

Nickel Catalyzed Copolymerization of Ethylene and Alkyl Acrylates

Bruce S. Xin,[†] Naomasa Sato,[‡] Akio Tanna,[‡] Yasuo Oishi,[‡] Yohei Konishi,[‡] and Fumihiko Shimizu*[‡]

Mitsubishi Chemical Group Science and Technology Research Center, Inc., 1000 Kamoshida-cho, Aoba-ku, Yokohama 227-8502, Japan

S Supporting Information

ABSTRACT: Ni(II) complexes bearing an *o*-bis(aryl)-phosphinophenolate ligand were synthesized as catalysts for copolymerization of ethylene and alkyl acrylates. When the P-bound aryl group was 2,6-dimethoxyphenyl group, one of the oxygen atoms in the methoxy groups coordinated to the nickel center on its apical position. This complex was a highly active catalyst without any activators to give highly linear and high molecular weight copolymers. The structures of the copolymers were determined by ¹H and ¹³C NMR to clarify that the alkyl acrylate comonomers were incorporated in the main chain and that the structures of the copolymers were significantly influenced by the structure of the aryl group in the ligand.

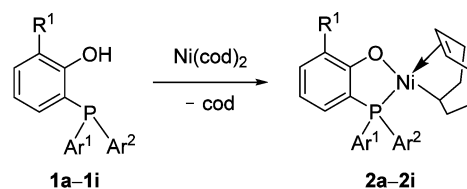
The development of olefin polymerization catalyst has enabled wide range control of polymer structures. In contrast, copolymerization of 1-alkenes with polar vinyl monomers via coordination–insertion mechanism is still a scientific challenge,¹ though it is attractive to produce value-added polyolefins with improved properties. Brookhart et al.² reported that Pd(II) α -diimine complexes can copolymerize ethylene with alkyl acrylates, but the obtained copolymers were highly branched and the comonomers were located at the ends of the branches. Pugh et al.³ reported that palladium modified with *o*-bis(2-methoxyphenyl)phosphinobenzenesulfonic acid was active for copolymerization of ethylene and alkyl acrylates to produce linear copolymers. This type of Pd complexes were further studied to enable copolymerization of ethylene and various polar vinyl monomers.⁴

Much effort has been done to find highly active Ni catalysts,^{1,5} particularly the one being capable of copolymerizing 1-alkenes with alkyl acrylates to give linear copolymers with high molecular weight. Such effort so far has given only a limited success in terms of catalyst activity, molecular weight, and linearity of the resulting copolymers.⁶

Among the approaches to seek for Ni catalysts, SHOP (Shell Higher Olefin Process) type Ni catalysts⁷ have some unique features: being highly active ethylene oligomerization or polymerization catalysts and tolerable in polar solvents. Furthermore, they can copolymerize ethylene with functional vinyl monomers, though being possible only when the vinyl unsaturation and the functional group are separated by a spacer of two or more methylene units.⁸

Here we report a novel class of Ni-based SHOP catalysts,⁹ the preparation of which is shown in Scheme 1 where the reaction of Ni(cod)₂ and *o*-bis(aryl)phosphinophenol **1a–1i** gave neutral σ , π -cyclooct-4-enyl Ni(II) complexes **2a–2i**

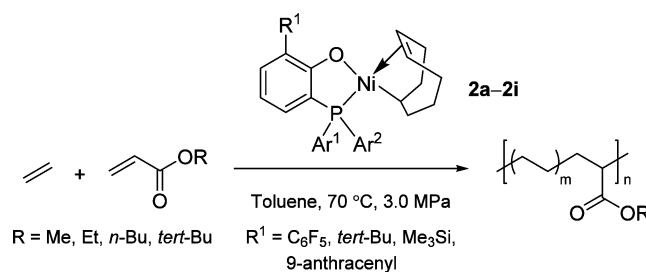
Scheme 1. Preparation of *o*-Bis(aryl)phosphinophenolate Nickel(II) Complexes



