Dalton
Transactions

RSC Publishing

PERSPECTIVE

View Article Online
View Journal | View Issue

Published on 18 February 2013. Downloaded by Memorial University of Newfoundland on 21/11/2013 16:03:41.

Cite this: *Dalton Trans.*, 2013, **42**, 8998

Aluminium coordination complexes in copolymerization reactions of carbon dioxide and epoxides

Nduka Ikpo, Jenna C. Flogeras and Francesca M. Kerton*

Al complexes are widely used in a range of polymerization reactions (ROP of cyclic esters and cationic polymerization of alkenes). Since the discovery in 1978 that an Al porphyrin complex could copolymerize propylene oxide with carbon dioxide, Al coordination compounds have been studied extensively as catalysts for epoxide-carbon dioxide copolymerizations. The most widely studied catalysts are Al porphyrin and Al salen derivatives. This is partially due to their ability to act as mechanistic models for more reactive, paramagnetic Cr catalysts. However, this in depth mechanistic understanding could be employed to design more active Al catalysts themselves, which would be beneficial given the wide availability of this metal. Polymerization data (% CO_3 linkages, M_n, M_w/M_n and TON) for these complexes are presented and mechanisms discussed. In most cases, especially those employing square-based pyramidal Al complexes, co-catalysts are required to obtain high levels of carbon dioxide incorporation. However, in some cases, the use of co-catalysts inhibits the copolymerization reaction. Lewis acidic Al phenolate complexes have been used as activators in CHO-carbon dioxide copolymerizations to increase TOF and this has recently led to the development of asymmetric copolymerization reactions. Given the ready availability of Al, the robustness of many complexes (*e.g.* use in immortal polymerizations) and opportunity to prepare block copolymers and other designer materials, Al complexes for copolymerization of carbon dioxide are surely worth a second look.

Received 7th January 2013,
Accepted 18th February 2013

DOI: 10.1039/c3dt00049d

www.rsc.org/dalton

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

Nduka Ikpo

Nduka Ikpo obtained an MSc in Instrumental Analytical Science from Robert Gordon University (RGU) Scotland under the supervision of Prof. Peter Robertson in 2003. He later joined the Kerton Group at Memorial University of Newfoundland (MUN), Canada, where he obtained an MSc in Synthetic/Green Chemistry in 2008 and is currently completing his PhD under the supervision of Francesca Kerton. His research interests focus on the development of novel (biocompatible) metal complexes for the ring-opening polymerization (ROP) of cyclic esters and co-polymerization of CO_2 and epoxides.

Jenna C. Flogeras

Jenna C. Flogeras was born in Saint John, New Brunswick, Canada in 1986. She obtained both her BSc and MSc in Chemistry from the University of New Brunswick (Fredericton) in 2009 and 2011, respectively. Her MSc research in the group of Professor Sean McGrady focused on hydrogen storage materials, specifically the supramolecular chemistry of amine-borane complexes; this research yielded two publications. In September 2011, she began her PhD studies with Francesca Kerton at MUN, and is currently working on the synthesis of environmentally-friendly bismuth(III) complexes for the production of biodegradable polymers and CO_2 activation.

This journal is © The Royal Society of Chemistry 2013

Published on 18 February 2013. Downloaded by Memorial University of Newfoundland on 21/11/2013 16:03:41.

