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Binuclear Ni catalyzed ethylene copolymerization with short chain alkenol monomers†

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Ethylene coordination copolymerization with vinyl polar monomers, particularly short chain alkenols, offers an attractive method for controlled synthesis of important hydroxy-functionalized polyethylenes under mild conditions. However, reports on short-chain alkenol copolymerization are limited due to issues like chelating coordination and β-O elimination. Here, we report the synthesis and characterization of binuclear Ni complexes for ethylene copolymerization with various alkenol monomers such as allyl-OH, 3-buten-1-ol, 4-penten-1-ol and 9-decen-1-ol. These complexes, upon activation with Et_2AlCl, achieved notable activity (as high as 592 kg (mol cat h atm)$^{-1}$) in ethylene/3-buten-1-ol copolymerization, producing copolymers with 1.7 mol% comonomer incorporation and a high molecular weight (M_n = 64.2 kg mol^{-1}). The activity and comonomer content were influenced by Et_2AlCl loading, reaction temperature, and alkenol monomer length, with longer alkenols such as 9-decen-1-ol yielding higher activity, comonomer incorporation and molecular weight. Activities up to 169 kg (mol cat h atm)$^{-1}$ were also achieved in ethylene/allyl-OH copolymerization with reduced molecular weight (M_n = 17.2 kg mol^{-1}). Microstructural analysis revealed predominant in-chain and chain-end polar monomer incorporation in all cases. Notably, ethylene/allyl-OH copolymers exhibited unique olefinic end groups and microstructures assignable to Friedel–Crafts reactions, which is likely due to an alternative chain termination pathway associated with the short chain length between the O atom and the active Ni center. For comparison, ethylene/allyl-OAc copolymers showed exclusively olefinic groups, indicating a β-OAc elimination mechanism. This process resulted in lower activity and molecular weight, suggesting catalyst poisoning from rapid chain termination.

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Introduction

Hydroxy-functionalized polyolefins, which bear hydroxyalkyl branches, often exhibit superior properties and performances to traditional non-polar polyolefins, such as adhesion and barrier properties.[1–4] They can be used as macroinitiators for the synthesis of polar–nonpolar graft block copolymers[5–8] and have recently been used for the synthesis of high performance reprocessable polyolefin vitrimers.[9–14]. Thus, hydroxy-functionalized polyolefins have been a unique target in catalytic and synthetic polyolefin research.[15–21] Ethylene coordination copolymerization with polar monomers, especially α,ω-alkenol monomers, provides an important pathway for the synthesis of functional polyolefins with well-defined structures under mild conditions.[3,22] Compared with long chain alkenol monomers, which are usually copolymerized with good activity and comonomer incorporation (early[23–31] and late[32–37] transition metal catalysis), short chain alkenols are abundant, cheap, industrially more relevant, and hence more attractive monomer candidates.

Despite the advantages of synthesizing hydroxy-functionalized polyolefins *via* coordination copolymerization, short chain alkenols are still challenging polar comonomers. Our laboratory reported[27,28] [ONX]Ti-catalyzed (ONX is a monoanionic tridentate ligand; X = S and P) ethylene copolymerization with 4-penten-1-ol and achieved an activity of 2800 kg (mol h atm)$^{-1}$ when the comonomer incorporation was 1.4 mol%. Duchateau *et al.* reported[29] $CGCTiCl_2$-catalyzed (CGC, constrained geometry catalyst) ethylene copolymerization with 3-buten-1-ol and allyl-OH and achieved activities of 792 kg (mol h atm)$^{-1}$ and 860 kg (mol h atm)$^{-1}$, when the comonomer incorporations were approximately 1.7 mol% and 3.1 mol%, respectively. Mu *et al.* reported[38] amine bis(phenolate) Zr catalyzed ethylene/3-buten-1-ol copolymerization and achieved an activity of 26 kg (mol h atm)$^{-1}$ when the comono-

