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Authors

Ghana, Priyabrata

Xiong, Shuoyan

Tekpor, Adjeoda

et al.

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Catalyst Editing via Post-Synthetic Functionalization by Phosphonium Generation and Anion Exchange for Nickel-Catalyzed Ethylene/Acrylate Copolymerization

Priyabrata Ghana,^{||} Shuoyan Xiong,^{||} Adjeoda Tekpor, Brad C. Bailey, Heather A. Spinney, Briana S. Henderson, and Theodor Agapie*[‡]



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ABSTRACT: Rapid, efficient development of homogeneous catalysts featuring desired performance is critical to numerous catalytic transformations but remains a key challenge. Typically, this task relies heavily on ligand design that is often based on trial and error. Herein, we demonstrate a “catalyst editing” strategy in Ni-catalyzed ethylene/acrylate copolymerization. Specifically, alkylation of a pendant phosphine followed by anion exchange provides a high yield strategy for a large number of cationic Ni phosphonium catalysts with varying electronic and steric profiles. These catalysts are highly active in ethylene/acrylate copolymerization, and their behaviors are correlated with the electrophile and the anion used in late-stage functionalization.

Polyolefin synthesis has been driven by advances in catalyst development.^{1–7} For homogeneous catalysts, this task relies heavily on ligand design, which has often involved leaps in discovery of privileged ligands followed by extensive steric and electronic tuning of the promising motif. Beyond electronic and steric tuning, strategies focused on chain-shuttling, metal–metal cooperativity, metal–substrate effect, and redox control have also been reported.^{8–19} Nonetheless, on-demand catalyst discovery or optimization remains limited because of challenges in predicting catalyst performance *a priori* given the mechanistic complexity of copolymerization. Further, the tunability of the catalyst design is limited by the synthetic methods accessible for introducing desired substituents.¹ Elaborated ligand structures, in many cases, result in an increased number of synthetic steps and cost of preparation.^{20–22} Redox changes or cation addition are powerful methods to switch catalyst performance but typically only between a limited number of catalyst states.^{10,23–25}

Ethylene/polar olefin copolymerization has been pursued to improve polyolefin material properties and introduce potential degradability, but precise catalytic control remains a challenge (Figure 1a,b).^{3–5,20,26–50} Ni catalysts have been a recent focus because of a variety of advantages, including lower cost, polar group tolerance, improved catalytic performance, and higher temperature stability.^{4,19,20,34,35,44,45,51–62} Herein, we report a versatile catalyst-editing strategy on the basis of postsynthetic functionalization of a phosphine moiety followed by anion exchange in a bisphosphinephenoxide-based Ni catalyst system active for ethylene/acrylate copolymerization (Figure 1c).^{20,55}

Our approach was based on phosphonium synthesis via the reaction of triarylphosphine with alkyl halides. The precursor, the bisphosphine phenol (POPH), can be prepared in four steps from commercial compounds.²⁰ Reaction of POPH with methyl iodide in benzene followed by anion exchange with a sodium salt, NaBAR₂₄^F, affords quantitative formation of

