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Thermodynamic and Kinetic Considerations in the Copolymerization of Ethylene and Carbon Dioxide

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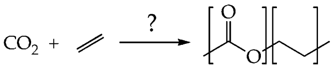
ABSTRACT: The thermodynamics of ethylene and carbon dioxide copolymerization are assessed with average bond dissociation energies, the Benson additivity method, and density functional theory (DFT) calculations (B3LYP 6-31G†). The DFT results suggest that formation of the alternating copolymer is exothermic ($\Delta H = -4.31$ kcal/mol per repeat unit), but endergonic at most temperatures (> -159 °C, the ceiling temperature), and therefore it is practically inaccessible because of entropic factors. However, these thermodynamic calculations show that the polymerization is favorable (exergonic) at room temperature (25 °C) when the molar quotient of ethylene/carbon dioxide exceeds 2.37 (29.7 mol % CO_2 or less). Various copolymerization conditions with catalytic amounts of late transition metal complexes (Fe, Co, Ni, Cu) in combination with MAO (methylaluminoxane) produced oligomers or polymers containing only ethylene. The lack of ester functionality, as confirmed by mass spectrometry and ^{13}C NMR, attests to the dubious nature of previous reports claiming up to 30 mol % incorporation of carbon dioxide.

Introduction

The vast majority of synthetic polymers are derived from petroleum feedstocks. Because these feedstocks are nonrenewable, there is considerable interest in developing routes to synthetic polymers that are based, partly or completely, on renewable resources. Carbon dioxide, present in 370 ppm in the terrestrial atmosphere,[1] has received considerable attention in this regard. Incorporating CO_2 into useful polymers not only takes advantage of a renewable, relatively inexpensive, and extremely abundant C_1 building block−it serves to remove a greenhouse gas from the atmosphere. Since Inoue's discovery of catalysts for the copolymerization of CO_2 and epoxides in 1969,[2] considerable research effort has been directed toward developing other catalysts that are capable of incorporating CO_2 into polymer chains. There have been multiple reports of copolymerizing CO_2 with high-energy comonomers such as epoxides[3] and aziridines[4] to form polycarbonates and polyurethanes, respectively.

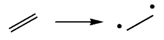
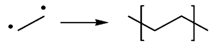
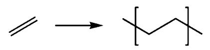
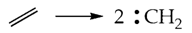
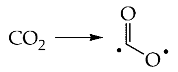
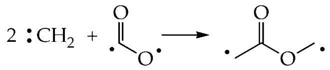
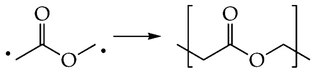
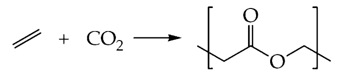
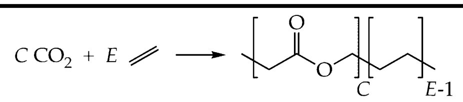
Our research program has considered theoretical and experimental facets of the corresponding copolymerization with ethylene, another high-energy comonomer.[5] Consequently, we were highly intrigued when in 2002, Zou and co-workers reported the copolymerization of ethylene and CO_2 to form high molecular weight polyesters with a significant degree of CO_2 incorporation (up to 30 mol %).[6] This paper reports our theoretical calculations on the thermodynamics of this copolymerization and provides a critical assessment of Zou's results in light of our inability to reproduce them.



Results and Discussion

Bond Dissociation Energy Thermodynamics. The calculated copolymerization enthalpy for ethylene and CO_2 can be determined by several methods. One approach employs average bond dissociation energies, such as those found in common organic chemistry textbooks.[7] Table 1 illustrates this calculation for the simplified polymer microstructure that avoids adjacent carbon dioxide monomers, a thermodynamically unfavorable arrangement (vide infra).[8−10] This approach yields eq 1, which gives the polymerization enthalpy *per monomer* as a function

Table 1. Average Bond Dissociation Energies (BDE) Used to Calculate Ethylene/Carbon Dioxide Copolymerization Thermodynamics

reaction	BDE[a]
	148 - 81 = 67
	- 81
	67 - 81 = -14
	148
	172 - 84 = 88
	-81 + -84 = -165
	-81
	148 + 88 - 165 - 81 = -10
	
$\Delta H_{poly} = [C(-10) + (E - 1)(-14)]/(C + E)$	(eq 1)
$\Delta G_{poly} = [C(-10\ \mathrm{kcal/mol}) + (E - 1)(-14\ \mathrm{kcal/mol})]/(C + E) - [T(-0.030\ \mathrm{kcal/molK})]$	(eq 2)

[a] Energies are in kcal/mol.

