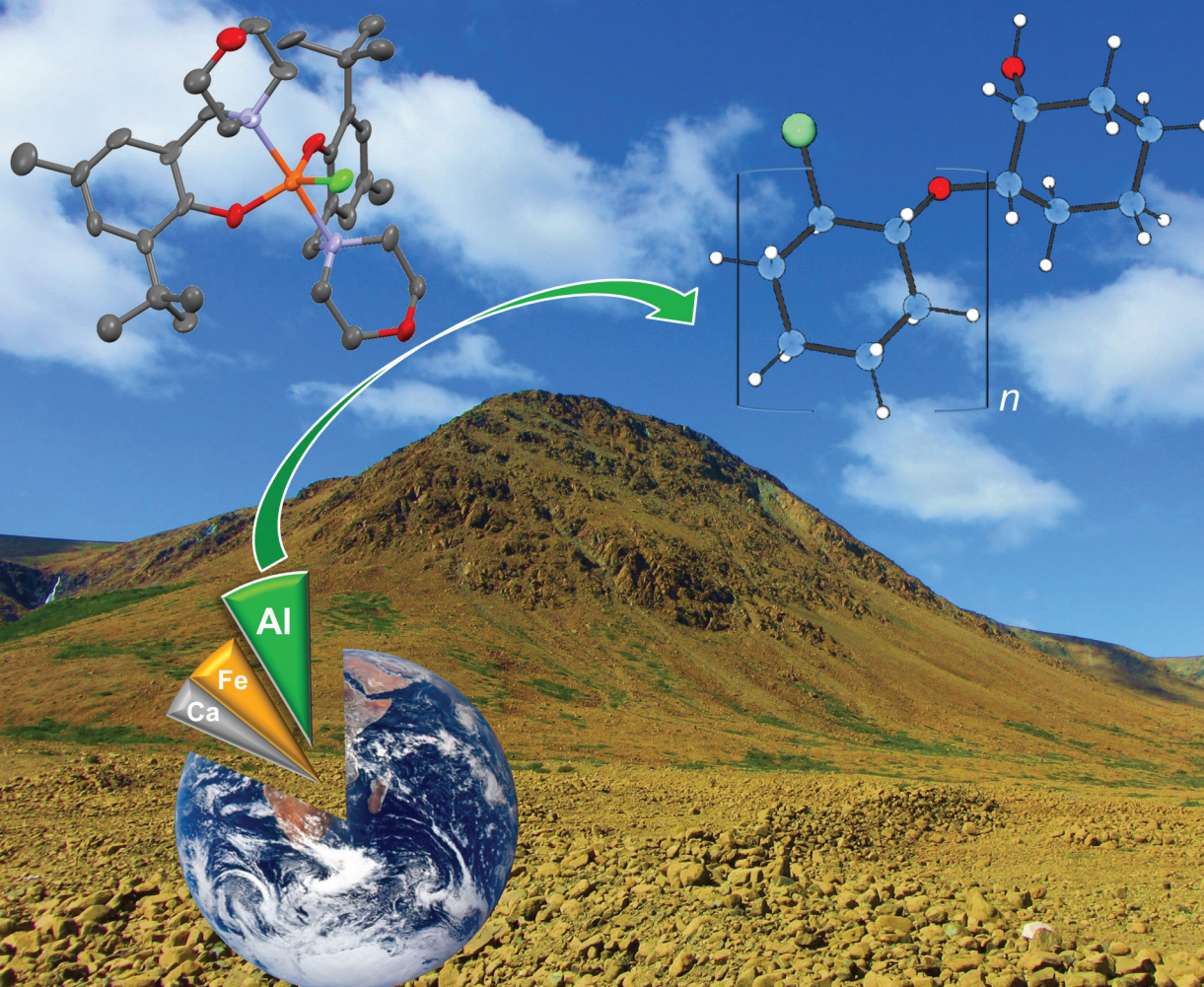


Dalton Transactions

An international journal of inorganic chemistry

www.rsc.org/dalton



Themed issue: Earth abundant element compounds in homogeneous catalysis

ISSN 1477-9226



COMMUNICATION

Francesca M. Kerton *et al.*

Ring-opening polymerization of cyclohexene oxide using aluminum amine–phenolate complexes