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mer incorporation was 1.1 mol%. Cui *et al.* reported[39] (Flu-CH_2CH_2-NHC-C_6H_4Me)Sc(CH_2SiMe_3)$_2$ catalyzed ethylene/3-buten-1-ol copolymerization and achieved an activity of 1168 kg (mol h atm)$^{-1}$ when the comonomer incorporation was 0.7 mol%. Imuta *et al.* reported[40] ethylene/allyl-OH copolymerization with an ansa-zirconocene catalyst and achieved an activity of 91.2 kg (mol h atm)$^{-1}$ when the comonomer incorporation was 1.2 mol%. Besides early transition metal catalysis, late transition metal catalysis was also reported in ethylene copolymerization with short chain alkenol comonomers in the absence of trialkylaluminum. Nozaki *et al.*[41] and Chen *et al.*[42] reported ethylene/allyl-OH copolymerization with a Pd/phosphine-sulfonate catalyst and a Pd/α-diimine catalyst and achieved activities of 1 and 15.6 g (mol h atm)$^{-1}$ when the comonomer incorporations were 5.7 mol% and 6.9 mol%, respectively. Overall, reports on ethylene copolymerization with short chain alkenol monomers are still very limited. Our group recently reported a series of tetranuclear Ni catalysts for ethylene copolymerizations with short chain protic monomers (vinyl acetic acid, acrylic acid, allyl-OH, 3-buten-1-ol, *etc.*), exhibiting great activity and comonomer incorporation.[43] Here, we further designed and synthesized a series of binuclear Ni complexes with varied substitutions and probed their ethylene copolymerization with various alkenol monomers in terms of activity, molecular weight, branch density, and comonomer incorporation, and probed the chain termination processes that may be associated with catalyst poisoning/low activity, especially in copolymerization with allyl-OH.

Results and discussion

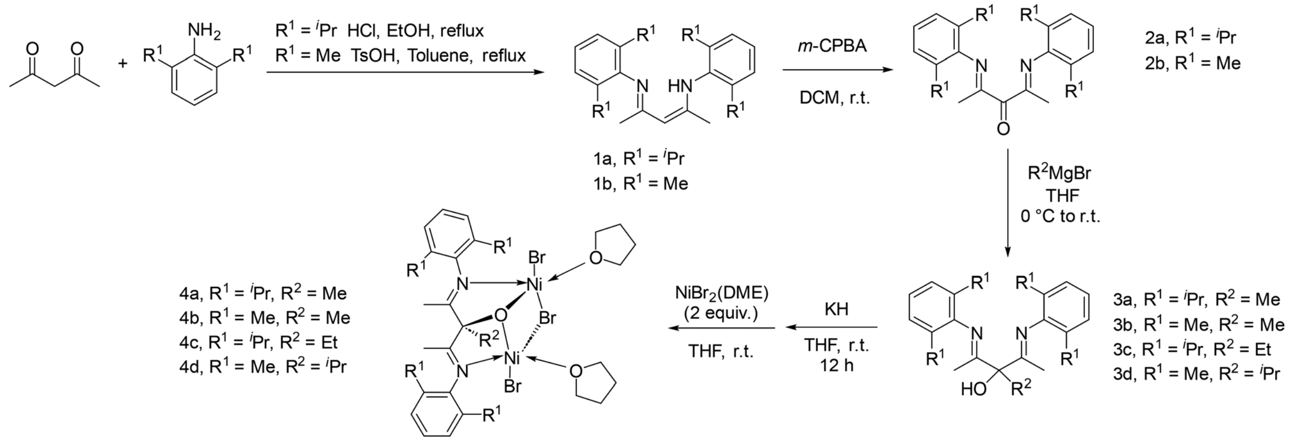
Synthesis and characterization of the ligands and Ni complexes

The synthesis of complex **4a** was recently reported by our group.[43] Ni complexes **4b–4d** were synthesized following the same procedure (Scheme 1), *i.e.* ligand deprotonation with 2.0 equiv. of KH, followed by the reaction with $NiBr_2$(DME),[44] all giving good yields, 73%, 65% and 46% for **4b**, **4c** and **4d**, respectively. Single crystals of **4c** and **4d** suitable for X-ray diffraction studies were grown from THF/*n*-hexane solution with the solid-state structure shown in Fig. 1. The two Ni atoms in the bimetallic Ni complex adopt a distorted trigonal bipyramidal configuration. The central O1 and Br2 atoms are equally shared by both nickel atoms. The Ni1⋯Ni2 distance for **4c** is 3.101 Å, much shorter than that in complex **4a** (3.259 Å), reflecting the dramatic effects of the R^2 substituent on the steric environment surrounding both Ni atoms.