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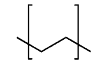
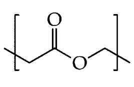
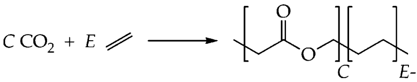
Table 2. Supergroups Based on Benson Groups Simplifying the Thermodynamic Treatment of Polymerization Systems Such as the Copolymerization of Ethylene and Carbon Dioxide[a]

supergroup	component groups	group additivity ΔH	supergroup additivity ΔH	supergroup ΔH_{poly}	group additivity S	supergoup additivity[b] S	supergroup ΔS_{poly}
	C–(C)$_2$(H)$_2$ C–(C)$_2$(H)$_2$	-5.0 -5.0	-10.0	-10.0 - (12.5) = -22.5	9.42 9.42	18.84	18.84 - (52.42) = -33.6
	C–(H)$_2$(C)(CO) CO–(C)(O) O–(C)(CO) C–(H)$_2$(O)(C)	-5.2 -35.2 -43.1 -8.1	-91.6	-91.6 - (12.5 - 94.0) = -10.1	9.6 14.78 8.39 10.3	43.07	43.07 - (52.43 + 51.10) = -60.5

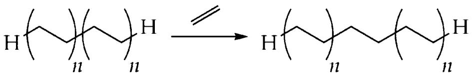


$$\Delta H_{poly} = [C(\text{-}10.1\ \text{kcal/mol}) + (E\text{-}1)(\text{-}22.5\ \text{kcal/mol})]/(C + E) \quad \text{(eq 3)}$$

$$\Delta G_{poly} = [C(\text{-}10.1\ \text{kcal/mol}) + (E\text{-}1)(\text{-}22.5\ \text{kcal/mol})]/(C + E) - T[C(\text{-}0.0605\ \text{kcal/molK}) + (E\text{-}1)(\text{-}0.0336\ \text{kcal/molK})]/(C + E) \quad \text{(eq 4)}$$

[a] Units given for enthalpy are kcal/mol; units given for entropy are cal/(mol K). The following experimental data are in kcal/mol: $\Delta H°_f$(ethylene) = 12.5 kcal/mol; $\Delta H°_f$(CO_2) = −94.0 kcal/mol; $S°$(ethylene) = 52.42 cal/(mol K); $S°$(CO_2) = 51.10 cal/(mol K).[14] [b] The entropic correction to S (given by $-R \ln \sigma$) is 0 since the symmetry number (σ) is 1 for these supergroups.

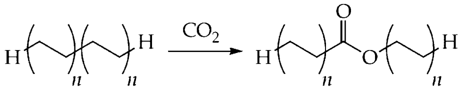
Table 3. Summary of DFT Thermodynamic Calculations for the Polymerization of Ethylene Monomer



	reactant chain		product chain		thermodynamic parameters		
n	H (kcal/mol)	S (cal/(mol K))	H (kcal/mol)	S (cal/(mol K))	ΔH^a (kcal/mol)	ΔS^a (cal/(mol K))	ΔG^b (kcal/mol)
1	−99345.32	73.138	−148646.71	88.308	−22.51	−39.935	−10.60
2	−197948.08	103.394	−247249.46	118.489	−22.51	−40.010	−10.58
3	−296550.83	133.381	−345852.15	146.851	−22.44	−41.635	−10.03
4	−395153.59	163.056	−444454.88	175.799	−22.42	−42.362	−9.79
5	−493756.35	192.712	−543057.61	204.641	−22.39	−43.176	−9.52
6	−592359.10	222.294	−641660.35	233.442	−22.38	−43.957	−9.27
7	−690961.71	247.814	−740263.08	262.191	−22.49	−40.728	−10.35
8	−789564.45	276.539	−838865.82	290.939	−22.49	−40.705	−10.36
9	−888167.18	305.323	−937468.55	319.690	−22.49	−40.738	−10.35
av for n = 1−9					−22.46	−41.472	−10.09

[a] Ethylene was calculated to have the following values for enthalpy and entropy: H = −49278.88 kcal/mol; S = 55.105 cal/(mol K). [b] At 298.15 K.