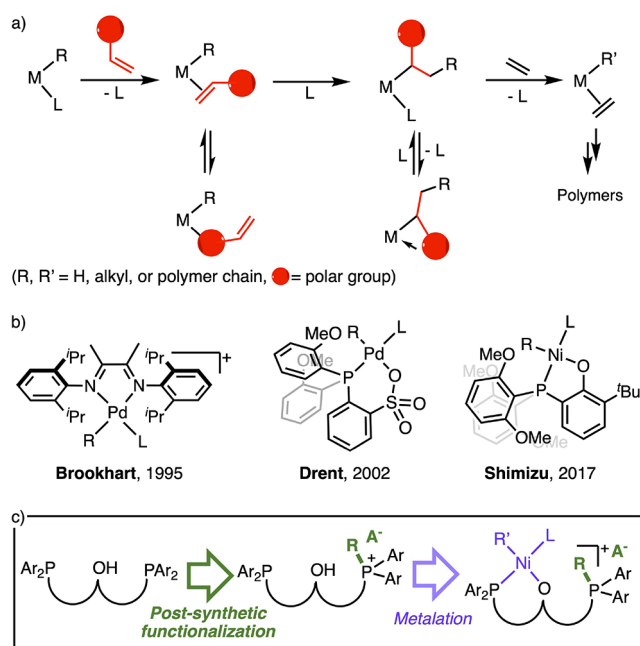


Figure 1. (a) Depiction of inhibitory effects of polar monomers in metal-catalyzed ethylene/polar olefin copolymerization. (b) Examples of Pd and Ni catalysts suitable for polar polyolefin synthesis. (c) Depiction of the catalyst editing strategy in this work and subsequent metalation.

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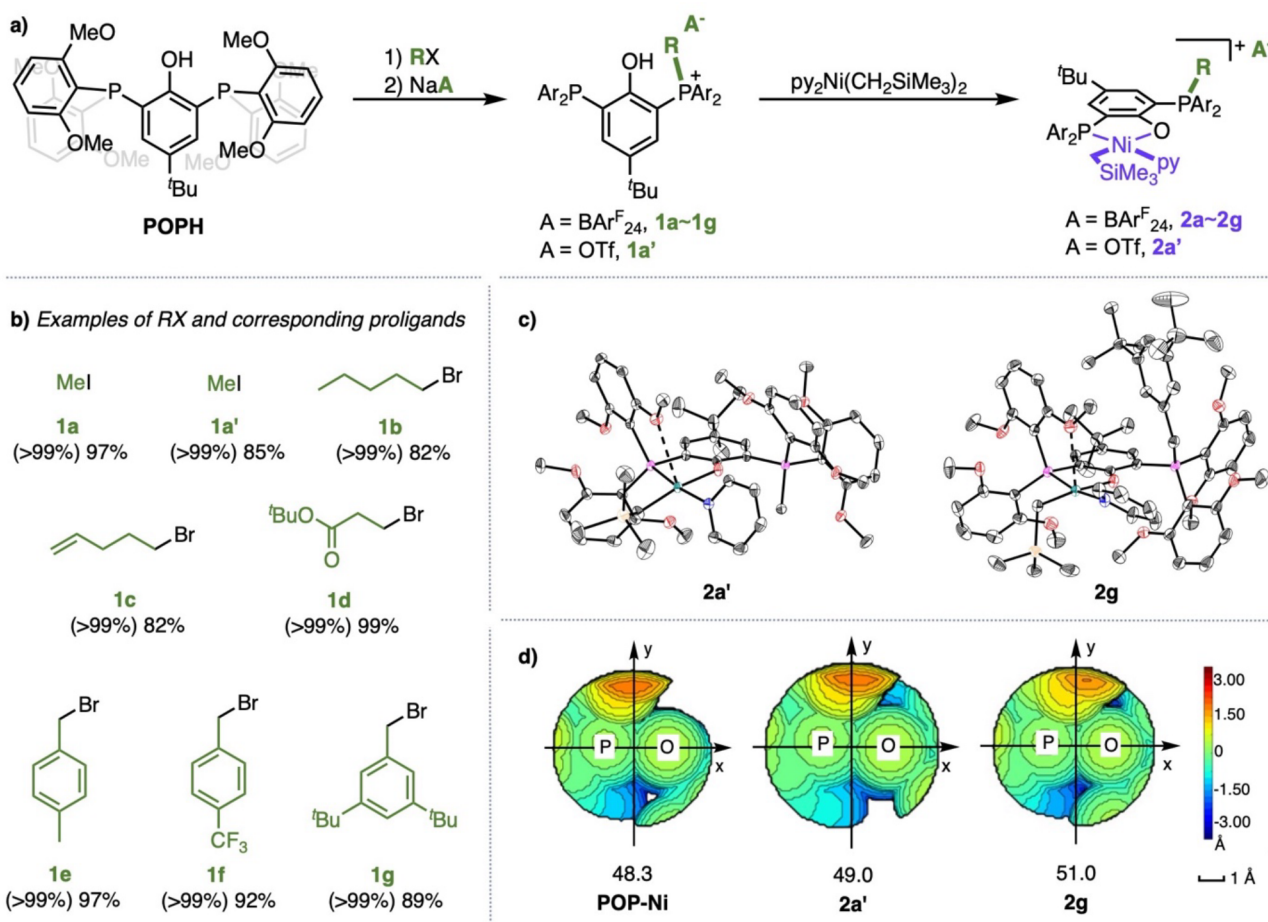