Introduction

Methods that can utilize carbon dioxide to produce chemicals and materials are of great interest currently, as it is a low cost, non-toxic, renewable resource.[1–4] In particular, interest in metal-catalysed copolymerization reactions of epoxides with carbon dioxide has grown tremendously over the past decade.[5–11] Recently, there has been significant interest in using main group complexes for this and related reactions, as such compounds contain earth-abundant metals and are often biocompatible. For example, copolymerization of cyclohexene oxide (CHO) with carbon dioxide (1 atm) in toluene has been performed successfully using n-Bu$_2$Mg in the presence of bis-(α,α-diarylprolinol) ligands and butanol as an additive.[12] A maximum TOF of 43 h^{-1} was obtained. Kinetics studies showed a zero-order dependence on carbon dioxide pressure and a first order dependence on CHO concentration. A bimetallic mechanism for the reaction was proposed, however, a structurally characterized bimetallic model complex was catalytically inactive in the reaction. More recently, Kember and Williams have reported remarkably active dimagnesium catalysts containing macrocyclic amine-phenolate ligands for the same copolymerization reactions and obtained TON of up to 6000 and TOF of 750 h^{-1}.[13] Furthermore, they were able to use water as a chain transfer agent and successfully prepare poly(cyclohexene carbonate) polyols with high selectivity. Historically however, of the main group metals, aluminium complexes have played an important role in the development of copolymerization reactions of carbon dioxide and should be investigated further. Importantly, aluminium complexes are known to catalyse a wide range of other polymerization reactions including ring-opening polymerization (ROP) of cyclic esters[14–26] and trimethylene carbonate,[18,27,28] and cationic polymerization of alkenes (incl. isoprene, benzofuran and styrenes).[22,29] Of particular relevance to research efforts towards copolymerization of epoxides with carbon dioxide are the range of aluminium complexes that are known to facilitate ROP of epoxides *i.e.* homopolymerization reactions.[29–32] This means aluminium-based systems for terpolymerization and other multi-monomer polymerizations utilizing carbon dioxide could potentially be developed. Such designer polymers could be of high-value and offer a way to circumvent the costs of the relatively expensive epoxide monomers used in most copolymerizations that use carbon dioxide. Herein, we present a summary of results to date concerned with copolymerizations of carbon dioxide by Al complexes. It should be noted that reactions yielding predominantly cyclic carbonates will not be discussed unless they are particularly pertinent to the discussion of the polymerizations presented. For reactions yielding cyclic carbonates, readers are advised to read a recent review of that field.[33]

Francesca M. Kerton

Francesca "Fran" Kerton was born in Sheffield, UK in 1974 and studied Chemistry with Environmental Science at the University of Kent (1995). She completed her PhD with G. A. Lawless on organometallic and polymer chemistry in early 1999. She travelled to Canada and pursued postdoctoral studies in the area of lanthanide chemistry with M. D. Fryzuk at the University of British Columbia. In 2000, she was appointed as a lecturer at the University of York, UK and was awarded a Royal Society University Research Fellowship in 2002. She moved to MUN in 2005 and became Associate Professor of Green Chemistry in 2010.

Porphyrin complexes

The copolymerization of propylene oxide (PO) with carbon dioxide using an Al porphyrin complex (Fig. 1) was first communicated in 1978 by Takeda and Inoue.[34] Reactions required a long time to achieve completion (19 days) and 40% carbonate linkages were found within the poly(propylene carbonate) produced (M_n = 3900 g mol^{-1}; M_w/M_n = 1.15).

Further studies by this group showed that (tetraphenylporphinato)aluminium chloride ((TPP)AlCl) was an effective catalyst for living ROP of PO and other epoxides. This led to the use of such species in the preparation of polyether-polycarbonate block copolymers (M_n = 5100–9000 g mol^{-1}, M_w/M_n = 1.10–1.22) and polycarbonates (Tables 1 and 2).[35,36] Due to the living nature of the polymerization, the molecular weight of the copolymer could be controlled by adjusting the mole ratio of epoxide to Al. They also showed that polyester-polycarbonate block copolymers could be prepared *via* initiation using a living poly(pthalic anhydride)-polyether block using (TPP)AlCl with EtPh$_3$PBr as a co-catalyst (Fig. 2). In the presence of a co-catalyst, twice as many living polymer chains were detected compared with using (TPP)AlCl alone and therefore, a bifacial polymerization mechanism was proposed. It was also noted that quaternary ammonium or phosphonium salts were necessary for significant levels of carbon dioxide incorporation into the copolymers. More recent studies by Chatterjee and Chisholm have suggested that one chain is growing per Al centre and that excess co-catalyst can lead to decreases in selectivity [away from poly(propylene carbonate) towards the

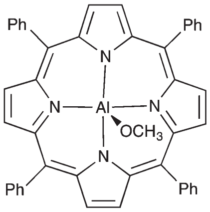


Fig. 1 Al porphyrin complex used by Takeda and Inoue in 1978 to produce poly(propylene carbonate).

Published on 18 February 2013. Downloaded by Memorial University of Newfoundland on 21/11/2013 16:03:41.