Table 4. Summary of DFT Thermodynamic Calculations for the Polymerization of Carbon Dioxide Monomer



	reactant chain		product chain		thermodynamic parameters		
n	H (kcal/mol)	S (cal/(mol K))	H (kcal/mol)	S (cal/(mol K))	ΔH^a (kcal/mol)	ΔS^a (cal/(mol K))	ΔG^b (kcal/mol)
1	−99345.32	73.138	−217660.43	92.154	13.83	−32.122	23.41
2	−197948.08	103.394	−316263.07	122.138	13.96	−32.394	23.61
3	−296550.83	133.381	−414865.89	151.288	13.89	−33.231	23.80
4	−395153.59	163.056	−513468.66	180.224	13.87	−33.970	24.00
5	−493756.35	192.712	−612071.42	208.926	13.87	−34.924	24.28
6	−592359.10	222.294	−710674.18	237.432	13.85	−36.000	24.59
7	−690961.71	247.814	−809276.94	265.852	13.71	−33.100	23.58
8	−789564.45	276.539	−907879.51	293.454	13.88	−34.223	24.09
9	−888167.18	305.323	−1006482.46	322.468	13.66	−33.993	23.80
av for n = 1−9					13.84	−33.773	23.91

[a] Carbon dioxide was calculated to have the following values for enthalpy and entropy: H = −118328.94 kcal/mol; S = 51.138 cal/(mol K). [b] At 298.15 K.

of the ethylene/carbon dioxide (E/C) quotient. The value of ΔG_{poly} (per monomer) can be determined by substituting eq 1 into $\Delta G = \Delta H - T\Delta S$ and assuming that $\Delta S = -0.030$ kcal/(mol K) per monomer incorporated (eq 2).[11] This method predicts an exergonic copolymerization for $E/C \approx 2.56$ or greater, suggesting that the perfectly alternating copolymer is thermodynamically inaccessible at reasonable polymerization temperatures (ceiling temperature ≈ −106°). However, it is clear that average bond dissociation energies poorly estimate the enthalpy of ethylene homopolymerization. This estimation suggests −14 kcal/mol, but the measured value is −22.348 kcal/mol.[12]

Benson Additivity Thermodynamics. A generally more reliable thermodynamic method employs Benson's group additivity rules.[13] In the thermodynamic analysis of polymers, the Benson method can be modified to account for *supergroups*

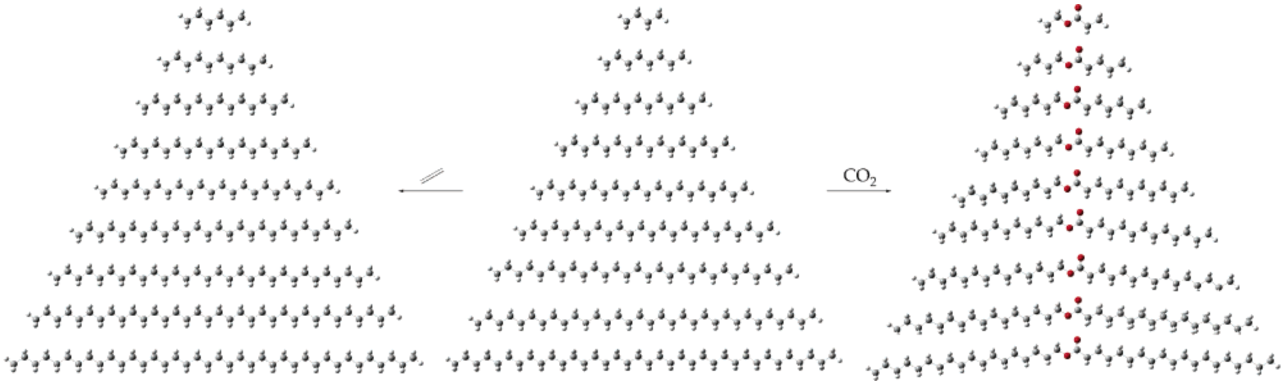


Figure 1. Geometry optimized structures (DFT B3LYP 6-31G†) for polyethylene and copoly[ethylene/carbon dioxide] oligomers.