Figure 2. (a) Synthesis route for phosphino-(phosphonium)phenol proligands **1a–1g** and **1a'**, as well as corresponding nickel catalysts **2a–2g** and **2a'** (Ar = dimethoxyphenyl). (b) Alkyl halides examined in this work, as well as corresponding NMR yields (in parentheses) and isolated yields. (c) Solid-state structures of **2a'** and **2g** (anion and hydrogen atoms omitted for clarity; cyan: Ni, pink: P, red: O, blue: N, khaki: Si). (d) Topographical maps and corresponding % V_{bur} of POP-Ni, **2a'**, and **2g** (see the Supporting Information section 6 for more details).

corresponding phosphino(phosphonium)-phenol, **1a** (Figure 2a, NMR yield > 99%, isolated yield: 97%), as indicated by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum featuring two characteristic signals for phosphine (−62.3 ppm) and phosphonium (8.4 ppm).^{63,64} Notably, formation of bisphosphonium species was not observed, potentially because of the low solubility of monophosphonium species in nonpolar solvents that hinders further reaction upon precipitation. Several alkyl bromides with longer alkyl chains, larger steric bulkiness, or electron-withdrawing substituents were also screened, which led to the near-quantitative generation of phosphino-(phosphonium)phenols **1b–1g** (Figure 2b). For Ni phenoxide catalysts, tuning the steric and electronic factors on the “O” side has shown promise for increasing catalytic activity and stability, though those ligands required multiple additional steps in the early stages of ligand synthesis.^{20,53} The current approach based on postsynthetic functionalization is a more facile strategy to increase structural diversity. Given the commercial availability of varieties of alkyl halides with a large window of steric and electronic profiles, PO ligands with a wide range of steric and electronic characteristics on the O side are readily accessible.

In addition, customization of the anion is also feasible by varying the Na salt employed. For example, anion exchange with NaOTf after the addition of methyl iodide generates the

corresponding phosphonium triflate, **1a'** (Figure 2a,b). We envisaged that the difference in anion may lead to difference in cation–anion interaction and consequently varying catalytic behavior.

Metalation of the cationic phosphino(phosphonium)-phenol proligands **1a–g** and **1a'** with one equivalent of $\text{Ni}(\text{py})_2(\text{CH}_2\text{SiMe}_3)_2$ in benzene or THF afforded the corresponding Ni complexes **2a–g** and **2a'** as orange solids (Figure 1a). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of these complexes display two characteristic doublet signals for two inequivalent phosphorus centers with an average $^4J_{\text{P,P}}$ coupling constant of ~13 Hz. The nickel-bound phosphines appear at around −7 ppm, which is consistent with reported Ni phosphine phenoxide complexes.^{20,34,53} The phosphonium groups appear in the same range (8–15 ppm) as observed in the corresponding proligands. Characterization of **2g** and **2a'** by single-crystal X-ray diffraction (scXRD) further confirms their identities as cationic Ni phosphino(phosphonium)-phenoxide complexes featuring a square planar geometry and a corresponding outer-sphere anion of BARF_{24}^- or OTf^- (Figure 2c).

