COMMUNICATION

Nickel Catalysts for Non-Alternating CO-Ethylene Copolymerization

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Supporting information for this article is given via a link at the end of the document. Deposition Number 2168374 contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service

Abstract: Transition metal-catalyzed copolymerization of CO and ethylene has a strong inherent propensity to produce the strictly alternating copolymer. In this work, nickel catalysts capable of both homopolymerization of ethylene and alternating copolymerization of CO and ethylene are developed to explore the possibility of non-alternating copolymerization of CO and ethylene under the assumption that comonomer incorporation in the polymer chain can be adjusted by the concentrations of the comonomers. Both polyketones with slightly more than 50% ethylene and "polyethylenes" with a small amount of CO incorporation are obtained but only under carefully controlled conditions and in low yields.

Carbon monoxide and ethylene are inexpensive raw materials available from both renewable and fossil feedstocks. Their copolymerization produces aliphatic polyketones that undergo photolytical degradation.[1] These features make such aliphatic polyketones attractive candidates as future sustainable commodity plastics. Either a radical initiator[1b, 2] or a transition-metal catalyst[3] can bring about the copolymerization. The copolymerization requires high temperatures and very high pressures when initiated by a radical but occurs under relatively mild conditions when catalyzed by a transition metal catalyst, typically a Pd or Ni catalyst. The radical-initiated copolymerization affords a branched statistical copolymer,[1b, 2a] and the Pd- or Ni-catalyzed usually produces a strictly alternating linear copolymer.[1b, 3a, 4] The latter exhibits a high crystallinity that renders the polymer brittle and a high melting temperature that limits the processing window.[1b, 5]

Transition-metal catalysts capable of copolymerizing ethylene and CO in the non-alternating fashion are therefore sought after. Pd catalysts were the first to be discovered to catalyze such non-alternating copolymerization.[6] Both polyketones with a more than 50% ethylene content and "polyethylenes" with a small amount of CO incorporation can be produced using either neutral Pd[6-7] or cationic catalysts.[8] Experimental[9] and theoretical[10] mechanistic investigations were carried out on the neutral Pd catalysts to understand the competition between alternating and non-alternating enchainments. The high cost of Pd is nevertheless incompatible with the goal of utilizing the non-alternating copolymers for commodity applications.

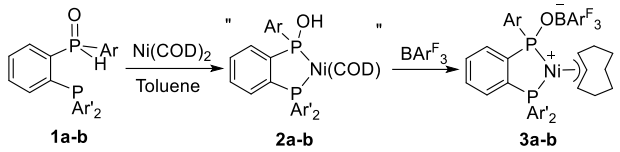
Very recently, Mecking and co-workers reported the ground-breaking discovery of Ni catalysts for the non-alternating copolymerization of CO and ethylene to produce "polyethylenes" with a small amount of CO incorporation.[11] In the present communication, we report a second type of Ni catalysts that enable the non-alternating copolymerization of CO and ethylene. Unlike Mecking's neutral Ni catalysts, the present Ni catalysts possess a net positive charge on Ni and are zwitterionic overall.

Results and Discussion

Our exploration begun with the assumption that if a catalyst capable of catalyzing both the homopolymerization of ethylene and the alternating copolymerization of CO and ethylene, the non-alternating copolymerization can be then realized by controlling the feed ratio of the comonomers. Given that "hard" O- and N-donors are weaker ligands than CO for Ni(II) and deactivation of such Ni catalysts under high-pressure CO is commonly observed,[12] we focused our attention on bidentate phosphine Ni catalysts. Although Ni catalysts for ethylene homopolymerization commonly bear hard Lewis base ligands,[13] Cámpora[14] and Hoffman and Schultz[15] have shown that cationic Ni complexes with sterically hindered diphosphinomethylene ligands do produce polyethylene or at least solid oligoethylenes. However, CO-ethylene copolymerization using these Ni catalysts is not mentioned in the literature. Our attempts reveal that such Ni compounds are completely deactivated when exposed to a CO atmosphere. We therefore sought to improve the steric hindrance in the axial direction of the zwitterionic Ni complexes, which we recently demonstrated to be effective catalysts for carbonylative polymerizations,[16] by placing the triarylborane moiety above the Ni(II) coordination plane.