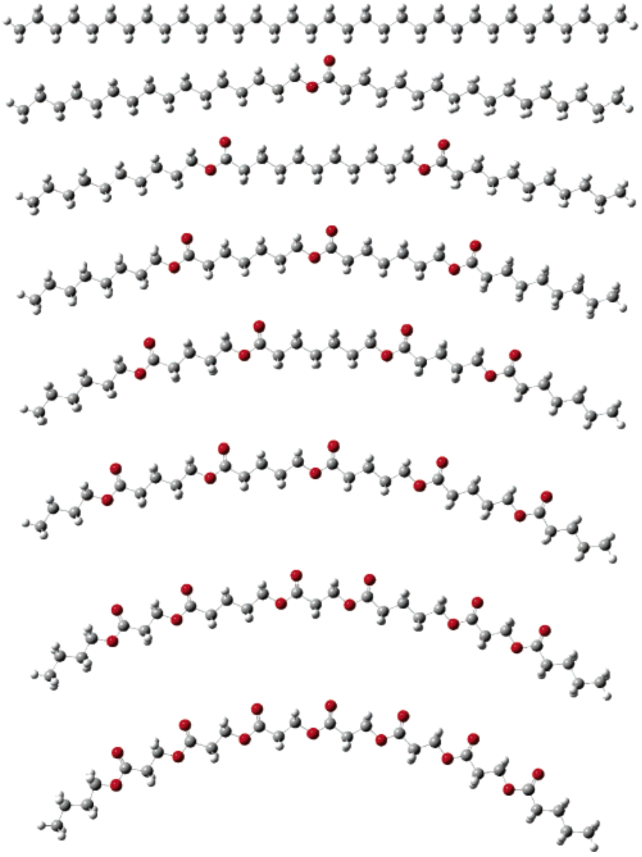


Figure 2. Geometry optimized structures (DFT B3LYP 6-31G†) for oligomers of length 17 with increasing carbon dioxide incorporation. The structures bend 8.8° per ester functional group.

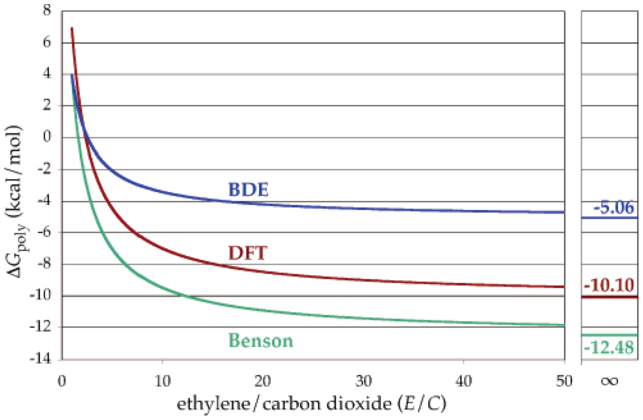


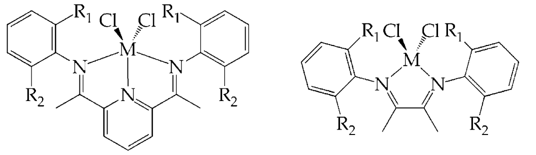
Figure 3. Gibbs free energy of polymerization (per monomer at 298.15 K) vs the ethylene/carbon dioxide quotient, as predicted by bond dissociation energies (BDE), the Benson additivity method, and DFT calculations. Note the asymptotic approach to the calculated Gibbs free energy of ethylene homopolymerization.

instead of simple groups. In the present case, one supergroup is taken as C$-$CH$_2$CH$_2-$C and a second is taken as C$-$CH$_2$C(O)OCH$_2-$C (Table 2). These groupings simplify the resultant enthalpic formula for copolymerization and predict the net enthalpy (in kcal/mol) *per monomer* incorporated as shown in eq 3. Note that this construct does not address the possibility of adjacent CO$_2$ monomers. This exclusion is valid because of the considerable endothermicity known for this kind of enchainment.[8−10] The formation of hypothetical poly(carbon dioxide) from carbon dioxide is calculated to be endothermic by 18.6 kcal/mol ($\mathrm{CO}-(\mathrm{O})_2 + \mathrm{O}-(\mathrm{CO})_2 - \Delta H°_f(\mathrm{CO}_2) = (-29.2) + (-46.2) - (-94.0)$).