Next, topographical analysis by Cavallo's SambVca 2.1 program was conducted with **2g**, **2a'**, and POP-Ni,^{65,66} an analogous neutral Ni catalyst derived from the bisphosphine phenol proligand (**1a**) that we reported previously.^{20,34,55} Compared with POP-Ni where substituents on the free

Table 1. Ethylene/Acrylate Copolymerization Results^a

entry	catalyst	[tBA]/M	T/°C	act. ^b	M _w /10 ³	PDI	% mol tBA	T _m /°C
1	2a	0.05	90	1130	84.7	2.5	0.59	123
2	2a	0.1	90	550	69.7	2.3	1.13	117
3	2b	0.025	90	1020	91.5	2.4	0.26	126
4	2b	0.05	90	470	85.0	2.7	0.60	122
5	2c	0.025	90	500	92.4	2.3	0.27	127
6	2c	0.05	90	240	80.7	2.3	0.55	122
7	2d	0.05	90	510	74.2	3.2	0.52	122
8	2d	0.1	90	220	59.5	2.9	1.03	117
9	2e	0.025	90	1050	42.0	2.6	0.25	124
10	2e	0.05	90	480	38.7	2.4	0.53	121
11	2e	0.1	90	240	37.2	2.4	0.99	117
12	2f	0.05	90	560	60.5	2.4	0.43	123
13	2f	0.1	90	300	52.1	2.2	0.83	120
14	2g	0.05	90	570	29.9	2.4	0.56	123
15	2g	0.1	90	280	28.7	2.4	0.84	119
16 ^c	2a'	0.025	90	210	8.2	2.8	0.35	121
17 ^c	2a'	0.05	90	120	9.0	4.1	0.76	117
18	2b	0.025	110	2190	41.2	2.1	0.29	124
19	2b	0.05	110	950	40.6	2.3	0.65	122
20	2c	0.025	110	1200	44.6	2.3	0.27	124
21	2c	0.05	110	530	41.0	2.2	0.52	122
22	2d	0.025	110	2000	40.3	2.7	0.40	124
23	2d	0.05	110	750	39.3	3.3	0.43	121
24	2e	0.05	110	790	19.8	2.0	0.6	120
25	2e	0.05	130	310	9.9	2.0	0.6	116
26 ^e	2e ^d	0.054	110	1060	22.1	2.3	0.50	121
27 ^f	POP-Ni ^g	0.05	90	660	55.1	2.2	2.11	111
28	POP-Ni ^g	0.05	100	300	40.4	2.2	2.32	110

^aUnless specified, V = 5 mL, [Ni] = 0.05 mM, ethylene pressure = 400 psi, and solvent is toluene. Polymerization was stopped after consuming a set amount of ethylene or at 1 h, whichever came first (reaction time: 13–60 min). Each entry represents multiple replicated runs. In each run, 30–121 mg of copolymer was produced. See the Supporting Information section S6 for detailed procedures and Table S3 for original catalytic runs. ^bActivity in kg/(mol·h). ^cBoth 0.25 mL of THF and 4.75 mL of toluene were added as the solvent. ^dA mixture of POPH (22.56 μmol), 4-methylbenzyl bromide, NaBAR^F₂₄, and py₂Ni(CH₂SiMe₃)₂ in a 1:1:1:1 ratio was used as *in situ* generated 2e. ^eV = 550 mL, [Ni] = 0.041 mM, ethylene pressure = 430 psi, [tBA] = 0.054 M, t = 60 min. ^fReported in ref 31 as entry 7. ^gPOP-Ni: a catalyst first reported in ref 31, prepared from ligand POPH and py₂Ni(CH₂SiMe₃)₂.

phosphine provide proximal steric hindrance from only one direction on the “O” side, phosphonium substituents in both 2g and 2a' occupy both bottom right and top right spaces of the Ni coordination sphere (Figure 2d). In addition, the percentage of buried volume (%V_{bur}) within 3.5 Å of the Ni center for 2a' (49.0) is slightly higher than that for POP-Ni (48.3), while that for 2g (51.0) is significantly higher. This trend is consistent with the relative bulkiness of phosphine/phosphonium substituents in these three complexes. Overall, the topographical analysis presented above confirms that the additional alkyl group on the phosphonium atom can impact the steric profile around the Ni center.

The nearly quantitative conversion of POPH in post-synthetic functionalization and of 1a–1g in metalation prompted investigation of one-pot synthesis of Ni phosphino-(phosphonium)-phenoxide complexes. Indeed, mixing POPH, 4-methylbenzyl bromide, and NaBAR^F₂₄ in 1:1:1 ratio followed by addition of one equivalent of Ni-(py)₂(CH₂SiMe₃)₂ led to the quantitative formation of 2e. Overall, the facile and selective formation of cationic Ni complexes combined with the high tunability and accessibility of the alkyl bromide and potentially the anion makes precise structural editing of this type of complexes possible.