Ethylene/3-buten-1-ol copolymerization

The four precatalysts are differentiated by the substituents R^1 and R^2. We first used **4a** as the primary precatalyst and Et_2AlCl (DEAC) as the cocatalyst for ethylene/3-buten-1-ol copolymerization studies (Table 1). The activity reached 474 kg (mol cat h atm)$^{-1}$ when 0.2 M of alkenol monomer was used for ethylene copolymerization at 1 atm and 30 °C, and 1.5 equiv. DEAC was used for pretreating the comonomer immediately before the reaction. The resulting copolymer shows a high molecular weight (M_n = 53.9 kg mol^{-1}) and 1.3 mol% alkenol comonomer content (entry 4). Here, we studied the effects of cocatalyst loading, comonomer amount, reaction temperature and time on the copolymerization. Note that hydroxy-functionalized PEs were acetylated using glacial acetic acid in the presence of H_2SO_4 at 120 °C before running GPC measurement (see the ESI for more details†).

On reducing the DEAC loading to 1 equiv./comonomer, the catalysis was not influenced in terms of activity, comonomer content, or product molecular weight (entry 2), but further reduction to 0.8 equiv. led to inactive catalysis (entry 1), suggesting the important stoichiometry requirement in pretreating the protic alkenol right before the polymerization. Further increasing the DEAC loading seems to have minor effects on catalysis, and thus we adopted 1.5 equiv. DEAC/comonomer for the subsequent studies. Upon increasing the alkenol amount from 0.1 to 0.2, 0.3 and then 0.4 M, the comonomer content increased from 0.4 mol% to 1.3 mol%,



Scheme 1 Synthesis of ligands and complexes.

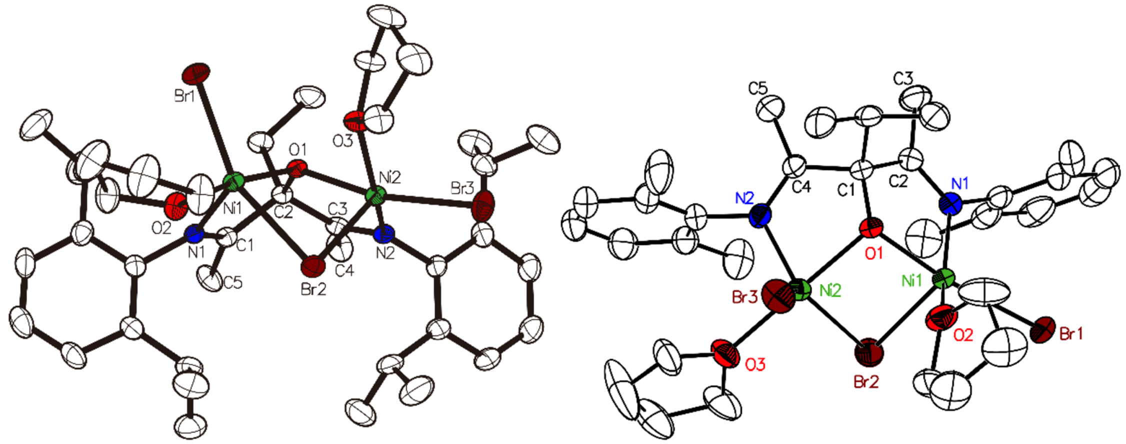


Fig. 1 Single crystal structures of **4c** and **4d**. H atoms are omitted for clarity.