The value of ΔG_{poly} (per monomer) can be estimated by substituting eq 3 into $\Delta G = \Delta H - T\Delta S$ and calculating ΔS_{poly} from *entropic* Benson group additivity values.[15] The result is eq 4, and it is apparent that formation of the perfectly alternating copolymer is thermodynamically forbidden at room temperature, but its formation at −106 °C (the ceiling temperature) and below is exergonic. Of course, most polymerization kinetics at this temperature are categorically slow. However, copolymers with greater *E*/*C* quotients are thermodynamically possible at room temperature (298.15 K). The Benson additivity method predicts that the copolymerization is exergonic for $E/C \approx 1.64$ and greater at room temperature. Simply stated, the exergonic polymerization of ethylene compensates for the endergonic incorporation of carbon dioxide.

DFT Thermodynamics. To assess the quality of the preceding Benson additivity approach, density functional theory (DFT) calculations (B3LYP 6-31G†) were performed on polyethylene and ethylene/CO$_2$ copolymer chains of varying lengths. From these calculations, the thermodynamic parameters ΔH, ΔS, and ΔG (at 298.15 K) were obtained for the insertion of one ethylene molecule or the insertion of one CO$_2$ molecule into a polyethylene chain. The results are summarized in Table 3 and Table 4, respectively. Figure 1 illustrates the geometry optimized oligomers from which these data derive. Figure 2 illustrates several geometry optimized oligomers of length 17 with increasing carbon dioxide incorporation. Note the curvature introduced by the ester functionality. Each ester group introduces a bend of approximately 8.8°.

The values in Table 3 provide an average ΔH_{poly} for ethylene of −22.46 kcal/mol, which correlates rather well to the published experimental value of −22.348 kcal/mol.[12] Similarly, the calculated ΔS_{poly} for ethylene (−41.47 cal/(mol K)) is a close match to the experimental value that includes the crystallization of the polyethylene chain (−41.6 cal/(mol K)),[16] as one might expect given the linearity of the geometry optimized ethylene



1: M = Fe, $R_1 = R_2 = {}^iPr$
2: M = Fe, $R_1 = R_2 = Me$
3: M = Co, $R_1 = {}^iPr$, $R_2 = H$
4: M = Fe, $R_1 = Me$, $R_2 = H$
5: M = Ni, $R_1 = R_2 = {}^iPr$
6: M = Cu, $R_1 = {}^iPr$, $R_2 = H$

Figure 4. Late transition metal complexes investigated for ethylene/carbon dioxide copolymerizations (upon activation with methylaluminoxane).

oligomers. The calculated thermodynamic parameters allow us to write eqs 5 and 6, which give ΔH_{poly} and ΔG_{poly} (per monomer) for the copolymerization of ethylene and carbon dioxide according to this DFT investigation. Thus, the copolymerization is expected to be exergonic for $E/C \approx 2.37$ and greater at room temperature. The ceiling temperature ($\Delta G_{poly} = 0$) for the 1:1 copolymer is calculated to be −159 °C. Figure 3 provides a graphical illustration of ΔG_{poly} vs the E/C ratio for each of the three calculational methods employed: bond dissociation energies, the Benson additivity method, and DFT. While these vary somewhat, they all suggest that the copolymerization thermodynamics are feasible at room temperature so long as a modest E/C quotient (1.64−2.56) is surpassed.

$$\Delta H_{poly} = [C(-22.46\ \text{kcal/mol} + 13.84\ \text{kcal/mol}) + (E - 1)(-22.46\ \text{kcal/mol})]/(C + E)$$

$$\Delta H_{poly} = [C(-8.62\ \text{kcal/mol}) + (E - 1)(-22.46\ \text{kcal/mol})]/(C + E) \quad (5)$$

$$\Delta G_{poly} = [C(-8.62\ \text{kcal/mol}) + (E - 1)(-22.46\ \text{kcal/mol})]/(C + E) - T[C(-0.03377\ \text{kcal/(mol K)}) + E(-0.04147\ \text{kcal/(mol K)})]/(C + E) \quad (6)$$