Cite this: *Dalton Trans.*, 2015, **44**, 12098

Received 16th January 2015,
Accepted 10th February 2015

DOI: 10.1039/c5dt00220f

www.rsc.org/dalton

Ring-opening polymerization of cyclohexene oxide using aluminum amine–phenolate complexes†‡

Hart Plommer, Immanuel Reim and Francesca M. Kerton*

Remarkably active (down to 0.001% Al) catalysts for ring-opening polymerization of cyclohexene oxide under neat reaction conditions are reported. High molecular weight polymers with uniform dispersity are produced. Kinetic data from NMR studies and MALDI-TOF MS data of the polymers provide some mechanistic insight.

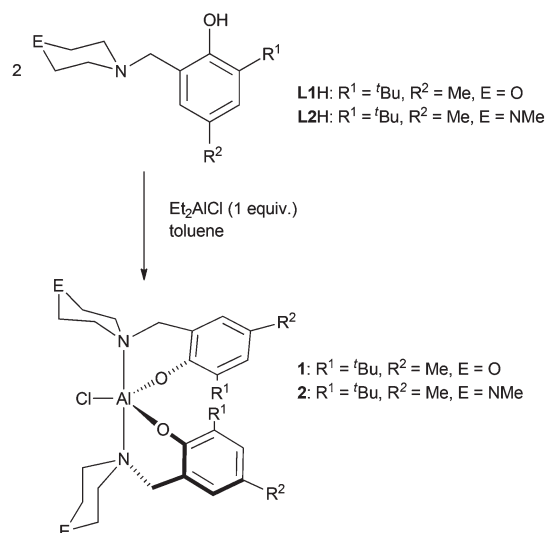
Aluminum is the most abundant of all metals in the earth's crust and its complexes can be used as Lewis acid catalysts or as co-catalysts for a range of reactions.¹ In particular, they have found broad applicability as homogeneous catalysts in polymerization processes.² Recently, significant attention has been given to their use in ring-opening polymerization (ROP) reactions of lactide (LA) and ϵ -caprolactone (CL) that yield biodegradable polyesters of controlled molecular weight and near uniform dispersity.³ They are also being widely explored as catalysts for reactions of carbon dioxide with epoxides that yield either polycarbonates or cyclic carbonate products.⁴ Aluminum species can also be active for polymerizations of propylene oxide (PO),⁵ cyclohexene oxide (CHO),^{3b,4h,6} and CHO-anhydride⁷ and PO-LA copolymerizations.⁸ The areas of polyether synthesis and stereoselective polymerization/copolymerizations of epoxides have recently been reviewed and provide good overviews of the concepts and possible mechanistic considerations in these reactions.⁹

We recently showed that chloro-aluminum complexes of *N*-piperazinyl and *N*-morpholinyl aminephenolate ligands, including **2** herein, were active in ROP of CL to yield polymers with the general formula $(\text{Cl}\{\text{CL}\}_n\text{OH})$ *i.e.* containing chloride end groups.¹⁰ We proposed that these reactions proceeded in a similar manner to ROP of trimethylene carbonate using aluminum-salen chloride catalysts,¹¹ which is to say that reactions

proceed *via* insertion into the Al–Cl bond. We also showed that one of the *N*-morpholinyl aminephenolate complexes was catalytically active in CO_2/CHO copolymerization to yield copolymers with a mix of ether and carbonate linkages (*i.e.* polyether-carbonates).¹⁰ Because of the relatively large number of ether linkages in these polymers, we decided to investigate the first step in this process in more detail, namely, the reaction of CHO with aluminum chloride complexes.

Complexes **1** and **2** are easily prepared in near quantitative yields *via* alkane elimination reactions of diethylaluminum chloride with two equivalents of the corresponding protio ligand (Scheme 1). Attempts to investigate the interaction of one equivalent of CHO with the aluminum complexes on an NMR scale in a range of solvents were unsuccessful due to the fluxional nature of the complexes. Therefore, larger amounts of CHO were added to samples and it was discovered that polyether forms.