Catalytic performance of these cationic complexes was examined in an ethylene/acrylate copolymerization. At 90 °C

(Table 1, entries 1–17), they show high activity [>100 kg/(mol·h)] in producing copolymers with moderate *tert*-butyl alcohol (tBA) incorporation (0.25%–1.13%).

Among these catalysts, 2a shows the highest activity [>1000 kg/(mol·h)] and produces copolymers with the highest M_w (up to 85 000), which is potentially related to the small, electron-donating methyl phosphonium substituent. Notably, 2a shows significantly higher activity [1130 kg/(mol·h)] compared to the neutral analogue, POP-Ni [660 kg/(mol·h)] and produces copolymers with higher M_w (84.7 × 10³ vs 55.1 × 10³) and lower acrylate incorporation (~0.6% vs ~2.2%) under identical polymerization conditions (Entry 1 vs 27), though these phenomena may be interrelated (i.e., the higher acrylate incorporation may lead to lower activity). Nevertheless, these differences demonstrate significant impacts of phosphonium vs phosphine on catalyst performance.

While producing copolymers with similar MW and acrylate incorporation, 2b and 2c show activity lower than that of 2a (Entry 1 vs 4 vs 6). Replacing the methyl group (2a) by a pendant ester group (2d) leads to higher PDI (Entry 1 vs 7 and 2.4 vs 3.2). Comparing 2a and 2e (entry 1 vs 10), the latter features a larger proximal benzyl group on the O side and produces copolymers with significantly lower M_w (~85 000 vs ~39 000). One rationale for this phenomenon is that bulky substituents on the O side may promote β-H elimination after