- 1a:** R¹ = C₆F₅, Ar¹ = Ar² = 2-MeOC₆H₄
1b: R¹ = C₆F₅, Ar¹ = Ar² = 2,6-(MeO)₂C₆H₃
1c: R¹ = C₆F₅, Ar¹ = 2,6-(MeO)₂C₆H₃, Ar² = 2-MeO-6-PhOC₆H₃
1d: R¹ = C₆F₅, Ar¹ = Ar² = 2-MeO-6-PhOC₆H₃
1e: R¹ = C₆F₅, Ar¹ = 2,6-(MeO)₂C₆H₃, Ar² = 2,6-(PhO)₂C₆H₃
1f: R¹ = C₆F₅, Ar¹ = 2-MeO-6-PhOC₆H₃, Ar² = 2,6-(PhO)₂C₆H₃
1g: R¹ = *tert*-Bu, Ar¹ = Ar² = 2,6-(MeO)₂C₆H₃
1h: R¹ = 9-anthracenyl, Ar¹ = Ar² = 2,6-(MeO)₂C₆H₃
1i: R¹ = Me₃Si, Ar¹ = Ar² = 2,6-(MeO)₂C₆H₃

almost quantitatively.¹⁰ We found that the complexes can copolymerize ethylene and alkyl acrylates with high activity to give highly linear copolymers with high molecular weight (Scheme 2).

Scheme 2. Copolymerization of Ethylene and Alkyl Acrylates with Complexes 2a–2i



The structure of **2a** and **2b** was determined by X-ray diffraction studies (Figure 1 and 2). In complex **2a**, the Ni(1)–C(31) distance (1.954(2) Å) reflects its σ -bond character and the C(27)–C(28) distance (1.364(4) Å) displays its double bond character. The σ -bond is located cis to the phosphorus atom because the strong trans influence of the phosphorus atom does not favor the existence of alkyl chain trans to the phosphorus atom.^{7c,8c} Complex **2b** has a similar structure to **2a**. The Ni(1)–C(33) distance (1.954(3) Å) reflects its σ -bond

Received: December 20, 2016

Published: February 20, 2017

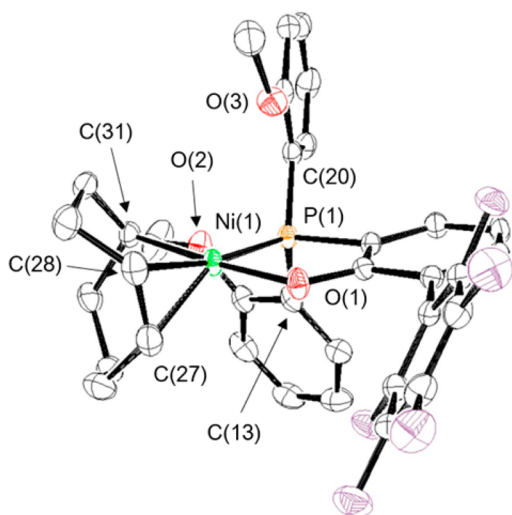


Figure 1. Structure of complex **2a**. The hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond distances (Å): Ni(1)–P(1) 2.1757(6), Ni(1)–O(1) 1.9383(16), Ni(1)–O(3) 3.166(2), Ni(1)–C(27) 2.132(3), Ni(1)–C(28) 2.118(2), Ni(1)–C(31) 1.954(2), C(27)–C(28) 1.364(4). Selected bond angle (deg): C(13)–P(1)–C(20) 106.76(11).

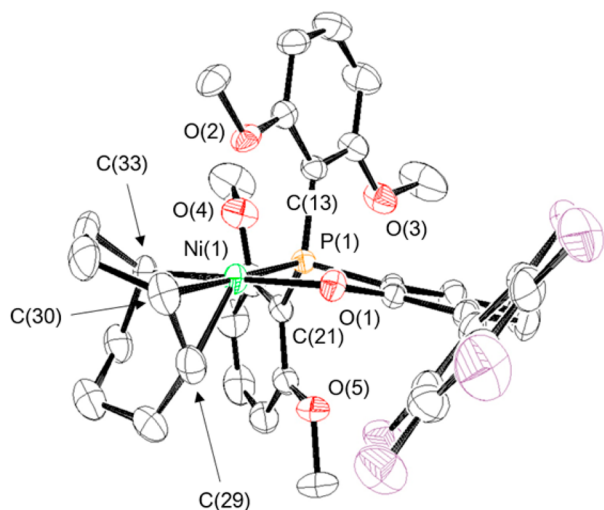


Figure 2. Structure of complex **2b**. The solvent and hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond distances (Å): Ni(1)–P(1) 2.1758(12), Ni(1)–O(1) 1.9663(18), Ni(1)–O(2) 2.530(2), Ni(1)–C(29) 2.037(4), Ni(1)–C(30) 2.055(5), Ni(1)–C(33) 1.954(3), C(29)–C(30) 1.375(6). Selected bond angle (deg): C(13)–P(1)–C(21) 110.66(17).

character whereas the C(29)–C(30) distance (1.375(6) Å) displays its double-bond character. The Ni(1)–O(2) distance in **2b** (2.530(2) Å) is significantly shorter than the sum of van der Waals radii of Ni–O, demonstrating that O(2) in **2b** coordinates to the nickel center on its apical position. The C(13)–P(1)–C(21) angle in **2b** (110.66(17)°) is wider than the corresponding angle C(13)–P(1)–C(20) in **2a** (106.76(11)°), suggesting that more sterically hindered structure in **2b** forces one of the aryl groups to be located in proximity to the nickel center, resulting in the coordination of the methoxy group.

