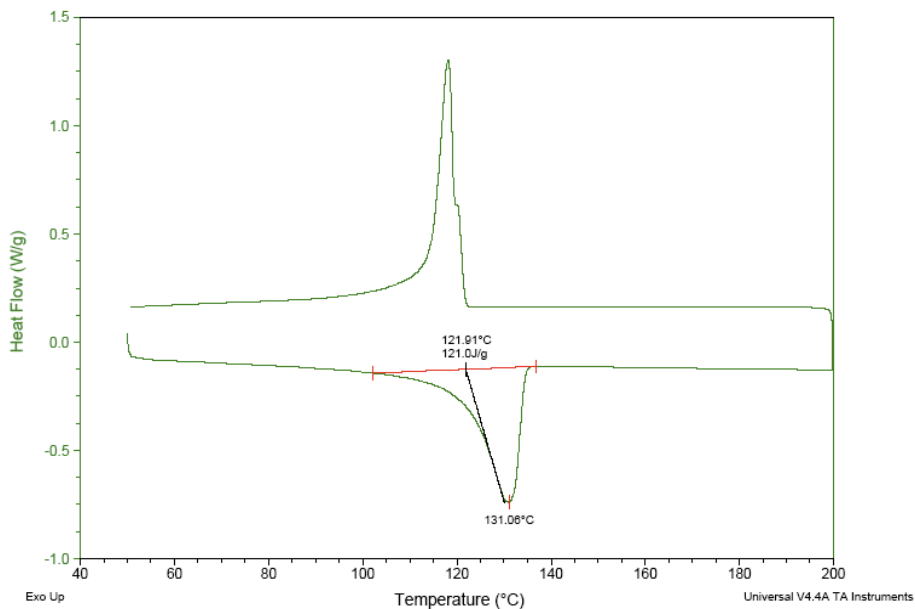


Figure S7. DSC curve of the polymeric product of entry 1, Table 1 ($M_n = 80500$; $M_w/M_n = 10.5$)

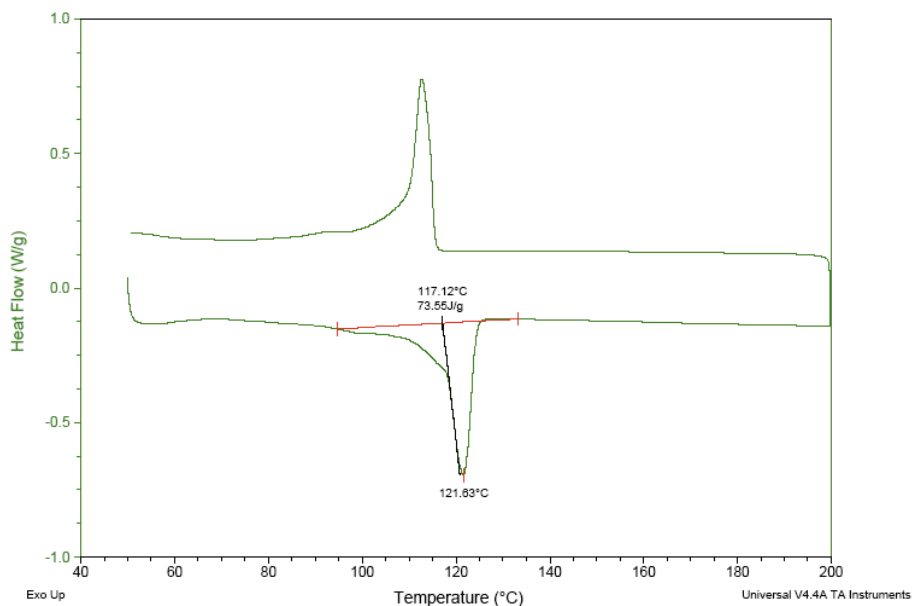


Figure S8. DSC curve of the polymeric product of entry 2, Table 1 ($M_n = 320$; $M_w/M_n = 14.0$)

Table S1. Expanded Table 1 – effects of alkyl groups of ZnR₂ on the product distribution (% = wt% out of total)

Entry	C ₆ (mg/ %)	1-hexene (mg/ %)	C ₈ (mg/ %)	1-octene (mg/ %)	C ₁₀ (mg/ %)	C ₁₂ (mg/ %)	C ₁₄ (mg/ %)	C ₁₆ (mg/ %)	C ₁₈ (mg/ %)	C ₂₀ (mg/ %)	C ₂₂ (mg/ %)	PE (mg/ %)	Total (mg/ %)*
1	25/ 1	25/ 1	1020/ 44	960/ 42	64/ 3	80/ 3	72/ 3	152/ 7	171/ 7	154/ 7	114/ 5	440/ 19	2295/ 100
2	40/ 1	40/ 1	1460/ 34	1400/ 33	260/ 6	522/ 12	400/ 9	406/ 10	383/ 9	313/ 7	267/ 6	200/ 5	4250/ 100
3	95/ 1	80/ 1	2710/ 37	2330/ 32	858/ 12	1050/ 14	733/ 10	660/ 9	530/ 7	370/ 5	248/ 3	Trace	7255/ 100
4	105/ 2	80/ 1	2460/ 49	2060/ 41	613/ 12	606/ 12	400/ 8	316/ 6	242/ 5	168/ 3	106/ 2	Trace	5015/ 100
5	25/ 3	25/ 3	570/ 64	520/ 58	18/ 2	11/ 1	11/ 1	25/ 3	24/ 3	11/ 1	-	200/ 22	895/ 100
6	33/ 3	33/ 3	630/ 69	580/ 63	33/ 4	41/ 4	27/ 3	33/ 4	28/ 3	26/ 3	-	65/ 7	920/ 100
7	34/ 3	34/ 3	660/ 69	610/ 64	50/ 5	55/ 6	47/ 5	39/ 4	36/ 4	28/ 3	-	5/ 1	955/ 100
8	30/ 3	30/ 3	580/ 66	525/ 60	58/ 7	59/ 7	51/ 6	41/ 5	34/ 4	22/ 2	-	Trace	880/ 100
9	60/ 3	50/ 2	1380/ 65	1170/ 55	292/ 14	251/ 12	87/ 4	39/ 2	23/ 1	-	-	Trace	2130/ 100
10	30/ 3	20/ 2	660/ 63	520/ 50	100/ 10	57/ 5	47/ 5	41/ 4	41/ 4	35/ 3	31/ 3	Trace	1040/ 100

* Fractions of cyclic C₆ products and branched C₁₂, C₁₄ oligomers were excluded for direct comparison between entries.

Table S2. Branched products in C₁₂ and C₁₄ (cf. amount of branched C₁₀: negligible)

Entry	251 Linear C ₁₂ (mg)	87 Linear C ₁₄ (mg)	210 Branched C ₁₂ (mg)	165 Branched C ₁₄ (mg)
1	80	72	70	98
2	522	400	240	343
3	1050	733	470	858
4	606	400	178	294
5	11	11	-	-
6	41	27	-	-
7	55	47	-	-
8	59	51	28	18