ROP of CHO was carried out using complexes **1** and **2** (Table 1) in the absence of solvent at room temperature. In



Scheme 1

Department of Chemistry, Memorial University of Newfoundland, St. John's, NL A1B 3X7, Canada. E-mail: fkerton@mun.ca

† For themed issue on Earth Abundant Element Compounds in Homogeneous Catalysis.

‡ Electronic supplementary information (ESI) available: Experimental details, MALDI-TOF mass spectrum and NMR spectra of PCHO, conversion *vs.* time plot, table of attempted ROP of other epoxides. See DOI: 10.1039/c5dt00220f

Table 1 Polymerization of CHO using **1**, **2**, **3**^a

Entry	Complex	[CHO]:[Al]	t/min	Conv./% (yield/%)	<i>M_n</i> ^b	<i>D</i> ^b	TOF/min ⁻¹
1	1	100 000 : 1	60	15 (13)	500	1.17	250
2	1	1000 : 1	1	58 (53)	180	1.20	580
3	2	1000 : 1	50	15 (6)	—	—	3
4	2	200 : 1	30	16 (3)	76.2	1.15	1
5	3	10 000 : 1	1260	<1%	—	—	—
6	3	1000 : 1	45	29	262	1.36	6
7	3	500 : 1	25	49	255	1.21	10
8	3	200 : 1	2	56	125	1.12	56
9 ^c	3	500 : 1	40	66	110	1.08	8

^a Reactions were performed neat at room temperature in the absence of solvent unless otherwise indicated in an inert atmosphere workstation. Conversions determined by ¹H NMR spectroscopy. Isolated yields indicated in parentheses. ^b Determined (in kg mol⁻¹) by GPC equipped with a multi-angle light scattering detector. ^c Reaction performed in the presence of 160 μL toluene. Note, 7% conversion was obtained after 18 h in 5 mL toluene.

most cases, polymerization occurred rapidly to yield a viscous monomer–polymer mixture that could no longer be stirred magnetically. For **2** however, the polymerizations were much slower, leading to less viscous solutions even after extended reaction times. This indicates that the nature of the outer-sphere heteroatom in the N-containing heterocycle has a significant effect on these reactions. Differences in reactivity between the *N*-piperazinyl and *N*-morpholinyl containing catalysts were also seen in ROP of CL and CO₂/CHO copolymerizations.¹⁰

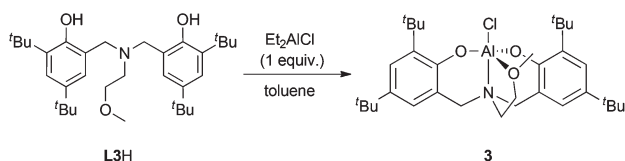
In an effort to determine the essential features of active complexes, **3** was prepared (Scheme 2). Amine-bis(phenolate) aluminum-alkyl and -alkoxide complexes similar to **3** have been prepared previously and used for ROP of lactide.¹² **3** showed good activity in ROP of CHO and using small amounts of toluene a higher conversion and less disperse polymer could be obtained compared to the neat reactions (entries 9 and 7). In contrast to **1**, catalyst loadings could not be reduced past 0.1 mol%.

The activities of these aluminum amine–phenolate complexes are clearly dependent on the nature of the ligand. Since the maximum conversion of CHO that can be attained during neat polymerization depends on the molecular weight of PCHO produced and the ability of CHO to solvate the catalyst and polymer, turnover frequencies (TOFs) are the most practical way to compare the catalysts. The conversion of 1000 equiv. of CHO was much quicker for **1** than **2** and **3** (Table 1, entries 2, 3 and 6) and TOF values are an order of magnitude higher for **1**. The observed reactivity trend for complexes **1**–**3** is in the order **1** ≫ **3** > **2**. This implies that, although chloro complexes of both monoanionic and dianionic aminephenolate ligands

give rise to active species, there is a more complex relationship between ligand structure and reactivity at play that warrants further investigation. Control polymerizations were performed using two simple chloro–aluminum reagents under similar reaction conditions to those employed with **1**–**3**. AlCl₃ (0.5 mol%) or Et₂AlCl (0.25 mol%) gave TOFs (min⁻¹) of 4 and 160, respectively, and a maximum *M_n* of 32 000 Da with relatively narrow dispersities (~1.3). These are significantly lower activities and molecular weights than achieved using **1** at similar loadings.