Copolymerization of ethylene and *tert*-butyl acrylate (tBA) was investigated with complexes **2a** and **2b** (Table 1). Notably,

Table 1. Copolymerization of Ethylene and Alkyl Acrylate with **2a** and **2b**^a

entry	cat. ^b	AA ^c	A ^d	M _w ^e	M _w /M _n	T _m ^f	[CM] ^g
1	2a	tBA	680	4	1.8	120.4	0.5
2	2b	tBA	390	185	2.0	118.2	1.1
3	2b	MA	86	68	2.0	104.0	4.5
4	2b	EA	203	99	2.1	111.0	2.8
5	2b	nBA	261	119	2.0	112.2	2.5

^aConditions: catalyst, 80 μmol; ethylene pressure, 3.0 MPa; temperature, 70 °C; alkyl acrylate, 42 mmol; solvent, 1000 mL of toluene; reaction time, 1 h. ^bCatalyst. ^cAlkyl acrylate as comonomer. ^dCatalyst activity (kg mol⁻¹ h⁻¹). ^ekg mol⁻¹. ^fMelting point of the copolymers (°C). ^gComonomer content in the copolymers determined by ¹³C and ¹H NMR (mol %).

no activators were needed for the copolymerization. Complex **2a** having one methoxy group at the 2-position of Ar¹ and Ar², respectively, gave a low molecular weight copolymer. Whereas **2b** having two methoxy groups at the 2,6-positions of Ar¹ and Ar², respectively, gave a much higher M_w over 100 kg mol⁻¹. The apical position of **2b** is sterically protected by the coordination of methoxy group. This would be the cause of higher M_w with **2b** than with **2a**.^{2,11} Other alkyl acrylates such as methyl acrylate (MA), ethyl acrylate (EA), and *n*-butyl acrylate (nBA) were also copolymerized with ethylene using **2b** (Table 1). The data shows that catalyst activity and M_w increase whereas acrylate incorporation decreases as the bulkiness of acrylate increases. The M_w/M_n of the copolymers is around two in each copolymer.

To investigate the effect of MeO–Ni interaction on the catalyst performance, we systematically replaced methoxy group(s) on Ar¹ and Ar² by phenoxy group(s) and observed the change in catalyst performance in the copolymerization of ethylene and tBA. Table 2 shows that catalyst activity and M_w increase whereas the tBA content ([tBA]) decreases with increasing the number of phenoxy groups.¹²

Table 2. Influence of Phenoxy Group(s) on the Copolymerization of Ethylene and *tert*-Butyl Acrylate^a

entry	cat. ^b	PhO ^c	A ^d	M _w ^e	M _w /M _n	[tBA] ^f
1	2b	0	390	185	2.0	1.1
2	2c	1	690	205	1.9	0.9
3	2d	2	2010	283	2.2	0.4
4	2e	2	2120	286	2.0	0.4
5	2f	3	3230	348	2.5	0.3

^aConditions: Same as in Table 1 except that the reaction time was 0.33 h for entries 2–5. ^bCatalyst. ^cThe number of phenoxy groups on Ar¹ and Ar². ^dCatalyst activity (kg mol⁻¹ h⁻¹). ^ekg mol⁻¹. ^fThe amount of *tert*-butyl acrylate in the copolymer determined by ¹³C and ¹H NMR (mol %).

We also investigated the influence of substituent R¹ adjacent to the phenolic OH group on the catalyst performance (Table 3). It seems to be that aromatic substituents as R¹ give a better performance regarding catalyst activity and/or comonomer incorporation.