The new zwitterionic nickel compounds were synthesized by reaction of the phosphine-secondary phosphine oxide ligands with $Ni(COD)_2$ followed by addition of tris[3,5-bis(trifluoromethyl)phenyl]borane in one pot as shown in Scheme 1. The reaction of **1a** and **1b** with $Ni(COD)_2$ presumably gives **2a** and **2b**, respectively. Intermediates **2a** and **2b** were not isolated or characterized in details, but precedents in the literature suggest coordination of the hydroxyphosphine tautomer of the secondary phosphine oxide to Ni.[17] Intramolecular protonation of the coordinated COD by the proton of the hydroxy group activated upon BAr^F_3 coordination followed by ring-walking of Ni gives the

Ni-(η^3-allyl) products, **3a** and **3b**. The conversions from **1a** to **3a** and **1b** to **3b** were quantitative according ^{1}H NMR. The isolated yields were 68% and 80% for **3a** and **3b**, respectively. Both compounds were fully characterized by NMR spectroscopy and elemental analysis (see Supplementary Materials).



a, Ar = 2-methoxyphenyl
b, Ar = 4-(dimethylamino)phenyl

Ar' = 2-methoxyphenyl;
Ar^F = 3,5-bis(trifluoromethyl)phenyl.

Scheme 1. Synthesis of Ni catalysts.

The structure of **3a** was further confirmed by single-crystal X-ray crystallography (Figure 1). In our initial design, the bis(trifluoromethyl)phenyl groups of the BAr$^F_3$ moiety is envisioned to shield the space above the Ni center. The X-ray structure of **3a** demonstrates that it is indeed the case in the crystalline state, but the bent B-O-P angle suggests the BAr$^F_3$ moiety may rotate away and provide a reduced degree of shielding in solution. The *o*-methoxy ancillaries on the phenyl groups also appear to augment the steric hindrance in the axial direction but can also rotate in and out of sterically shielding the Ni coordination plane.

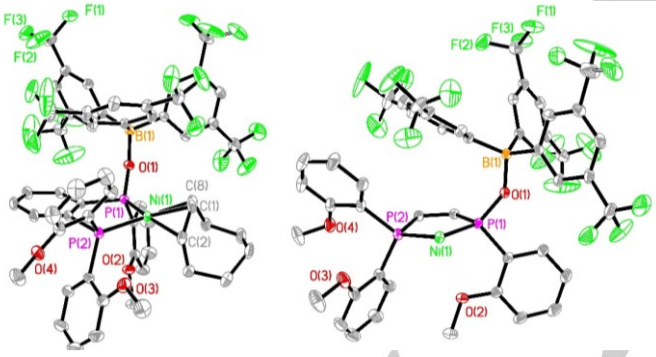


Figure 1. X-ray single-crystal structures of **3a** with 35% probability ellipsoids. Left: Side view. Hydrogen atoms are omitted for clarity. Right: Front view showing the steric hindrance over and under Ni. The allylic cylcooctyl in the front and the fused phenyl in the back as well as hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni(1)-P(1) = 2.1383(6), Ni(1)-P(2) = 2.1862(6), Ni(1)-C(1) = 1.9790(18), Ni(1)-C(2) = 2.086(2), Ni(1)-C(8) = 2.0483(19), B(1)-O(1) = 1.511(2), O(1)-P(1) = 1.5610(13), P(1)-Ni(1)-P(2) = 91.330(19), C(1)-C(2)-C(8) = 122.32(18), B(1)-O(1)-P(1) = 140.76(12).

Compounds **3a** and **3b** indeed catalyze the homopolymerization of ethylene in the absence of CO (entries 1 - 3, Table 1) and the alternating copolymerization of ethylene and CO (entries 4 and 5), but non-alternating copolymerization proved to be extremely challenging. At the CO/ethylene pressure ratio of 15:300 and 80 °C, both **3a** and **3b** produce the alternating copolymer within 2 h (entries 4 and 5) and then the ethylene homopolymer after CO is completely consumed. When the polymerization temperature is raised to130 °C, a small amount of repetitive ethylene units become detectable in the product (entries 6 and 7). These repetitive ethylene units must have been formed after CO is depleted to a certain extent because the polymerization produces a strictly alternating copolymer when it is carried out in a large reactor under otherwise identical conditions (entry 8), i.e., the initial absolute amount of CO is increased, and the CO pressure remains high when the polymerization is stopped.