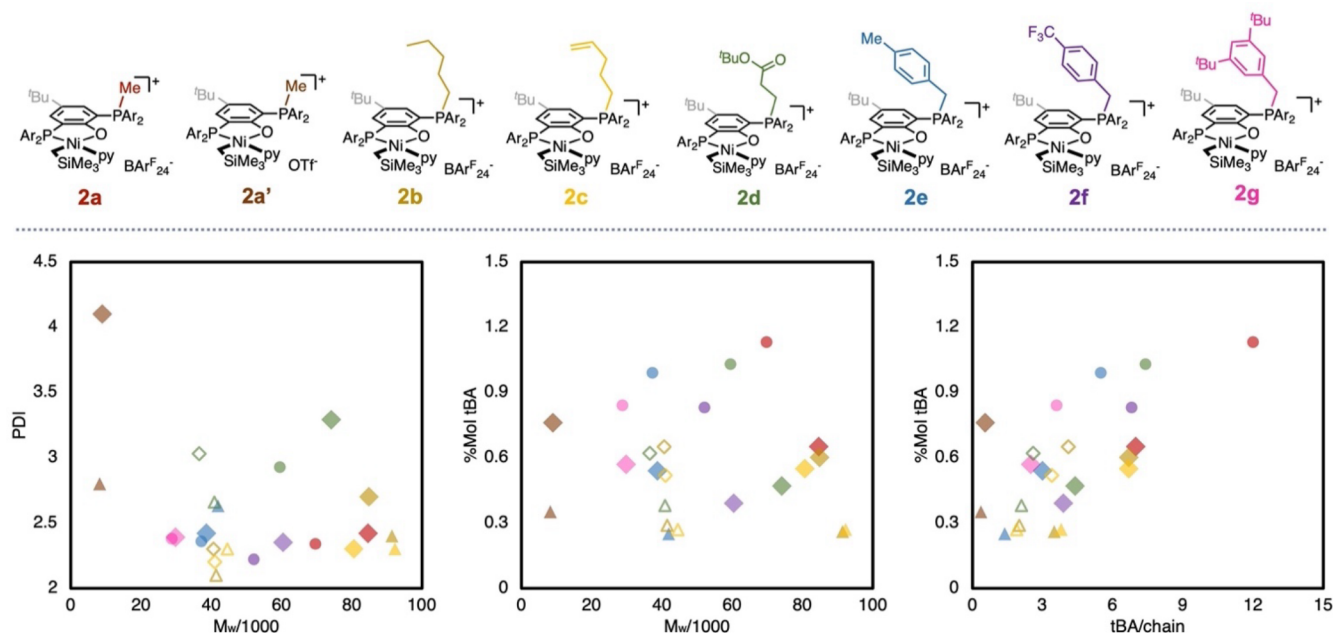


Figure 3. Correlation between structure of cationic Ni catalysts and polymer characteristics [M_w , polydispersity index (PDI), incorporation ratio of acrylate, and number of acrylate units per chain] and correlations between catalyst structures and polymer characteristics. $T = 90\text{ }^\circ\text{C}$ (filled shapes) or $110\text{ }^\circ\text{C}$ (empty shapes); [tBA] = 0.025 M (triangles), 0.05 M (diamonds), or 0.1 M (circles). See Table 1 for catalysis runs and detailed polymerization conditions.

monomer insertion and, thus, lead to decreases in MW. Relatedly, we have previously reported a P,O–Ni catalyst with a rigid aryl group on the O side, which produces copolymers with a significantly lower MW relative to less rigid analogues, and a similar case is observed with cationic complexes herein.²⁰ Notably, this previous example requires an ~ 10 -step synthesis, while similar steric control can be achieved here with a catalyst-editing strategy with only one additional step, a notable step economy. Further increasing the steric hindrance by introducing two *tert*-butyl groups on the phenyl moiety (**2e** vs **2g**) leads to even lower M_w (39 000 vs 30 000), thereby demonstrating the broad range of MW tuning with this facile catalyst-modification strategy.

Introduction of electron-withdrawing substituents, such as perfluoro-alkyl or aryl group, is known to enhance activity or polymer MW for neutral Ni and Pd catalysts.^{34,53,67,68} For this catalyst system, replacing the methyl by trifluoromethyl (**2e** vs **2f**), indeed, leads to a moderate increase of catalyst activity (by $\sim 20\%$) and significant increase of copolymer MW (by $\sim 50\%$), albeit with a decrease in acrylate incorporation. These differences indicate that electronic tuning available through this approach also impacts catalyst behavior.

Although direct interaction between the cationic catalyst and the outer-sphere anion was not observed in solid-state structures of **2g** and **2a'**, the cation species in **2a** and **2a'** that feature the identical structure exhibit slightly different chemical shifts in ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (Figures S1–S3 vs S22–S24). This potentially implies differences in the cation–anion interaction. Notably, switching the anion leads to a dramatic difference in catalyst performance. Compared with **2a**, catalyst **2a'** featuring weakly coordinating OTf^- instead of BARF_{24}^- as the anion is much less active and produces copolymers with significantly lower MW and higher PDI (Entry 1 vs 17). One rationale is that the OTf^- anion is more coordinating than BARF_{24}^- and competes with olefins for binding to the nickel center and, thus, slows

catalysis and promotes chain transfer. Further screening of other anions, as well as mechanistic elucidation of this effect, is currently ongoing.

Notably, a catalyst system can be generated *in situ* from a 1:1:1:1 mixture of POPH, 4-methylbenzyl bromide, NaBARF_{24} , and $\text{Ni}(\text{py})_2(\text{CH}_2\text{SiMe}_3)_2$ and shows high activity [1010 kg/(mol·h)] in ethylene/acrylate copolymerization at $110\text{ }^\circ\text{C}$ (Table 1, entry 26). These results highlight the versatility of the reported postsynthetic ligand modification strategy. With this one-pot procedure, parallel generation and screening of a large number of new catalysts can be accessed via high-throughput methods.