The structure of the copolymers obtained with **2a**–**2i** had the following common features:¹³ (i) a highly linear structure, (ii) isolated alkyl acrylate unit in the main chain,¹⁴ (iii) no branches including alkyl acrylate comonomers, and (iv) no branches having three or more carbons. More detailed structures of the copolymers **2A** and **2B** are summarized in

Table 3. Influence of R¹ on the Copolymerization of Ethylene and *tert*-Butyl Acrylate^a

entry	cat. ^b	R ¹	A ^c	M _w ^d	M _w /M _n	[tBA] ^e
1	2b	C ₆ F ₅	390	185	2.0	1.1
2	2g	<i>tert</i> -Bu	173	169	2.2	1.4
3	2h	9-anth ^f	246	146	2.0	1.9
4	2i	Me ₃ Si	185	125	2.1	1.2

^aConditions: Same as in Table 1 except that alkyl acrylate was 41 mmol for entries 2–4. ^bCatalyst. ^cCatalyst activity (kg mol⁻¹ h⁻¹). ^dkg mol⁻¹. ^eSame as in Table 2. ^f9-Anthracenyl.

Table 4, where 2A and 2B were obtained with 2a and 2b in the copolymerizations described in Table 1 entries 1 and 2,

Table 4. Detailed Structure of Ethylene/tBA Copolymers Determined by ¹H and ¹³C NMR

detailed structure		2A	2B
tBA (mol %)	total [tBA]	0.5	1.1
	internal [tBA]	0.4	1.0
	terminal [tBA]	0.1	0.01
branch (1/1000C)	methyl	3.8	0.5
	ethyl	0.2	n.d. ^a
chain end structure (1/1000C)	saturated	6.8	0.1
	vinyl	3.2	0.06
	1-propenyl	2.6	0.02
	tBA	0.5	0.06

^aNot detected.

respectively (see also Figures S30–S60 in the SI). Both the amount of tBA at the chain end (terminal tBA) and the branches were also influenced by the structure of Ar¹ and Ar².

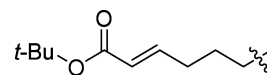
In 2A, the amount of terminal tBA was 20% (0.1/0.5). On the other hand, terminal [tBA] was only 0.9% (0.01/1.1) in 2B. Based on the fact that 2B has much less terminal tBA and much higher M_w than 2A, it is likely that ethylene insertion after tBA insertion is the rate-determining step^{15a,16} in the copolymerization of ethylene and tBA and that this step is accelerated with 2b compared to 2a probably because of the transient coordination of the apical methoxy group.¹⁵ Both methyl and ethyl branches were observed in 2A and the total amount of branches were 4.0 per 1000 carbons in the main chain. Whereas in 2B, only methyl branch was observed, being only 0.5 per 1000 carbons in the main chain.

The amount of branch in 2B is notably less than the case reported by Johnson et al.^{6,8c} It is well-known that methyl-branching occurs via (i) β-H elimination to form a terminal-vinyl polymer species (a macromer), (ii) reinsertion of the macromer in 2,1-fashion, and (iii) successive insertion of monomers into the newly formed metal–polymer bond,^{17,18} and that further branching occurs via a similar mechanism. Accordingly, significantly less branches in 2B would suggest the following two possibilities in the copolymerization with 2b: (a) less frequent β-H elimination than in the cases of Johnson et al., or (b) higher probability of 1,2-reinsertion than 2,1-reinsertion after the formation of a macromer.

Analysis of the chain end structures for 2A and 2B (Table 4) revealed that the number of saturated ends (6.8/1000C for 2A and 0.1/1000C for 2B) is roughly equal to the sum of vinyl groups, 1-propenyl groups, and terminal tBAs (6.3/1000C for 2A and 0.14/1000C for 2B). It suggests that one end of the copolymer is a saturated ethyl group, meaning that the

initiation step of the copolymerization is the insertion of ethylene into the Ni–H bond.^{19,20} It also suggests that the termination is β-H elimination from the last inserted ethylene or tBA.

The structure of terminal tBA in 2A (Figure 3) shows that the insertion of terminal tBA is 2,1-fashion.³ In the case of vinyl

**Figure 3. Structure of terminal tBA for copolymer 2A determined by ¹H NMR.**

monomers bearing electron-withdrawing groups, 2,1-insertion is generally favored with regard to the insertion into Pd-alkyl bonds.^{8c} Further, 2,1-insertion is favorable to avoid the steric repulsion between the growing polymer chain and the ester group in the comonomer.²¹ It is therefore reasonable to assume that 2,1-insertion of tBA prevailed in the main chain.