To avoid gelation and potentially increase conversions, some solution polymerizations with **1** were attempted using CH₂Cl₂, toluene or THF as reaction media. Reaction rates were significantly reduced and for a 200 : 1 ratio of CHO : **1** in 5 mL solvent conversions of 28% (CH₂Cl₂), 18% (toluene) and <1% (THF) were obtained after 20 h. The latter may be due to THF preferentially coordinating to the Al centre over CHO. Darensbourg and Chung have recently reinvestigated the basicities of a range of ethers and esters,¹³ and this statement is in agreement with the reported p*K_b* values. A difference in reactivity for ROP reactions in CH₂Cl₂ and toluene was also observed by Martínez *et al.*⁶ in their study of multinuclear Al complexes for CHO polymerizations, *e.g.* 96% yield in CH₂Cl₂ and 75% yield in toluene. They found that the addition of benzenesulfonyl chloride to toluene improved activities, reaching similar conversions to those performed in CH₂Cl₂ with no chloride additive. This suggests that the chloride group is important in these ROP reactions.

Of note is the very low loadings of **1** that could be used, 0.001 mol% relative to CHO (Table 1, entry 1), giving low conversion (15%) of CHO but yielding a polymer with very high *M_n* (500 000 Da) and uniform dispersity. The only catalysts reported to date for CHO polymerization that can produce such high molecular weight polymers (albeit at longer reaction times) are group 4 benzotriazole–phenolate complexes, which could achieve *M_n* values of up to 980 000 Da.¹⁴ Other systems reported that give PCHO with high molecular weights include the rare earth catalysts of Cui and co-workers¹⁵ that attain *M_n* up to 147 000 Da with a dispersity of 2.38, as well as



Scheme 2



the Zn and Mg catalysts prepared by Bochmann and co-workers¹⁶ that achieve up to 380 000 Da with a dispersity of 3.8. It should be noted that previous authors invariably report M_n determined *via* GPC calibrated with polystyrene standards, and therefore some care must be taken in making direct comparisons with our results based on multi-angle light scattering.

The polymerization of various other epoxides (PO, styrene oxide, limonene oxide, and epichlorohydrin) was attempted using **1–3** (Table S1†). In all cases, including microwave heated reactions conducted at 60 °C with propylene oxide and at 130 °C with limonene oxide, no polymer was detected by ¹H NMR. Catalysts for ROP of CHO containing a range of other metals such as iron,¹⁷ zinc, magnesium,¹⁶ uranium,¹⁸ titanium, zirconium, and hafnium¹⁴ are able to polymerize a number of different epoxides (*e.g.* PO, epichlorohydrin). Therefore, it was somewhat surprising that **1** could not polymerize any of the other monomers studied. It is well known that the ring-opening reactions of CHO are more facile than PO. It has been suggested that this is due to the release of extra strain energy upon polymerizing the bicyclic CHO monomer,¹⁹ but more recently others have shown that the strain energies of CHO and PO are essentially the same.²⁰ This is also reflected by nearly identical enthalpies of polymerization: −96.7 kJ mol^{−1} for CHO²¹ and −94.5 kJ mol^{−1} for PO (calculated using thermodynamic data in the NIST chemistry webbook). Therefore, differences in reactivity must be due to kinetic effects and thus determination of reaction pathways computationally would aid in discerning the differences observed experimentally. One possible reason for the differences in epoxide reactivity is steric *i.e.* the CHO monomer is slimmer, due to its bicyclic nature, than the other monomers studied,^{18a} and this means it can coordinate to the metal centre more readily prior to ring-opening by a nucleophile.