Copolymerization Results. Pyridine−diimine complexes **1**−**3** (Figure 4) were synthesized and investigated upon activation with MAO (methylaluminoxane, 450−2000 equiv). Complexes of this type are known to be active for the homopolymerization of ethylene[17] and are reported to be active for the copolymerization of ethylene and CO_2.[18] We conducted several successful control experiments whereby the complexes were used to homopolymerize ethylene before attempting to repeat the ethylene/carbon dioxide copolymerization work of Zou et al. The monomers were introduced via a gas cylinder previously charged with equimolar amounts of ethylene and carbon dioxide. Many reactions were performed with various durations, temperatures, and pressures. However, the resulting polymers contained only ethylene, as evidenced by the lack of a carbonyl peak in the ^{13}C NMR spectra (Figure 5), despite the fact that more pressing conditions were used than those previously reported.[6]

Table 5. Summary of Polymerization and Oligomerization Runs with 1−6/MAO[a]

entry	precatalyst (mg)	monomer(s)	time (min)	temp (°C)	pressure (psi)
1	**1** (5)	E,C	60	25	75
2	**1** (4)	E,C	60	25	65
3	**1** (7)	E	45	25	105
4	**2** (5)	E,C	360	25	60
5[b]	**2** (5)	E,C	55	25	60
6	**2** (5)	E,C	120	25	88
7	**2** (5)	E,C	90	25	100
8	**2** (9)	E,C	60	25	100
9[c]	**2** (5)	E	25	25	105
10	**3** (10)	E,C	60	25	150
11[d]	**4** (10)	E,C	60	25	150
12[c]	**4** (20)	E,C	60	70	100
13	**4** (5)	E,C	60	25	60
14[b]	**5** (5)	E,C	80	25	60
15	**5** (5)	E,C	60	25	70
16	**6** (5)	E,C	60	25	60

[a] E = ethylene, C = CO_2, in 85 mL of toluene with 0.74 g MAO. The E,C feed gas contains equimolar amounts of ethylene and CO_2. [b] In 85 mL of dichloromethane. [c] In 25 mL of toluene. [d] With 1.1 g of MAO.

In an attempt to simplify the characterization of the products formed from the attempted copolymerization reactions, catalyst systems were employed that are known to produce ethylene oligomers. It has been shown that by employing a less sterically demanding ligand, the rate of chain transfer increases relative to the rate of propagation.[19] As a result, oligomers and low molecular weight polymers are obtained which are more readily characterized because of increased solubility in organic solvents compared to high molecular weight materials. We then synthesized complex **4**, which bears only a single methyl group on each aryl ring. After activation with MAO (450−1200 equiv), **4** routinely produced toluene-soluble oligomers under various polymerization conditions with a 1:1 ethylene:carbon dioxide monomer feed (Table 5, entries 11−13). These oligomers were subjected to GC−MS analysis to detect any CO_2 incorporation. A typical chromatogram, along with the representative mass for each GC peak, is shown in Figure 6. The masses correspond to unsaturated ethylene oligomers having the structure $H(CH_2CH_2)_n(CH{=}CH_2)$ with $n = 5$ to 18. No carbon dioxide incorporation was detected by GC−MS.

Additionally, late transition metal α-diimine complexes have been shown to be active for the polymerization and oligomerization of ethylene.[20] Complexes **5** and **6** were synthesized in order to test their ability to incorporate CO_2 into a growing