To summarize, we discovered a novel nickel catalyst system bearing a bidentate *o*-bis(aryl)phosphinophenolate ligand being capable of copolymerizing ethylene with alkyl acrylates without any activators. The resulting copolymers were highly linear and alkyl acrylate comonomers were incorporated in the main chain. Catalyst performance and the structure of the resulting copolymers were greatly influenced by the structure of the aryl groups in the ligand.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b13051.

Experimental procedures, NMR of the products, and X-ray crystallography (PDF)
Data for C₃₄H₃₀F₅NiO₃P and C₃₆H₃₄F₅NiO₅P/2.5C₆H₆ (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*1809430@cc.m-kagaku.co.jp

ORCID

Naomasa Sato: 0000-0001-5179-7441

Akio Tanna: 0000-0002-7134-7605

Yasuo Oishi: 0000-0001-7140-9661

Yohei Konishi: 0000-0002-7752-5193

Fumihiko Shimizu: 0000-0002-2223-7418

Present Addresses

[†]PetroChina Petrochemical Research Institute.

[‡]MCHC R&D Synergy Center, Inc.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Mitsubishi Chemical Corporation and Japan Polychem Corporation for the support of this work. We also thank Dr. Hiromasa Tanahashi, Prof. Kazushi Mashima, and Prof. Kyoko Nozaki for their helpful discussions.

■ REFERENCES

(1) Camacho, D. H.; Guan, Z. *Chem. Commun.* **2010**, 46, 7879–7893.

(2) (a) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267–268. (b) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888–899.

(3) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 744–745.

(4) (a) Rünzi, T.; Fröhlich, D.; Mecking, S. *J. Am. Chem. Soc.* **2010**, *132*, 17690–17691. (b) Daigle, J.-C.; Piche, L.; Claverie, J. P. *Macromolecules* **2011**, *44*, 1760–1762. (c) Ito, S.; Munakata, K.; Nakamura, A.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 14606–14607. (d) Anselment, T. M. J.; Anderson, C. E.; Rieger, B.; Boeddinghaus, M. B.; Fässler, T. F. *Dalton Trans.* **2011**, *40*, 8304–8313. (e) Kochi, T.; Noda, S.; Yoshimura, K.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 8948–8949. (f) Borkar, S.; Newsham, D. K.; Sen, A. *Organometallics* **2008**, *27*, 3331–3334. (g) Shen, Z.; Jordan, R. F. *Macromolecules* **2010**, *43*, 8706–8708. (h) Luo, S.; Vela, J.; Lief, G. R.; Jordan, R. F. *J. Am. Chem. Soc.* **2007**, *129*, 8946–8947. (i) Friedberger, T.; Wucher, P.; Mecking, S. *J. Am. Chem. Soc.* **2012**, *134*, 1010–1018. (j) Skupov, K. M.; Piche, L.; Claverie, J. P. *Macromolecules* **2008**, *41*, 2309–2310.

(5) (a) Mu, H. L.; Pan, L.; Song, D. P.; Li, Y. S. *Chem. Rev.* **2015**, *115*, 12091–12137. (b) Ito, S.; Ota, Y.; Nozaki, K. *Dalton Trans.* **2012**, *41*, 13807–13809. (c) Ketz, B. E.; Ottenwaelder, X. G.; Waymouth, R. M. *Chem. Commun.* **2005**, 5693–5695. (d) Benson, S.; Payne, B.; Waymouth, R. M. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 3637–3647. (e) Tao, W.-J.; Nakano, R.; Ito, S.; Nozaki, K. *Angew. Chem., Int. Ed.* **2016**, *55*, 2835–2839.

(6) (a) Johnson, L.; Bennett, A.; Dobbs, K.; Hauptman, E.; Ionkin, A.; Ittel, S.; McCord, E.; McLain, S.; Radzewich, C.; Yin, Z.; Wang, L.; Wang, Y.; Brookhart, M. *Polym. Mater. Sci. Eng.* **2002**, *86*, 319. (b) Wang, L.; Hauptman, E.; Johnson, L. K.; Marshall, W. J.; McCord, E. F.; Wang, Y.; Ittel, S. D.; Radzewich, C. E.; Kunitsky, K.; Ionkin, A. S. *Polym. Mater. Sci. Eng.* **2002**, *86*, 322. (c) Liu, W.; Malinoski, J. M.; Brookhart, M. *Organometallics* **2002**, *21*, 2836–2838. (d) Long, B. K.; Eagan, J. M.; Mulzer, M.; Coates, G. W. *Angew. Chem., Int. Ed.* **2016**, *55*, 7106–7110.