Table 1 Ethylene/3-buten-1-ol copolymerization with Ni catalyst **4a** [a]

Entry	Comon. (M)	DEAC/ comon. ratio	Temp. (°C)	t (min)	Yield (g)	Act. [b]	M_n [c] (kg mol^{-1})	$Đ$ [c]	Comon. content [d] (mol%)	FG/chain	Branch [d] (CH$_3$/1000C)
1	0.2	0.8	30	10	None	—	—	—	—	—	—
2	0.2	1.0	30	10	0.405	486	46.3	2.4	1.4	23	75
3	0.2	1.25	30	10	0.393	472	46.7	2.4	1.4	23	81
4	0.2	1.5	30	10	0.395	474	53.9	2.2	1.3	25	75
5	0.2	2.0	30	10	0.306	367	38.3	2.4	1.4	19	82
6	0.2	2.5	30	10	0.314	377	35.5	3.1	1.2	15	82
7	0.1	1.5	30	10	0.700	840	79.0	2.3	0.4	11	79
8	0.3	1.5	30	10	0.220	264	27.0	2.3	2.9	28	74
9	0.4	1.5	30	10	0.143	172	16.7	2.2	4.7	28	70
10	0.2	1.5	20	10	0.523	628	68.1	1.9	1.1	27	70
11	0.2	1.5	40	10	0.256	307	27.2	2.9	1.9	18	80
12	0.2	1.5	50	10	0.146	175	15.9	2.9	2.7	15	80
13	0.2	1.5	30	5	0.259	622	34.0	1.9	1.6	19	78
14	0.2	1.5	30	15	0.434	347	52.7	3.2	1.3	24	81
15	0.2	1.5	30	20	0.489	293	56.3	3.1	1.3	26	78
16	0.2	1.5	30	30	0.510	204	56.3	3.3	1.2	24	74

[a] Conditions: cat. **4a** (5 μmol), toluene (total volume 50 mL), water bath, and ethylene (1 atm). All experiments were performed in duplicate. [b] kg (mol cat h atm)$^{-1}$. [c] Determined by high temperature GPC. [d] Calculated from ^{1}H NMR.

2.9 mol% and then 4.7 mol% at the expense of activity, which dropped from 840 to 474, 264 and then 172 kg (mol cat h atm)$^{-1}$, respectively (Fig. 2A). When the reaction temperature was gradually increased from 20 °C to 50 °C (entries 10, 4, 11 and 12), the activity was gradually reduced from 628 to 175 kg (mol cat h atm)$^{-1}$, but the comonomer content increased from 1.1 to 2.7 mol% (Fig. 2B). This may be due to the reduced ethylene solubility at higher temperatures and limited thermal stability of the active species. When the reaction time gradually increased from 5 to 30 min (entries 13, 4 and 14–16), the activity was also reduced from 622 to 204 kg (mol cat h atm)$^{-1}$ and the comonomer content was slightly reduced from 1.6 to 1.2 mol%. Interestingly, the molecular weight of the resulting copolymer increased from 34.0 to 56.3 kg mol^{-1} with a slightly broadened $Đ$, suggesting reduced catalytic efficiency over reaction time (Fig. 2C and D).

Effects of the alkenol comonomer length and catalyst structure

Next, we explored using all the catalysts **4a–4d** for ethylene copolymerization with various alkenol monomers such as allyl-OH, 3-buten-1-ol, 4-penten-1-ol and 9-decen-1-ol (Table 2). We first analyzed the effects of the polar monomer linker length, and then the catalyst on the copolymerization activity, comonomer content, and molecular weight as well as the introduced FG other than –OH.

The length of the alkenol monomer exhibited significant effects on catalysis, and overall similar trends were observed in terms of activity, comonomer content and product molecular weight, regardless of the Ni catalyst used. Here, we used catalyst **4a** as an example. Upon switching the monomer from allyl-OH to 3-buten-1-ol, 4-penten-1-ol and then 9-decen-1-ol, the activity increased from 82 to 474, 497 and then 587 kg