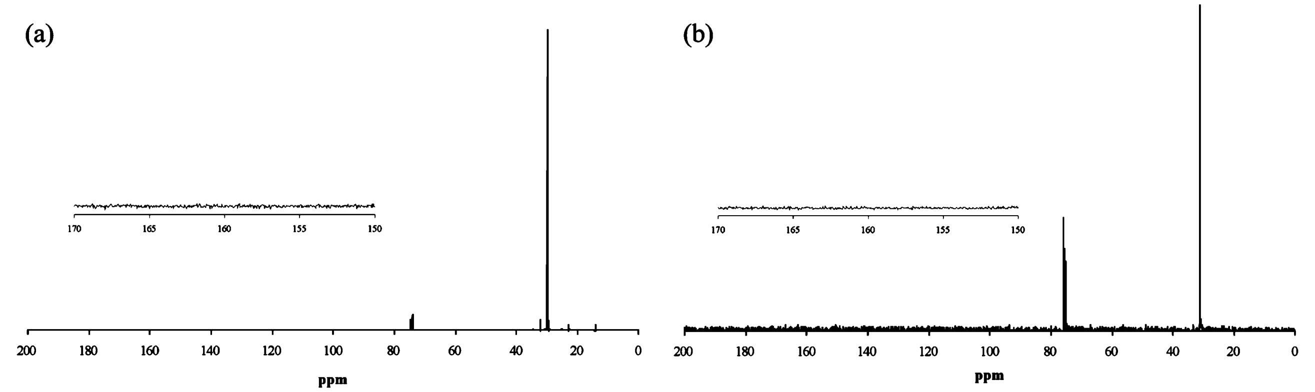


Figure 5. ^{13}C NMR spectra of the polymers produced by **1**/MAO (a, Table 5, entry 1; b, Table 5, entry 2), showing the absence of carbonyl peaks.

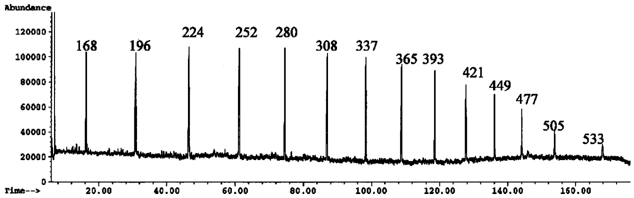


Figure 6. GC−MS of the oligomers produced by **4**/MAO (Table 5, entry 11) with the masses for each peak. Shown are unsaturated ethylene oligomers with DP = 6 through 19. No CO_2 incorporation is evident.

polyethylene chain. Here also, lower molecular weight products were desired because their increased solubility facilitates characterization. After activation with MAO (1100−1300 equiv), complexes **5** and **6** produced waxy solids and toluene-soluble oligomers, respectively. Neither high-temperature NMR nor GC−MS provided any evidence of CO_2 incorporation (see Supporting Information).

Conclusions

The thermodynamic parameters for the incorporation of ethylene and the incorporation of carbon dioxide into a polyethylene chain were calculated using average bond dissociation energies, the Benson additivity method, and DFT calculations. These calculations indicate that formation of the perfectly alternating ethylene/CO_2 copolymer is thermodynamically impossible at reasonable polymerization temperatures. However, the favorable thermodynamics for ethylene can offset the unfavorable thermodynamics of carbon dioxide and polymers with ethylene/carbon dioxide quotients greater than 2.37 (less than 29.7 mol % CO_2) should be feasible at room temperature (DFT analysis). The implications of these thermodynamic results on small molecule catalysis are twofold: (1) the 1:1 coupling of olefins (or alkynes) with carbon dioxide should be thermodynamically restricted; and (2) the 1:1 coupling of dienes (or enynes or diynes) with carbon dioxide may be feasible−in several cases, this has been demonstrated.[21]

All attempts to reproduce the copolymerization results by Zou et al.[6] have failed. Using identical and similar catalysts under identical and more stringent conditions, we were unable to detect any CO_2 incorporation into the polymeric and oligomeric products by ^{13}C NMR or GC−MS. These results are not surprising given the reports that olefins can be polymerized by similar palladium complexes in supercritical CO_2 to form the expected polyolefins.[22]

While the thermodynamics of ethylene and carbon dioxide copolymerization are feasible for sufficiently large ethylene/CO_2 quotients, an effective kinetic pathway has yet to be found. Given our current understanding of organometallic chemistry, it is difficult to envisage a mechanism that would allow such an enchainment process. We have proposed a pathway that relies on the inverse insertion of carbon dioxide into a metal−carbon bond[23]—thus allowing maintenance of a metal−carbon bond throughout the propagation. Our efforts in this direction continue, but the challenges of this copolymerization will most likely be resolved by high-throughput, combinatorial methods. The motivations for achieving this copolymer are numerous and include the prospect of readily producing aliphatic polyesters that exhibit the mechanical properties of polyethylene, but are biodegradable[24] because of the ester functionality located in the polymer backbone.