(7) (a) Keim, W. *Angew. Chem., Int. Ed.* **2013**, *52*, 12492–12496. (b) Kuhn, P.; Sémeril, D.; Matt, D.; Chetcuti, M. J.; Lutz, P. *Dalton Trans.* **2007**, 515–528. (c) Wan, D.-W.; Gao, Y.-S.; Li, J.-F.; Shen, Q.; Sun, X.-L.; Tang, Y. *Dalton Trans.* **2012**, *41*, 4552–4557.

(8) (a) Klabunde, U.; Ittel, S. D. *J. Mol. Catal.* **1987**, *41*, 123–134. (b) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169–1203. (c) Nakamura, A.; Ito, S.; Nozaki, K. *Chem. Rev.* **2009**, *109*, 5215–5244.

(9) (a) Shimizu, F.; Xin, S.; Tanna, A.; Goromaru, S.; Matsubara, K. Patent WO2010/050256, May 6, 2010. (b) Shimizu, F.; Xin, S.; Tanna, A.; Goromaru, S.; Matsubara, K. U.S. Patent 8,618,319, Dec. 31, 2013.

(10) (a) Singleton, D. M. U.S. Patent 4,472,525, Sep. 18, 1984. (b) Peuckert, M.; Keim, W. *Organometallics* **1983**, *2*, 594–597. (c) Heinicke, J.; Koesling, M.; Brüll, R.; Keim, W.; Pritzkow, H. *Eur. J. Inorg. Chem.* **2000**, 299–305. (d) The complexation was confirmed by ³¹P NMR in this work. (See also the [Supporting Information](#).)

(11) (a) Deng, L.; Woo, T. K.; Cavallo, L.; Margl, P. M.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, *119*, 6177–6186. (b) Camacho, D. H.; Salo, E. V.; Ziller, J. W.; Guan, Z. *Angew. Chem., Int. Ed.* **2004**, *43*, 1821–1825.

(12) Both steric and electronic effects should be taken into account. Considering the sterically congested circumstance around the Ni in **2b**, it may be reasonable to assume that ethylene is more likely to undergo insertion than bulky tBA and that this tendency is enhanced with increasing the number of bulkier phenoxy groups. However, we do not have any clue to rule out an electronic explanation.

(13) All the NMR charts of the copolymers are shown in the [Supporting Information](#).

(14) Guironnet, D.; Roesle, P.; Rünzi, T.; Göttker-Schnetmann, I.; Mecking, S. *J. Am. Chem. Soc.* **2009**, *131*, 422–423. No series of alkyl acrylate comonomers were observed in the copolymers, meaning that the possibility of contamination of alkyl acrylate homopolymer is excluded.

(15) (a) Ota, Y.; Ito, S.; Kuroda, J.; Okumura, Y.; Nozaki, K. *J. Am. Chem. Soc.* **2014**, *136*, 11898–11901. (b) Skupov, K. M.; Marella, P.

R.; Simard, M.; Yap, G. P. A.; Allen, N.; Conner, D.; Goodall, B. L.; Claverie, J. P. *Macromol. Rapid Commun.* **2007**, *28*, 2033–2038. This paper says that the C=O chelation after the 2,1-insertion of an acrylate blocks the polymerization until the termination by chain-walking mechanism. Note that it is also described that C=O chelation may be broken by the transient coordination of the apical methoxy group. See also the discussion regarding the rate determining step in the copolymerization.

(16) Nakamura, A.; Anselment, T. M. J.; Claverie, J.; Goodall, B.; Jordan, R. F.; Mecking, S.; Rieger, B.; Sen, A.; van Leeuwen, P. W. N. M.; Nozaki, K. *Acc. Chem. Res.* **2013**, *46*, 1438–1449.

(17) Noda, S.; Nakamura, A.; Kochi, T.; Chung, L. W.; Morokuma, K.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 14088–14100.

(18) Guan, Z.; Cotts, P. M.; McCord, E. F.; McLain, S. J. *Science* **1999**, *283*, 2059–2062.

(19) The initial activation of **2a–2i** may proceed with the formation of Ni–H species via β -H elimination of cyclooctenyl group, though we have not detected isolated cyclooctadiene. Meanwhile, no cyclooctenyl chain end was observed in the copolymers. (See the [Supporting Information](#).)

(20) Müller, U.; Keim, W.; Krüger, C.; Betz, P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1011–1013.

(21) von Schenck, H.; Strömberg, S.; Zetterberg, K.; Ludwig, M.; Åkermark, B.; Svensson, M. *Organometallics* **2001**, *20*, 2813–2819.