MALDI-TOF mass spectra were obtained on the polymers in order to identify end-groups, as no phenolate or other end groups were seen in their ¹H NMR spectra. It has been reported that laser desorption techniques induce significant fragmentation of polyethers and consequently only small oligomers are seen when using this technique,⁸ but these methods have been useful in identifying chloride end groups in polyethers and copolymers. The MALDI-TOF spectrum of the PCHO formed using **3** (Table 1, entry 9), Fig. S1,† is described here. The spectrum shows two prominent series of peak distributions with a mass difference between them of 36 Da, which corresponds to the mass of HCl. Successive peak distributions of either series are separated by 98 Da which equals the mass of the CHO monomer. These data are consistent with the formation of sodium adducts of both cyclic PCHO ($\{CHO\}_nNa^+$) [*e.g.* $n = 8$, m/z 807.58 (expt), m/z 807.52 (calcd)] and PCHO chains, the latter being capped with hydroxyl and chloride end groups ($Cl\{CHO\}_nH-Na^+$) [*e.g.* $n = 8$, m/z 843.55 (expt), m/z 843.50 (calcd)]. Since HCl was unable to catalyze these reactions under identical conditions, the identification of a chloride end group confirms the role of the chloride ligand in ring-opening of the epoxide. In previous research,

P(CL) polymers containing chloride end groups could be made with complex **2**.¹⁰

The polymers obtained with **1–3** were analyzed by DSC. Glass transition temperatures obtained were 68–69 °C, in agreement with values found for PCHO by Kim *et al.*,²² who polymerized CHO to give PCHO with M_n in the range of 12 400 to 24 900. No exotherm corresponding to a crystallization process could be observed on cooling, indicating that these polymers are amorphous. The stereochemistry of the PCHO was analyzed *via* ¹H and ¹³C NMR spectroscopy (Fig. S2 and S3†). No stereocontrol was achieved in these polymerizations, as three peaks at δ 3.53, 3.44, and 3.37 in the ¹H NMR spectra were observed corresponding to the methine protons are characteristic of syndiotactic (*rr*), heterotactic (*rm* and *mr*), and isotactic (*mm*) triads. The atactic nature of the polymer was also confirmed by the presence of three broad peaks at δ 78.8, 77.7, and 75.6 (methine carbons) in the ¹³C NMR spectra. The stereochemistry is in accordance with the finding of others using similar achiral Al catalysts.^{4h,6}

Kinetic studies on the ROP of CHO using **2** were carried out under neat conditions using a co-axial NMR tube containing CDCl₃ for locking. The slower reactivity of this catalyst meant it was a practical choice for NMR monitoring. Rates of stirring could not be readily controlled within the spectrometer and may have led to inhomogeneity that produced scattering and curvature in the data for two samples. These studies show that the polymerization is first-order in [Al], indicated by the linear relationship between k_{obs} and [2] (Fig. 1). The slope of this graph gives a propagation rate of 0.0568 M^{−1} min^{−1} and the intercept is close to the origin suggesting that minimal catalyst deactivation occurred through the presence of impurities. More studies are needed to determine whether the reactions proceed *via* a monometallic (intramolecular) or bimetallic (intermolecular) mechanism. Namely, whether the chloride initiator originates on the same Al centre as the coordinated CHO or on a neighbouring complex. For recently reported ROP of epoxides using [UO₂Cl₂(THF)₃] as a catalyst,^{18b} an intermolecular process is favoured and we think that a similar mechanism is at work in our catalyst system.

In summary, we have shown that amine-phenolate complexes of aluminum containing ancillary chloride ligands are active catalysts for ROP of CHO under neat conditions. In some cases, very low catalyst loadings (0.001%) can be used and high molecular weight amorphous polymers (M_n up to 500 000) are obtained. The reactions are generally inhibited in the presence of solvents, especially THF, and are first order in [Al]. The reactions are initiated by nucleophilic attack of the coordinated epoxide by a chloride anion, as evidenced by MALDI-TOF analysis of the resulting polymers. Further studies are needed to unequivocally determine whether the reaction proceeds *via* a monometallic or bimetallic process, and to determine the extent of reactivity across a wider range of aluminum amine-phenolate species.

We thank NSERC, Memorial University, Canada Foundation for Innovation, and RDC-Newfoundland for funding. Immanuel Reim thanks DAAD Rise for a scholarship.