Table 1 Copolymerization of CHO with carbon dioxide using Al-containing catalysts[a]

Al species	Co-catalyst	Conditions	%-CO_3 linkages	M_n (kg mol^{-1})	M_w/M_n	TON, TOF (h^{-1})
(TPP)AlCl Inoue, 1986[36]	$EtPh_3PBr$	25 °C, 49 bar, 336 h, CH_2Cl_2	n.r.	6.20	1.06	100, 0.30
(TPP)AlCl Wang, 2008[41]	Et_4NBr and 0.125 equiv. Me-Al(2,6-di-^{t}Bu-4Me-phenolate)$_2$	60 °C, 40 bar, 9 h, CH_2Cl_2	97	5.8	1.07	404, 45
(TPP)AlCl Wang, 2008[41]	Et_4NBr and 0.125 equiv. Me-Al(2,6-di-^{t}Bu-4Me-phenolate)$_2$	60 °C, 20 bar, 9 h, CH_2Cl_2	95	5.1	1.07	383, 43
(^{t}Bu)(NO_2)-salenAlCl Darensbourg, 2005	Bu_4NCl	80 °C, 34 bar, 8 h, neat	96	n.r.	n.r.	283, 35
(^{t}Bu)(NO_2)-salenAlCl Darensbourg, 2005[43]	DMAP	80 °C, 34 bar, 8 h, neat	97	n.r.	n.r.	222, 28
(Salophen)AlMe Sugimoto, 2005[44]	Et_4NOAc	80 °C, 50 bar, 24 h, CH_2Cl_2	94	Bimodal 18.3 7.3	Bimodal 1.10 1.40	240, 10
$\{(ONO)^{*Ph}AlMe\}_2$[b] Sugimoto, 2012[48]	Bis-imidazole, Me-Al-(2,6-di-^{t}Bu-4Me-phenolate)$_2$	25 °C, 50 bar, 24 h, toluene	59[b]	6.00	1.54	94, 3.9
$(CyO)_2AlCl$ Beckman, 1999[49]	None	60 °C, 83 bar, 24 h, toluene	8.3	4.53	2.62	n.r.
Al(^{i}OPr)$_3$ Zevaco, 2005[53]	None	60 °C, 96 bar, 18 h, neat	22	10.4	1.40	~4000, 222
(mdtbp)AlCl Zevaco, 2006[54]	None	93 °C, 86 bar, 18 h, toluene	21	8.33	2.30	855, 48
(dmca)AlCl Kuran, 1998[55]	None	35 °C, 61 bar, 264 h, toluene	18	1.93	n.r.	6.5, 0.6 day^{-1}
$\{(ON)^{OtBuMe}\}_2AlCl$ Kerton, 2012[20]	None	60 °C, 40 bar, 16 h, neat	54	29.0	3.16	335, 21

[a] Conditions and data as reported in (or calculated from) original paper, n.r. = not reported. [b] *Note*: 74% ee. Reaction optimized for ee and not % carbonate linkages. In reactions with lower asymmetric induction, >99% carbon dioxide incorporation could be obtained.

Table 2 Copolymerization of PO with carbon dioxide using Al-containing catalysts[a]

Al species	Co-catalyst	Conditions	%-CO_3 linkages	M_n (kg mol^{-1})	M_w/M_n	TON, TOF (h^{-1})
(TPP)AlOMe Inoue, 1978[34]	None	20 °C, 8 bar, 456 h, neat	40	3.90	1.15	84, 4.4 day^{-1}
(TPP)AlCl Inoue, 1986[36]	$EtPh_3PBr$	25 °C, 49 bar, 336 h, CH_2Cl_2	>99	3.50	1.09	61, 0.18 h^{-1}
(TPP)Al$(PO)_2$Cl Ree, 1999[38]	Et_4NBr	25 °C, 52 bar, 168 h, CH_2Cl_2	72	3.30	1.24	166, 0.99 h^{-1}
(TPP)AlCl Chisholm, 2004[39]	DMAP	25 °C, 50 bar, 40 h, neat	96	3.0–9.0	1.1–1.4	n.r.
(TFPP)AlCl Chisholm, 2011[37]	PPN^+Cl^-	25 °C, 50 bar, 48 h, neat	97	Bimodal 41.4, 16.1	Bimodal 1.04, 1.05	150, 3.13 h^{-1}[b]
(dmca)AlCl Kuran, 1998[55]	None	35 °C, 61 bar, 168 h	13	5.62	n.r.	19, 2.7 day^{-1}
$\{(C_6H_5)_3CO\}_2AlOC_6H_{10}O^iPr$ Beckman, 2000[51]	None	40, 82 bar, 24 h	56	2.08	1.64	n.r.