Encouraged by the accessibility and efficiency of steric and electronic tuning with this postsynthetic strategy, we further explored ethylene/acrylate copolymer synthesis under varying acrylate concentrations and temperatures (Figure 3, Table 1). Catalysts **2b**–**2e** show 50%–120% higher activity at $110\text{ }^\circ\text{C}$ than at $90\text{ }^\circ\text{C}$ (Entries 19, 21, 23, and 24 vs 4, 6, and 7, Table 1), thereby demonstrating higher thermal stability than typically reported optimized temperatures for most Ni catalysts ($<100\text{ }^\circ\text{C}$). Catalyst **2e** is even active in copolymerization at $130\text{ }^\circ\text{C}$ (Entry 25, Table 1), though the ethylene uptake data suggest decomposition over time (Figures S27 and S28). Specifically, analogous neutral catalyst, POP-Ni, shows $\sim 60\%$ lower activity at $100\text{ }^\circ\text{C}$ than at $90\text{ }^\circ\text{C}$ (Entry 27 vs 28, Table 1). This scenario suggests that converting the free phosphine to phosphonium is beneficial for the thermal stability. By tuning acrylate concentration and reaction temperature, ethylene/acrylate copolymers with a wide range of M_w and acrylate incorporation are accessible (Figure 3). Microstructural analysis of the resulting ethylene/acrylate copolymers reveals that these cationic catalysts produce mostly linear copolymers with a small amount of methyl branching (Table S4). In contrast, POP-Ni produces copolymers with virtually no methyl branching. This difference further demonstrates significant impacts of phosphonium versus phosphine on

catalyst performance. Notably, copolymers produced by cationic Ni catalysts reported herein feature a significant amount of vinyl chain end (~37–54%) and 2-propenyl chain end (33–58%) but low levels of terminal tBA (3–18%). Therefore, β -H elimination after ethylene rather than acrylate insertion is more significant for this catalyst system. Overall, tuning the substituents on the phosphonium group by changing the alkyl halide employed in postsynthetic ligand functionalization allows for the preparation of ethylene/acrylate copolymers with broad range of characteristics, such as MW, MWD, and acrylate incorporation (Figure 3).

In summary, we have demonstrated an efficient late-stage functionalization strategy to synthesize a series of cationic P,O-nickel complexes starting from our previously reported POPH ligand. This synthetic method provides a facile and step-efficient pathway to tune the electronic and steric profiles of P,O-nickel complexes that are efficient catalysts for ethylene/*tert*-butyl acrylate copolymerization. Among the eight different variants reported here, the methyl variant, **2a**, shows the highest activity and M_w copolymers. Increasing the steric bulk close to the nickel center, such as in **2g** with 3,5-ditertbutylbenzyl group, enhances the rate of chain termination, which leads to low M_w copolymers. Although the acrylate incorporation is low to moderate, a broad spectrum of activity, as well as M_w and molecular weight distribution (MWD) of the copolymers produced suggests that this late-stage functionalization strategy can be very useful for tuning polymerization catalysts for the synthesis of desired functional polyolefins.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.4c03416>.

Experimental section, synthetic procedures, characterization data, ligand exchange studies, and polymerization studies (PDF)

Accession Codes

CCDC 2296096 and 2296313 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

Theodor Agapie – Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States; orcid.org/0000-0002-9692-7614; Email: agapie@caltech.edu

Authors

Priyabrata Ghana – Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States; Present Address: Department of Chemistry, IIT Gandhinagar Pajal, Gandhinagar-382055, India

Shuoyan Xiong – Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States; orcid.org/0000-0002-2579-4260

Adjeoda Tekpor – Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

Brad C. Bailey – Chemical Science, Core R&D, The Dow Chemical Company, Midland, Michigan 48667, United States

Heather A. Spinney – Chemical Science, Core R&D, The Dow Chemical Company, Midland, Michigan 48667, United States

Briana S. Henderson – Chemical Science, Core R&D, The Dow Chemical Company, Midland, Michigan 48667, United States

Complete contact information is available at:

<https://pubs.acs.org/10.1021/jacs.4c03416>

Author Contributions

^{||}P.G. and S.X. contributed equally.

Notes

The authors declare the following competing financial interest(s): A patent application including phosphonium-based ligands and corresponding nickel complexes was filed.

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