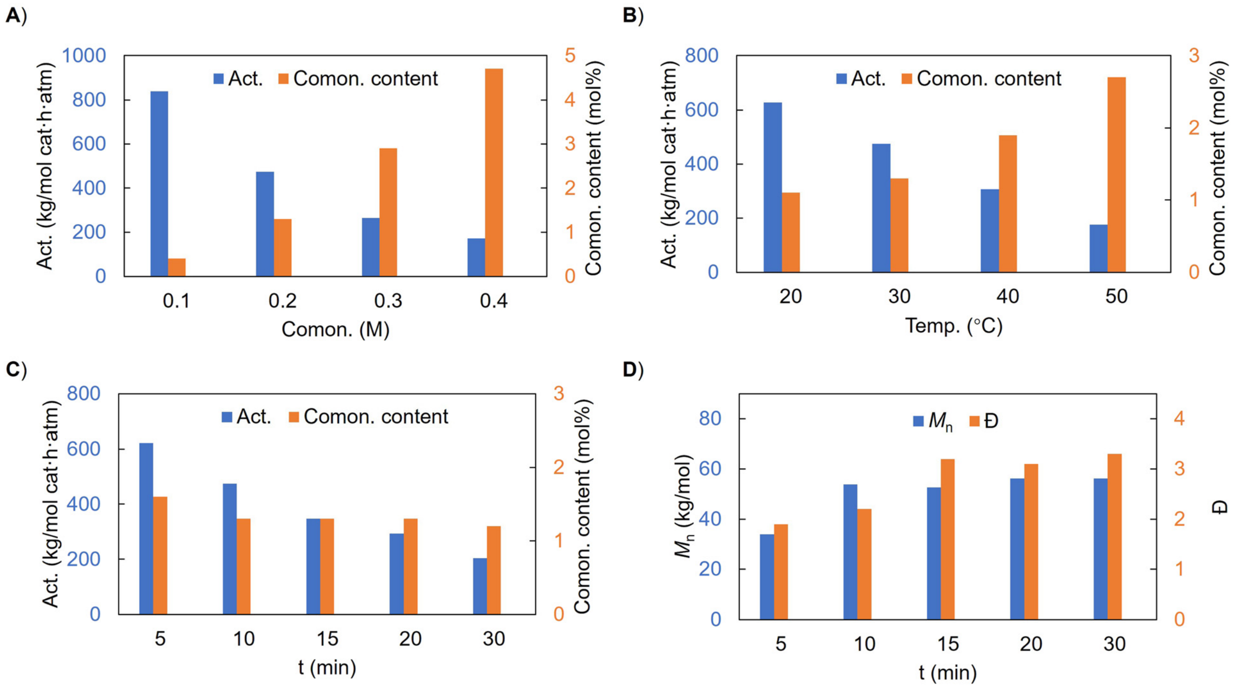


Fig. 2 Effects of comonomer amount (A), reaction temperature (B) and time (C and D) on **4a** catalyzed ethylene/3-buten-1-ol copolymerization.

Table 2 Ethylene/alkenol copolymerization with Ni catalysts.[a]

Entry	Cat. (μmol)	Comon.	Yield (g)	Act.[b]	M_n[c] (kg mol^{-1})	$Đ$[c]	Comon. content[d] (mol%)	Branch[d] (CH_3/1000C)
1	**4a** (10)	Allyl-OH	0.136	82	7.1	2.9	0.4[e]	82
2	**4b** (10)	Allyl-OH	0.062	37	3.8	1.9	0.6[e]	89
3	**4c** (10)	Allyl-OH	0.281	169	17.2	2.3	0.4[e]	84
4	**4d** (10)	Allyl-OH	0.204	122	13.9	1.9	0.4[e]	96
5[f]	**4a** (10)	Allyl-OH	0.028	17	1.7	1.9	1.6[e]	85
6	**4a** (5)	3-Buten-1-ol	0.395	474	53.9	2.2	1.3	75
7	**4b** (5)	3-Buten-1-ol	0.086	103	14.1	2.5	2.0	75
8	**4c** (5)	3-Buten-1-ol	0.493	592	64.2	1.6	1.7	76
9	**4d** (5)	3-Buten-1-ol	0.267	320	42.9	1.7	1.7	87
10	**4a** (5)	4-Penten-1-ol	0.414	497	57.0	2.3	1.1	76
11	**4b** (5)	4-Penten-1-ol	0.117	140	20.1	5.0	1.8	71
12	**4c** (5)	4-Penten-1-ol	0.481	577	65.2	1.5	1.7	75
13	**4d** (5)	4-Penten-1-ol	0.269	323	47.1	1.6	1.7	88
14	**4a** (5)	9-Decen-1-ol	0.489	587	71.0	2.7	1.3	74
15	**4b** (5)	9-Decen-1-ol	0.154	185	25.7	4.3	1.5	69
16	**4c** (5)	9-Decen-1-ol	0.590	708	79.5	1.4	2.9	67
17	**4d** (5)	9-Decen-1-ol	0.337	404	49.7	1.4	1.7	87