[a] Conditions and data as reported in (or calculated from) original paper, n.r. = not reported. [b] Reaction achieved 100% conversion of PO and therefore, actual TON and TOF values might be higher than those calculated and presented here.

cyclic product].[37] Further details are discussed below. However, it should be noted that Inoue and co-workers proposed their mechanism based on the use of Al-living polymer macroinitiators and different co-catalysts compared with those studied by Chatterjee and Chisholm.

Interestingly, it should be noted that to date the methoxide complex shown in Fig. 1 and the related chloride complex, (TPP)AlCl, have not been structurally characterized, so structural comparisons with other active Al catalysts cannot be made. However, one could assume that they contain Al in a square-based pyramidal environment and therefore, they are structurally related to many of the highly active (salen)AlCl species discussed below. However, the activity of these TPP containing catalysts are poor for PO copolymerizations with reaction times of 12–40 days and typically low molecular weight polymers (or oligomers) are produced (M_n 1200–9000), Table 2.

Ree and co-workers followed up the work of the Inoue group with an in-depth study of PO-carbon dioxide copolymerization using (TPP)AlCl or its PO adduct, (TPP)Al$(PO)_2$Cl, with

This journal is © The Royal Society of Chemistry 2013

Published on 18 February 2013. Downloaded by Memorial University of Newfoundland on 21/11/2013 16:03:41.

Et_4NBr as a co-catalyst.[38] They also studied the individual components of the catalyst system including the free ligand, $TPPH_2$, which was inactive, and Et_4NBr, which produced a low yield of cyclic propylene carbonate. In the absence of the co-catalytic quaternary salt, (TPP)AlCl and (TPP)Al$(PO)_2$Cl afforded oligomeric products (M_n 3000–3600) with a high percentage of ether linkages (76–80%). In the presence of Et_4NBr, the Al catalysts produced oligomeric products (M_n 1900–3300) with a high percentage of carbonate linkages (70–75%). These results demonstrated that the quaternary salt plays an important role in reducing the amount of ether linkages in the copolymer product.

More recently, Chisholm and Zhou performed elegant NMR studies to ascertain the preliminary steps in such copolymerization reactions using (TPP)AlCl and proposed a suitable reaction mechanism, Fig. 3.[39] Reaction of (TPP)AlCl with PO in $CDCl_3$ forms the two regioisomers $AlOCHMeCH_2Cl$ and (TPP) $AlOCH_2CHMeCl$ in a ratio of 9 : 1. Kinetic studies showed the ring-opening of PO by (TPP)AlX complexes (X = Cl or OR) is first-order with respect to [Al] and DMAP (4-dimethylaminopyridine) was found to significantly enhance the rate of ring-opening. The binding of the neutral co-catalyst DMAP to potential copolymerization intermediates was found to follow the order $O_2CR > O_2COR \gg OR$, which is approximately the inverse order of the basicity of the oxygen donor ligands. Carbon dioxide reacts reversibly with (TPP)AlOR species and the extent of reaction is dependent on the concentration of the gas. Chisholm and Zhou showed that this equilibrium shifts dramatically to the right (towards Al-carbonate formation) in the presence of DMAP, Fig. 3, $k_1 > k_{-1}$. They also noted that upon removal of CO_2 pressure and solvent, the alkoxide (TPP) AlOR reformed and that the insertion/deinsertion reaction was kinetically rapid compared with PO ring-opening, Fig. 3. The amount of carbonate linkages within the PPC product is also dramatically affected by the presence of DMAP in the reaction mixture and MS data for the polymer showed that a strictly alternating copolymerization can be achieved (100% carbonate linkages) in the presence of 1 equiv. DMAP. They concluded that the co-catalyst plays a number of roles in these reactions including: (1) Increasing the equilibrium concentration of the alkylcarbonate-Al species at the expense of the alkoxide-Al groups, and (2) increasing the rate of ring-opening of PO by the alkylcarbonate nucleophile relative to the alkoxide group, thus leading to alternating copolymerization of PO and carbon dioxide over production of polyether segments (*i.e.* cycle A in the proposed mechanism, Fig. 3, is shut down). Ultimately, this understanding could lead to the design of better catalyst systems for PPC synthesis and higher levels of carbon dioxide incorporation. However, it should be noted that for some purposes, polymers with a lower level of carbonate linkages may also be desirable and therefore, these data will also be useful in obtaining ‘designer’ polymers with dialed in levels of carbonate groups relative to ethers.