Experimental Section

All air-sensitive procedures were performed under a purified nitrogen atmosphere in a glovebox or by using standard Schlenk line and vacuum line techniques. Methylaluminoxane (MAO) (Albemarle, 30% in toluene) was concentrated to dryness and used as a solid. 2,6-Diisopropyl aniline (Acros, 92%) was fractionally distilled at 145 °C under dynamic vacuum prior to use. When required, solvents were distilled from an appropriate drying agent into oven-dried Straus flasks: ethanol and methanol from magnesium sulfate, tetrahydrofuran (THF) from sodium/benzophenone, and toluene from elemental sodium. All other chemicals and solvents were used as received. All compounds were prepared according to literature procedures. The general procedures are as follows.

Pyridyl—Diimine Ligand Synthesis.[25] **Method A.** To a solution of 2,6-diacetylpyridine (3.00 g, 18.4 mmol) in 30 mL of dry ethanol was added the appropriate amount (46 mmol, 2.5 equiv) of a substituted aniline and 5 drops of glacial acetic acid. The resulting solution was refluxed for 18 h and then concentrated to approximately half the original volume. The mixture was cooled to 0 °C and then filtered to isolate the solid product.

Method B. To a solution of 2,6-diacetylpyridine (3.00 g, 18.4 mmol) in 200 mL of dry toluene was added the appropriate amount (46 mmol, 2.5 equiv) of a substituted aniline and 0.1 g of *p*-toluenesulfonic acid. The resulting solution was azeotropically distilled using a Dean−Stark trap until 90% of the calculated amount of water was collected. The solution was poured into a separatory funnel and the organic layer was rinsed with 100 mL of a dilute aqueous sodium bicarbonate solution (3.0 g in 100 mL water). The aqueous layer was rinsed with diethyl ether (2 × 100 mL). All organic layers were combined and concentrated to dryness.

α-Diimine Ligand Synthesis.[19,20] To a solution of 2,3-butanedione (43.05 g, 0.50 mol) in 250 mL of dry methanol was added the appropriate amount of a substituted aniline (1.1 mol, 2.2 equiv). The resulting solution was shaken at room temperature for 36 h, after which time a solid precipitate formed. The reaction was heated until homogeneous, then slowly cooled to 0 °C. It was then filtered to isolate the solid product.

Precatalyst Synthesis.[19,20,25] Inside the glovebox, 10 mmol of the ligand and 10 mmol of the metal dichloride were combined in a 100 mL round-bottom flask and a swivel frit apparatus was attached. The apparatus was brought out of the box and evacuated. Approximately 70 mL of an appropriate solvent (dry ethanol or THF) were condensed in at −196 °C, and the reaction mixture was slowly warmed to room temperature. The resulting slurry was either stirred at room temperature for 16 h *or* refluxed for 30 min. The swivel frit apparatus was flipped and all soluble material was washed to the lower collection flask. The solvent was reduced to approximately half its original volume. The swivel frit was flipped again and the solution was filtered to isolate the solid product.

General Polymerization and Oligomerization Procedures. ***CAUTION!*** All polymerizations should be carried out in a fume hood behind a blast shield. Polymerizations were carried out in an 85 mL glass Lab-Crest (Andrews Glass Co.) cylindrical polymerization reactor equipped with a 2 in. cylindrical stir bar able to provide ample surface agitation while stirring. In the glovebox, the vessel was charged with the appropriate amount of precatalyst, MAO, and solvent. The reactor was assembled and brought out of the box. Rapid stirring was begun and the reactor was pressurized with ethylene or a 1:1 mixture of ethylene and CO_2. The reaction was quenched by slowly venting the vessel and adding ∼5 mL of an acidic methanol solution (methanol plus 10% aqueous concentrated HCl). The insoluble polymer was collected by filtration. For oligomerizations, the quenched reaction mixture was poured into a separatory funnel and the aqueous layer was removed. The organic layer was washed with a 10% sodium bicarbonate solution, dried over $MgSO_4$, stripped of solvent under high vacuum, and subjected to analysis.

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Supporting Information Available: Text giving theoretical and synthetic details, figures and tables of DFT optimized structures, and figures showing additional characterization data (^{13}C NMR, GC−MS) for the formed oligomers and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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