[a] Conditions: alkenol monomer (0.2 M), DEAC (0.3 M), toluene (total volume 50 mL), water bath (30 °C), ethylene (1 atm), and 10 min. All experiments were performed in duplicate. [b] kg (mol cat h atm)$^{-1}$. [c] Determined by high temperature GPC. [d] Calculated from ^{1}H NMR. [e] Olefinic end group was observed in the polymer samples; please see the ESI† for detailed analysis. [f] Allyl-OH, 0.4 M; DEAC, 0.6 M.

(mol cat h atm)$^{-1}$ (Fig. 3A), and the molecular weight (M_n) of the resulting copolymer also increased from 7.1 to 53.9, 57.0 and then 71.0 kg mol^{-1} (entries 1, 6, 10 and 14). Besides the remarkable effects of the allyl-OH monomer on activity and M_n, it also exhibited unique effects on the comonomer content and introduced FG (Fig. 3B). The comonomer content is much lower (0.4 mol% for allyl-OH) than those of other longer alkenol monomers (1.0–1.3 mol%); copolymer ^{1}H NMR suggested that some of the –OH groups were converted to olefinic groups in the case of allyl-OH, likely resulting from β-OAl elimination.[45–48] In contrast, copolymerization with other longer alkenol monomers leads to exclusively –OH groups.

The catalysts bear different R^1 and R^2 substituents, which exhibited varied effects on copolymerization. For all the alkenol monomers, the activity decreases in the order of **4c** > **4a**, **4d** > **4b**, *i.e.* the bulkier the R^1 and R^2 groups of the catalyst, the higher the activity. Overall, the four catalysts' comonomer enchainment capabilities are similar. It is worth noting

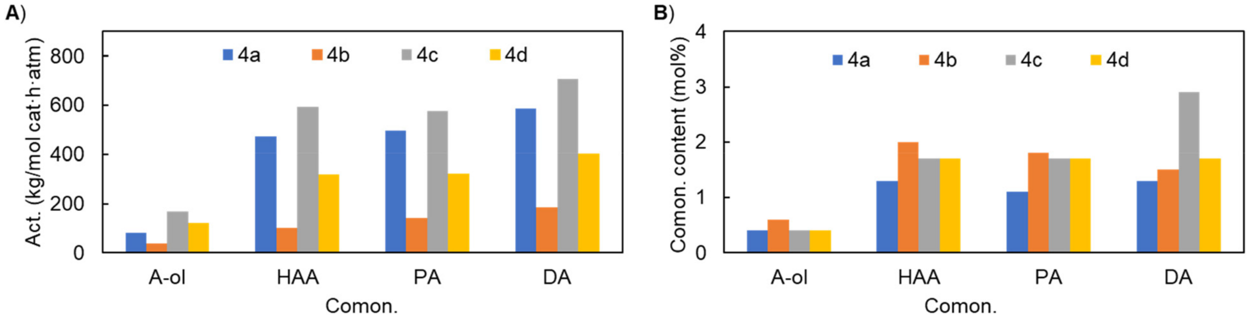


Fig. 3 Effects of catalyst structures on ethylene copolymerization activity (A) and comonomer content (B) with various alkenol monomers (A-ol = allyl-OH; HAA = 3-buten-1-ol; PA = 4-penten-1-ol; and DA = 9-decen-1-ol).

that the resulting copolymers (entries 11 and 15, Table 2) derived from catalyst **4b** showed non-uniform comonomer composition through GPC traces and DSC thermograms (Fig. S80 and S84†), likely reflecting the formation of non-uniform catalytically active centers.