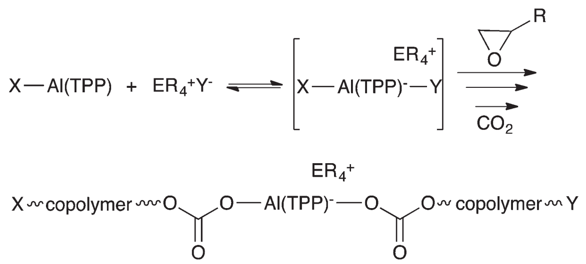


Fig. 2 Proposed bifacial mechanism for copolymerization using a (TPP)AlCl-phosphonium or ammonium halide catalyst system.

In 2011, Chatterjee and Chisholm compared the reactivity of (TPP)AlCl with two related porphyrin systems, (TFPP)AlCl and (OEP)AlCl, Fig. 4, in order to ascertain ligand effects on PO-carbon dioxide copolymerizations.[37] In the presence of 0.5 equiv. of co-catalyst, the fluorinated compound (TFPP)AlCl was found to be very active in the copolymerization of PO with carbon dioxide even at 10 bar pressure, which was due to the increased Lewis acidity of the Al centre in this species compared with (TPP)AlCl and (OEP)AlCl. Indeed, the binding constant for the azide ion [of bis(triphenylphosphoranylidene) ammonium azide ($PPN^+N_3^-$)] with (TFPP)AlCl determined by IR spectroscopy was two orders of magnitude greater than with

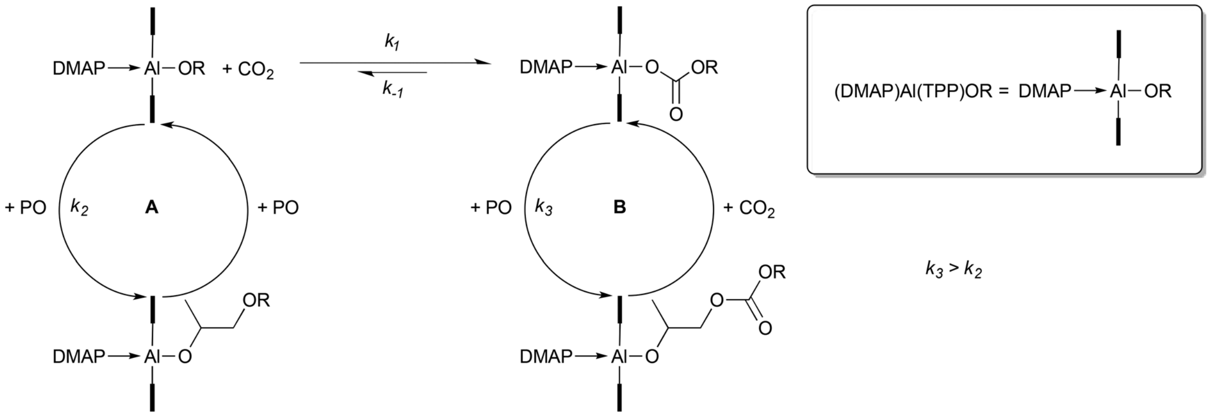


Fig. 3 Proposed Mechanism for PO-carbon dioxide copolymerization by (TPP)AlX systems in the presence of DMAP.

Published on 18 February 2013. Downloaded by Memorial University of Newfoundland on 21/11/2013 16:03:41.