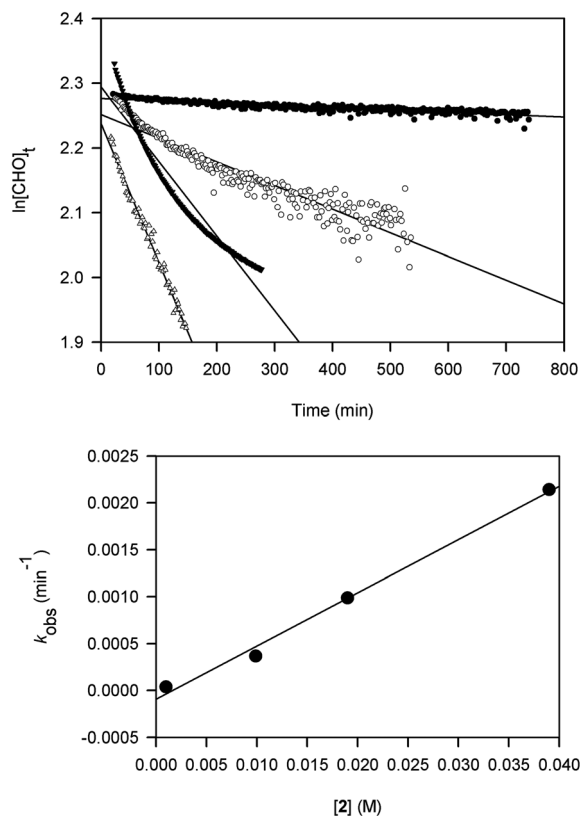


Fig. 1 Plots of $\ln[\text{CHO}]_t$ against time at catalyst loadings 0.01 (●), 0.1 (○), 0.2 (▼) and 0.4 (△) mol% using **2** (top) and k_{obs} (min^{-1}) against $[\text{2}]$ (M) (bottom).