The conditions for obtaining non-alternating copolymers with various CO and ethylene contents were further explored. Since **3b** appears slightly better than **3a** for incorporating the extra ethylene units, we used **3b** as the catalyst for the subsequent copolymerization study. Simultaneously increasing P_E to 900 psi and decreasing P_{CO} to 2 psi only resulted in a moderate increase in the ethylene content in the polyketone product (entry 9). Further decreasing P_{CO} to 1 psi resulted in two fractions in the product (entry 10), a polyketone with a slightly more than 50% ethylene content and a "polyethylene" with a small amount of CO incorporation. The two fractions have very different solubilities and can be easily separated by extraction of the polyketone fraction with hexafluoroisopropanol (HFIPA). The ^{1}H NMR of the two fractions are shown in Figure 2. The peaks of the ^{1}H NMR spectra are assigned based on their chemical shifts, coupling patterns, and ^{1}H-^{1}H COSY NMR. When P_{CO} was further reduced to 0.5 psi (entry 11), "polyethylene" with a small amount of CO incorporation was produced as the only product.

The molecular weights of the polyethylene and "polyethylene" with a small amount of CO were characterized by high-temperature gel permeation chromatography (GPC). The relatively broad molecular weight distributions of the polyethylene

Table 1. Copolymerization of CO and ethylene.

Entry[a]	Cat	P_{CO} (psi)	P_E (psi)	Temp (°C)	Time (h)	Yield (g)	CO/E	$M_w/10^3$ (g/mol)	$Đ$ [b]
1	**3a**	-	300	80	1	0.54	-	29.6 [b]	3.73 [b]
2	**3a**	-	300	80	4	4.03	-	17.5 [b]	2.39 [b]
3	**3b**	-	300	80	1	0.82	-	11.2 [b]	2.65 [b]
4	**3a**	15	300	80	2	0.28	50.0 : 50.0	98 [d]	-
5 [c]	**3b**	15	300	80	2	0.46	50.0 : 50.0	59 [d]	-
6	**3a**	15	300	130	2	0.26	49.6 : 50.4	60 [d]	-
7	**3b**	15	300	130	2	0.19	49.1 : 50.9	35 [d]	-
8 [c]	**3b**	15	300	130	2	0.52	50.0 : 50.0	48 [d]	-
9 [c]	**3b**	2	900	150	1	0.07	47.7 : 52.3	52 [d]	-
10	**3b**	1	900	130	0.5	trace 0.04	44.7 : 55.3 1.8 : 98.2	- 4.0 [b]	- 1.58 [b]
11	**3b**	0.5	900	130	0.5	0.06	2.7 : 97.3	4.1 [b]	1.65 [b]

[a] Polymerization condition: catalyst = 10 μmol, THF = 20 mL,125mL autoclave unless otherwise specified. [b] Determined by GPC in 1,3,5-trichlorobenzene at 140 °C after universal calibration using polystyrene standards. [c] 500 mL autoclave used. [d] Weight-average molecular weight determined by static light scattering.

products in entries 1 and 3 (*Đ* > 2) are likely due to a slow initiation process that involves β-hydrogen elimination of the allylic cylcooctyl group to afford 1,3-cyclooctadiene and the Ni hydride, which initiates the polymerization. The slow initiation accompanied by formation of 1,3-cyclooctadiene was confirmed by in situ ^{1}H NMR under 1 atm of ethylene at 50 °C. When the polymerization was allowed to continue for 4 h (entry 2) under the conditions identical to entry 1, the *Đ* decreased to 2.39. The initiation is fast in the presence of CO (*Đ* < 2 in entries 10 and 11). No end group originating from the allylic cylcooctyl group was observed in any of the products in Table 1.