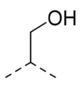
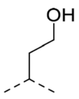
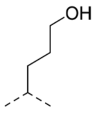
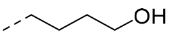
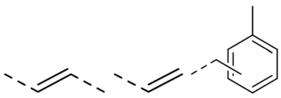
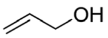
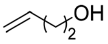
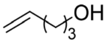
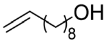
We also inspected the microstructure of ethylene copolymers with various alkenol comonomers. Representative samples derived from catalysis with catalyst **4c** were chosen for a qualitative comparison (Table 3). Besides the hydroxyalkyl branch generated from regular alkenol insertion without chain walking (in-chain incorporation), *i.e.* $(CH_2)_nOH$ from $CH_2{=}CH(CH_2)_nOH$ (n = 1, 2, and 3) enchainment, a chain-end hydroxyl group, $-(CH_2)_nOH$ ($n > 3$), was observed in all the copolymer products. Structures I, II, III and IV were assigned by combined ^1H, ^{13}C and 2D NMR characterization, and according to the literature.[40–43]

The in-chain incorporation was observed in the ethylene copolymerizations with all the types of alkenol comonomers, likely occurring *via* path a and path b during the catalysis (Fig. 4). The chain-end incorporation was observed in all the cases as well, regardless of the alkenol comonomer, suggesting a strong tendency to undergo path c in all the copolymerizations, *i.e.* 2,1-insertion of the polar comonomer followed by chain walking before the next monomer insertion. In contrast to other alkenols, ethylene copolymers with allyl-OH showed additional functional groups such as olefinic end groups[41,49,50] and even microstructures assignable to the Friedel–Crafts reaction of alkenes with arenes[51–54] (path d). It is likely associated with the short chain length between the olefin double bond and the –OH group, which leads to chelating coordination and other chain termination pathways. Note that the GPC traces of several polymer samples, especially for allyl-OH copolymers, exhibited broadened or even multiple peaks, likely reflecting the formation of non-uniform catalytically active centers and/or complicated chain transfer/termination processes.

Ethylene/allyl-OAc copolymerization

On the other hand, we were curious about the chemistry associated with the functional group during the copolymerization as it is related to catalyst poisoning by back-biting and β-X elimination of the introduced functional group. Thus, we studied allyl-OAc in the copolymerization with DEAC as the masking reagent and cocatalyst. Copolymerization afforded polymers with exclusively olefinic groups and no –OAc group was detected by ^1H NMR (Table 4). An olefin double bond and aromatic protons were detected instead. Due to the complexity of the reaction product and difficulty in analysis of the trace

Table 3 Characteristic microstructures in the copolymer samples.[a]

Entry	Monomer	 I	 II	 III	 IV	
1		✓	n.d.	n.d.	✓	✓
2		n.d.	✓	n.d.	✓	n.d.
3		n.d.	n.d.	✓	✓	n.d.
4		n.d.	n.d.	n.d.	✓	n.d.

[a] The samples are from entries 3, 8, 12 and 16 in Table 2 for the ethylene copolymers with allyl-OH, 3-buten-1-ol, 4-penten-1-ol and 9-decen-1-ol, respectively. The microstructures were identified by polymer ^1H NMR and ^{13}C NMR. Please see detailed assignments in the ESI.†