Notes and references

- (a) M. R. Mason, Aluminum: Organometallic Chemistry, in *Encyclopedia of Inorganic Chemistry*, John Wiley & Sons, Ltd, 2006; (b) J. Lewinski and A. E. H. Wheatley, *Top. Organomet. Chem.*, 2013, **41**, 1–58.
- S. Dagorne and C. Fliedel, *Top. Organomet. Chem.*, 2013, **41**, 125–171.
- (a) M. H. Chisholm, J. C. Gallucci, K. T. Quisenberry and Z. Zhou, *Inorg. Chem.*, 2008, **47**, 2613–2624; (b) B. Liu, H. Li, C.-S. Ha, I. Kim and W. Yan, *Macromol. Res.*, 2008, **16**, 441–445; (c) H. Du, A. H. Velders, P. J. Dijkstra, J. Sun, Z. Zhong, X. Chen and J. Feijen, *Chem. – Eur. J.*, 2009, **15**, 9836–9845; (d) K. Phomphrai, P. Chumsaeng, P. Sangtrirutnugul, P. Kongsaree and M. Pohmakotr, *Dalton Trans.*, 2010, **39**, 1865–1871; (e) A. D. Schwarz, Z. Chu and P. Mountford, *Organometallics*, 2010, **29**, 1246–1260; (f) M.-H. Thibault and F.-G. Fontaine, *Dalton Trans.*, 2010, **39**, 5688–5697; (g) C. Bakewell, R. H. Platel, S. K. Cary, S. M. Hubbard, J. M. Roaf, A. C. Levine, A. J. P. White, N. J. Long, M. Haaf and C. K. Williams, *Organometallics*, 2012, **31**, 4729–4736; (h) M. Bouyahyi, T. Roisnel and J.-F. Carpentier, *Organometallics*, 2012, **31**, 1458–1466; (i) M. Lamberti, I. D'Auria, M. Mazzeo, S. Milione, V. Bertolasi and D. Pappalardo, *Organometallics*, 2012, **31**, 5551–5560; (j) W. Alkarekshi, A. P. Armitage, O. Boyron, C. J. Davies, M. Govere, A. Gregory, K. Singh and G. A. Solan, *Organometallics*, 2013, **32**, 249–259; (k) X. Liu, C. Jian, D. Yu, J. Zhang, N. Tang, C. Wang and J. Wu, *Inorg. Chem. Commun.*, 2013, **36**, 206–211; (l) L. Postigo, M. d. C. Maestre, M. E. G. Mosquera, T. Cuenca and G. Jimenez, *Organometallics*, 2013, **32**, 2618–2624; (m) K. Bakthavachalam, A. Rajagopal and N. Dastagiri Reddy, *Dalton Trans.*, 2014, **43**, 14816–14823; (n) M. J. Go, S. H. Kim, Y. Y. Kang, H.-R. Park, Y. Kim and J. Lee, *Inorg. Chem. Commun.*, 2014, **44**, 139–142; (o) S.-Y. Hsu, C.-H. Hu, C.-Y. Tu, C.-H. Lin, R.-Y. Chen, A. Datta and J.-H. Huang, *Eur. J. Inorg. Chem.*, 2014, **2014**, 1965–1973; (p) C. Romain, C. Fliedel, S. Bellemin-Laponnaz and S. Dagorne, *Organometallics*, 2014, **33**, 5730–5739; (q) H. Kampova, E. Riemlova, J. Klikarova, V. Pejchal, J. Merna, P. Vlasak, P. Svec, Z. Ruzickova and A. Ruzicka, *J. Organomet. Chem.*, 2015, **778**, 35–41.
- (a) W. Kuran, T. Listos, M. Abramczyk and A. Dawidek, *J. Macromol. Sci., Part A: Pure Appl. Chem.*, 1998, **35**, 427–437; (b) J. H. Jung, M. Ree and T. Chang, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, **37**, 3329–3336; (c) T. Sârbu and E. J. Beckman, *Macromolecules*, 1999, **32**, 6904–6912; (d) M. H. Chisholm and Z. Zhou, *J. Am. Chem. Soc.*, 2004, **126**, 11030–11039; (e) H. Sugimoto, H. Ohtsuka and S. Inoue, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 4172–4186; (f) T. A. Zevaco, A. Janssen, J. Sypien and E. Dinjus, *Green Chem.*, 2005, **7**, 659–666; (g) J. Melendez, M. North and R. Pasquale, *Eur. J. Inorg. Chem.*, 2007, 3323–3326; (h) T. A. Zevaco, J. K. Sypien, A. Janssen, O. Walter and E. Dinjus, *J. Organomet. Chem.*, 2007, **692**, 1963–1973; (i) M. North and R. Pasquale, *Angew. Chem., Int. Ed.*, 2009, **48**, 2946–2948; (j) W. Clegg, R. W. Harrington, M. North and R. Pasquale, *Chem. – Eur. J.*, 2010, **16**, 6828–6843; (k) C. Chatterjee and M. H. Chisholm, *Inorg. Chem.*, 2011, **50**, 4481–4492; (l) K. Nishioka, H. Goto and H. Sugimoto, *Macromolecules*, 2012, **45**, 8172–8192; (m) M. North, P. Villuendas and C. Young, *Tetrahedron Lett.*, 2012, **53**, 2736–2740; (n) D. Tian, B. Liu, Q. Gan, H. Li and D. J. Darensbourg, *ACS Catal.*, 2012, **2**, 2029–2035; (o) M. A. Fuchs, C. Altesleben, T. A. Zevaco and E. Dinjus, *Eur. J. Inorg. Chem.*, 2013, **2013**, 4541–4545; (p) N. Ikpo, J. C. Flogeras and F. M. Kerton, *Dalton Trans.*, 2013, **42**, 8998–9006; (q) C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adan, E. Martin and A. W. Kleij, *J. Am. Chem. Soc.*, 2013, **135**, 1228–1231; (r) J. A. Castro-Osma, C. Alonso-Moreno, A. Lara-Sánchez, J. Martínez, M. North and A. Otero, *Catal. Sci. Technol.*, 2014, **4**, 1674; (s) S. H. Kim, D. Ahn, M. J. Go, M. H. Park, M. Kim, J. Lee and Y. Kim, *Organometallics*, 2014, **33**, 2770–2775; (t) X. Sheng, Y. Wang, Y. Qin, X. Wang and F. Wang, *RSC Adv.*, 2014, **4**, 54043–54050; (u) C. J. Whiteoak, N. Kielland, V. Laserna, F. Castro-Gomez, E. Martin, E. C. Escudero-Adan, C. Bo and A. W. Kleij, *Chem. – Eur. J.*, 2014, **20**, 2264–2275.
- (a) M. Akatsuka, T. Aida and S. Inoue, *Macromolecules*, 1994, **27**, 2820–2825; (b) M. H. Chisholm and D. Navarro-