The polyketone samples are only soluble in exotic solvents such as HFIPA. As the result, GPC becomes prohibitively expensive, and only the weight-average molecular weight of these samples were measured by static light scattering. The molecular weights of the polyethylene and "polyethylenes" with a small amount of CO are lower than those of the polyketones by one order of magnitude. Facile coordination of CO apparently suppresses chain transfer via *β*-hydrogen elimination. The molecular weights of the polyethylene and "polyethylene" with a small amount of CO are too low to be useful, but the polyketones are within the range of useful molecular weights and smilar to the commercial CO-ethylene-propylene terpolymer.[3a] The low molecular weight of the polyethylene indicates that shielding in the axial direction of the Ni coordination plane is only moderate as discussed above.

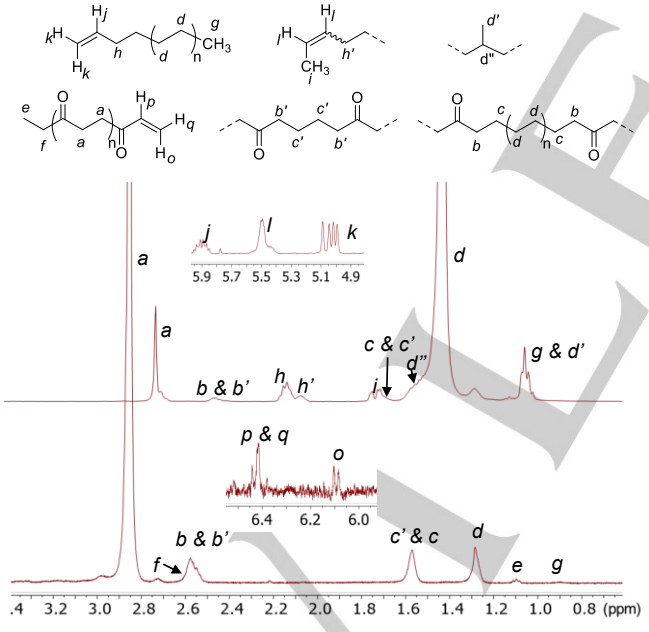


Figure 2. ^{1}H NMR spectra of the ethylene-CO copolymer. Top: "polyethylene" fraction from entry 10, Table 1 in $C_2D_2Cl_4$ at 125 °C. Bottom: polyketone fraction from entry 10, Table 1 in $CDCl_3$/TFA-d (10/1 volume ratio) at room temperature.

The above polymerization data demonstrate that the present Ni catalysts have a strong preference for the alternating copolymerization, unfortunately but not surprisingly as most known Pd and Ni catalysts do. At temperatures below 130 °C, the non-alternating chainment is not detectable. Assuming first-order kinetics in the respective comonomer and that the solubility of ethylene is 5 times of that of CO at such high temperatures,[18] the rate constant ratio of alternating enchainment (CO insertion following an ethylene insertion) and non-alternating enchainment (ethylene insertion following a preceding ethylene insertion), k_{EC}/k_{EE}, can be estimated to be on the order of ~10^4 – 10^5 at 150 °C for **3b** based on entry 10, Table 1. In comparison, k_{EC}/k_{EE} can be approximately estimated to be ~10^2 at 100 °C according to the polymerization data of Sen for the original neutral (P~SO_3)Pd catalyst reported by Drent and Pugh,[6, 9] ~10^2 – 10^3 for the formally cationic (P~P=O)Pd catalyst reported by Chen,[8] and ~10^3 – 10^4 for the neutral Ni catalyst reported by Mecking.[11]

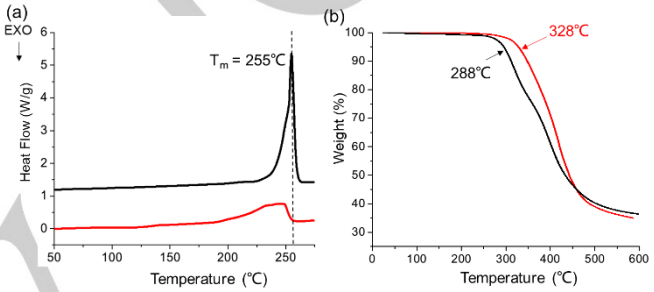


Figure 3. Comparison of thermal properties of alternating polyketone (Table 1, entry 4) and non-alternating polyketone (Table 1, entry 9). (a) DSC traces, the vertical line at 255 °C is added as a guide to the eye. (b) TGA traces, the temperatures are the temperatures, at which 5% weight loss occurred. The traces are in black for the alternating copolymer and in red for the non-alternating.