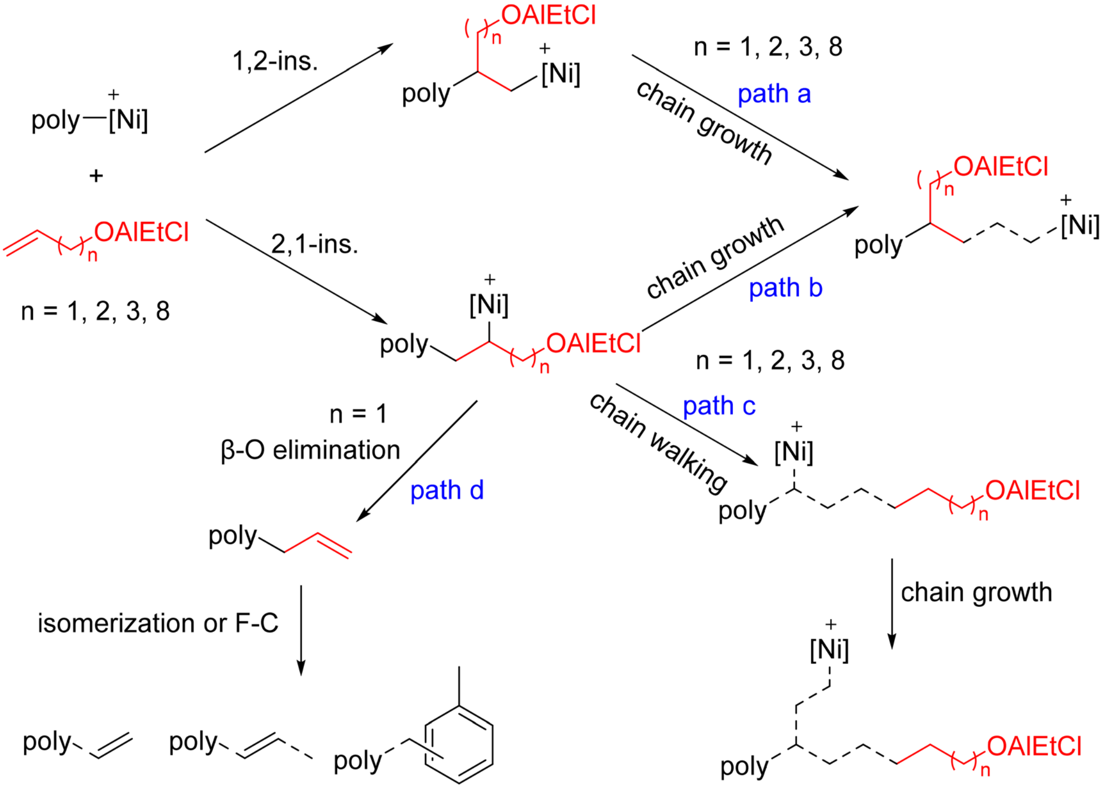


Fig. 4 Possible polar monomer enchainment pathways (insertion, chain walking, and chain transfer). The active species is shown as $[Ni]^+$ for clarity purposes.

Table 4 Ethylene/allyl-OAc copolymerization with Ni catalysts[a]

Entry	Cat. (μmol)	Allyl-OAc (M)	Temp. (°C)	Yield (g)	Act.[b]	M_n[c] (kg mol^{-1})	$Đ$[c]
1	**4a** (5)	0.2	30	0.150	180	11.9	2.1
2	**4b** (5)	0.2	30	0.098	118	6.1	2.1
3	**4c** (5)	0.2	30	0.170	204	18.2	2.1
4	**4d** (5)	0.2	30	0.124	149	10.0	1.8
5	**4a** (10)	0.4	20	0.178	107	7.8	1.9
6	**4a** (10)	0.4	30	0.136	82	5.8	2.0
7	**4a** (10)	0.4	40	0.071	43	4.0	2.0

[a] Conditions: toluene (total volume 50 mL), DEAC/comon. = 1.5, water bath, ethylene (1 atm), and 10 min. All experiments were performed in duplicate. [b] kg (mol cat h atm)$^{-1}$. [c] Determined by high temperature GPC.

peaks, their quantitative analysis was not pursued. The polymer M_n ranged from 4.0 kg mol^{-1} to 18.2 kg mol^{-1}, which is lower than that of the corresponding ethylene/alkenol copolymers (Table 2), reflecting a disadvantaged chain propagation *vs.* chain transfer. Thus, β-OAc elimination is invoked whenever an allyl acetate monomer is enchained,[55] which affords olefin-ended PE. The lower activity in Ni catalyzed ethylene copolymerization with either allyl-OH or allyl-OAc *vs.* ethylene copolymerization with longer chain alkenols is likely associated with the facile chain transfer/termination and poisoning of the Ni species.

Conclusion

Binuclear Ni complexes paired with DEAC offer a great catalyst system for ethylene coordination copolymerization with short-chain alkenols and controlled synthesis of hydroxy-functionalized polyethylenes. Despite challenges like chelating coordination and β-O elimination, these complexes exhibit notable activity, producing copolymers with high molecular weights. Microstructural analysis reveals insights into copolymerization mechanisms, highlighting the influence of the catalyst structure and reaction conditions on activity, comonomer incorporation and polymer molecular weight. Understanding these factors is crucial for optimizing activity and mitigating catalyst poisoning, thereby advancing the development of functional polyolefins. Further investigations focusing on the elucidation and modulation of the polar monomer enchainment process and novel catalyst design are underway.

Data availability

Data are available upon request from the authors.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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