- Llobet, *Macromolecules*, 2002, **35**, 2389–2392; (c) W. Braune and J. Okuda, *Angew. Chem., Int. Ed.*, 2003, **42**, 64–68; (d) L. Tang, E. P. Wasserman, D. R. Neithamer, R. D. Krystosek, Y. Cheng, P. C. Price, Y. He and T. J. Emge, *Macromolecules*, 2008, **41**, 7306–7315; (e) J.-T. Issenhuth, J. Pluinage, R. Welter, S. Bellemin-Laponnaz and S. Dagorne, *Eur. J. Inorg. Chem.*, 2009, **2009**, 4701–4709; (f) S. Dagorne, M. Bouyahyi, J. Vergnaud and J.-F. Carpentier, *Organometallics*, 2010, **29**, 1865–1868; (g) N. Nakata, Y. Saito and A. Ishii, *Organometallics*, 2014, **33**, 1840–1844.
- 6 G. Martínez, S. Pedrosa, V. Tabernero, M. E. G. Mosquera and T. Cuenca, *Organometallics*, 2008, **27**, 2300–2305.
 - 7 E. H. Nejad, C. G. W. van Melis, T. J. Vermeer, C. E. Koning and R. Duchateau, *Macromolecules*, 2012, **45**, 1770–1776.
 - 8 M. H. Chisholm, D. Navarro-Llobet and W. J. Simonsick Jr., *Macromolecules*, 2001, **34**, 8851–8857.
 - 9 (a) A.-L. Brocas, C. Mantzaridis, D. Tunc and S. Carlotti, *Prog. Polym. Sci.*, 2013, **38**, 845–873; (b) M. I. Childers, J. M. Longo, N. J. Van Zee, A. M. LaPointe and G. W. Coates, *Chem. Rev.*, 2014, **114**, 8129–8152.
 - 10 N. Ikpo, S. M. Barbon, M. W. Drover, L. N. Dawe and F. M. Kerton, *Organometallics*, 2012, **31**, 8145–8158.
 - 11 D. J. Darensbourg, P. Ganguly and D. Billodeaux, *Macromolecules*, 2005, **38**, 5406–5410.
 - 12 (a) C.-T. Chen, C.-A. Huang and B.-H. Huang, *Dalton Trans.*, 2003, 3799–3803; (b) Z. Tang and V. C. Gibson, *Eur. Polym. J.*, 2006, **43**, 150–155; (c) E. D. Cross, G. K. Tennekone, A. Decken and M. P. Shaver, *Green Mater.*, 2013, **1**, 79–86.
 - 13 D. J. Darensbourg and W.-C. Chung, *Polyhedron*, 2013, **58**, 139–143.
 - 14 S. Pappuru, E. R. Chokkapu, D. Chakraborty and V. Ramkumar, *Dalton Trans.*, 2013, **42**, 16412–16427.
 - 15 D. Cui, M. Nishiura and Z. Hou, *Macromolecules*, 2005, **38**, 4089–4095.
 - 16 Y. Sarazin, M. Schormann and M. Bochmann, *Organometallics*, 2004, **23**, 3296–3302.
 - 17 E. Ertürk, M. A. Tezeren, T. Tilki, T. Erdogan and A. C. Gören, *Polym. Int.*, 2012, **61**, 795–799.
 - 18 (a) R. J. Baker and A. Walshe, *Chem. Commun.*, 2012, **48**, 985–987; (b) J. Fang, A. Walshe, L. Maron and R. J. Baker, *Inorg. Chem.*, 2012, **51**, 9132–9140.
 - 19 Z. Liu, M. Torrent and K. Morokuma, *Organometallics*, 2002, **21**, 1056–1071.
 - 20 M. W. Lehenmeier, C. Bruckmeier, S. Klaus, J. E. Dengler, P. Deglmann, A.-K. Ott and B. Rieger, *Chem. – Eur. J.*, 2011, **17**, 8858.
 - 21 F. Andruzzi, L. Shaofeng, G. Pilcher and F. Heatley, *Makromol. Chem.*, 1987, **188**, 2643–2650.
 - 22 B. Y. Liu, H. Q. Li, C. S. Ha, I. Kim and W. D. Yan, *Macromol. Res.*, 2008, **16**, 441–445.