It is interesting, however, that even a small amount of additional ethylene units gives rise to notable changes in thermal properties of the copolymer. Differential scanning calorimetry (DSC) analysis shows that the non-alternating polyketones have much broader melt transitions than the perfectly alternating polyketone. The melt process of the non-alternating copolymer starts at below 200 ºC and is finished at the peak melting temperature of the alternating copolymer (T_m = 255 °C). Further, thermogravimetric analysis (TGA) reveals that the decomposition of the alternating copolymer at 288 °C is absent or at least not obvious for the non-alternating copolymers. These results are consistent with the previous reports that a reduced carbonyl content decreases the melting temperature and improves the thermal stability of the copolymer[8].

Conclusion

The ability to catalyze both the homopolymerization of ethylene and the alternating copolymerization of CO and ethylene is a necessary condition for a catalyst to catalyze the non-alternating copolymerization of CO and ethylene. When the kinetic preference for alternating enchainment is strong (i.e., k_{EC}/k_{EE} >> 1), the window of CO concentration is exceedingly small for producing the non-alternating product. The present catalyst, which is only the second example of a Ni catalyst capable of producing such non-alternating copolymers, is the worst in this regard among the few known catalysts that display some ability to produce the non-alternating CO-ethylene

copolymer. Composition drift is too drastic to overcome in the small window, making it impractical to produce a substantial amount of non-alternating copolymer of relatively homogeneous compositions. Moving forward, catalysts with a smaller k_{EC}/k_{EE} than what is displayed by the currently known catalysts must be developed, and precise continuous feed can help once improved catalysts are available.

Experimental Section

General procedure for synthesis of **3a** and **3b**: The corresponding phosphine oxide **1** (1.05 mmol) and $Ni(COD)_2$ (0.29 g, 1.05 mmol) were dissolved in toluene (10 mL). The solution was stirred at room temperature overnight. Tris[3,5-bis(trifluoromethyl)phenyl]borane (0.68 g, 1.05 mmol) was added as a solid to the solution at room temperature. The solution was stirred for another 12 h. The solvent was removed in vacuo. The crude product was dissolved in dichloromethane (10 mL) and filtered through celite. The solution was concentrated to ~5 mL in vacuo. The product was recrystallized by slow diffusion of a layer of hexane (10 mL) on top of the dichloromethane solution at room temperature. The yields for **3a** and **3b** were 0.80 g (62%) and 1.04 g (80%), respectively.

The typical procedure of polymerization: A catalyst (10 mg) was charged in a Parr high-pressure reactor in a glovebox. The reactor was connected to a Schlenk line in a well-ventilated fume hood. Under a steady flow of nitrogen, solvent was injected into the reactor. The reactor was then placed in the oil bath at a set temperature for 15 minutes to allow the temperature of the solution to equilibrate. Next, the reactor was pressurized to the desired pressure as specified in Table 1. The reaction mixture was stirred with a magnetic stirrer. After the desirable period of reaction time, the polymerization was stopped by releasing the pressure into a well-ventilated fume hood. **Caution: Highly toxic $Ni(CO)_4$ may be present as the result of catalyst decomposition under high-pressure CO.** The reactor was opened, and the mixture in the reactor was exposed to air and continued to be stirred for a minimum of 2 h to allow oxidative decomposition of any trace amount of $Ni(CO)_4$. Then, methanol was poured into the reactor to precipitate the polymer. The polymer was filtered, washed with methanol and dried under vacuum.

Acknowledgements

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Keywords: non-alternating copolymerization, nickel catalyst, polyketone

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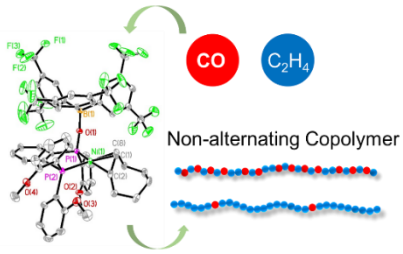

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