the other two related Al catalysts. Mass spectrometric studies of the resulting polymers from these catalysts led to the conclusion that one polymer chain was growing per Al centre. Interestingly, when (TPP)Al(OEt) was used with ionic co-catalysts (*e.g.* $PPN^+N_3^-$, PPN^+Cl^-) for either homopolymerization or copolymerization of PO, it was shown by IR and MS that the resulting polymers contained no end groups resulting from incorporation of the co-catalytic nucleophile (*i.e.* no azide or chloride incorporation). Chisholm and Chatterjee also concluded that the epoxide and growing polymer chain (alkyl-carbonate group) were bound to the same face of the Al(porphyrin) species. These elegant studies were only possible due to advances in mass spectrometric and other techniques since the initial discovery of these catalysts in the late 70s, and provide strong evidence against a bifacial mechanism for PO-carbon dioxide copolymerization using Al-porphyrin containing catalysts. It should be noted that mechanisms are strongly dependent on a number of factors (especially ligand and monomer) and therefore, these conclusions do not exclude bifacial mechanisms for other monomers or other catalyst systems. Chisholm and Chatterjee also determined that in the presence of carbon dioxide, the polycarbonate chains bound to the Al centre do not degrade to form cyclic propylene carbonate (PC). However, when the carbon dioxide was vented (removed), the poly(propylenecarbonate) did degrade to PC. Therefore, as they had already shown that alkyl-carbonate–Al bonds readily deinsert carbon dioxide (in the absence of the gas), [39] they showed that the backbiting reaction to form PC proceeds *via* an alkoxide–Al bond. It should also be noted that interesting gas-phase studies concerned with the coordination of PO with LAl^+ cations have been reported by Chen, Chisholm and co-workers.[40] Using data from electrospray tandem mass spectrometry, binding of PO to $(TPP)Al^+$ ions was determined to be stronger than to $(salen)M^+$ ions, which is likely due to the better donor properties of salen relative to TPP.

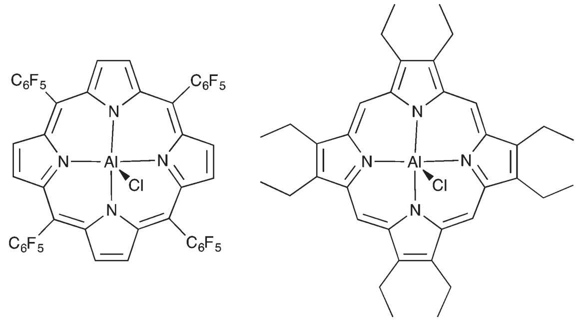


Fig. 4 Structure of (TFPP)AlCl (left) and (OEP)AlCl (right) studied by Chisholm and Chatterjee for copolymerization of PO with carbon dioxide.

As has been discussed above, a co-catalyst is essential for enabling high levels of carbon dioxide incorporation into copolymers prepared using (TPP)AlCl. Recently, the Wang research group has shown that the presence of a bulky Lewis acid [*e.g.* methylaluminium bis(2,6-di-*tert*-butyl-4-methylphenolate)] can have a further beneficial effect on the outcome of CHO-carbon dioxide copolymerization reactions.[41] A maximum TOF of 44.9 h^{-1} could be achieved compared with 36.1 h^{-1} for the same reaction with no additional Lewis acid. The authors propose that the enhanced reaction rate is due to activation of the incoming CHO monomer by the added Lewis acid prior to ring-opening at the (TPP)Al-alkylcarbonate reactive site. A similar Lewis acid acceleration effect had previously been observed by Inoue and co-workers for the homopolymerization of epoxides.[42] Of particular note in the copolymerization studies was very little dependence on reaction rate with varying carbon dioxide pressure,[41] this implies that such approaches may be useful in preparing catalyst systems for copolymerization using Al at carbon dioxide pressures close to ambient. At present, moderately high pressures are needed for these reactions (Tables 1 and 2) compared with state of the art systems employing other metal centres.

Schiff base complexes

In 2005, Darensbourg and Billodeaux studied an array of Al complexes for copolymerization of CHO with carbon dioxide, where the backbone of the ligand was varied alongside the 3- and 5-positions on the phenolate rings.[43] Several of the compounds were structurally characterized and all contained Al in a square-based pyramidal environment as expected. The most active of the Al-salen complexes reported in this study contained nitro groups in the 5-position and *t*-butyl groups in the 3-position, Fig. 5(a). As in previously reported salen systems, it is thought that the nitro groups serve to increase the electrophilicity of the metal centre whereas the t-butyl groups are required to increase solubility of the catalyst in solvent (or CHO). Interestingly, replacement of the ethylenediimine backbone with 1,2-phenylenediimine led to a dramatic decrease in catalytic activity. However, no obvious trends could be correlated between ligand variations and also changes in co-catalyst. Typically for a particular catalyst in combination with an ionic

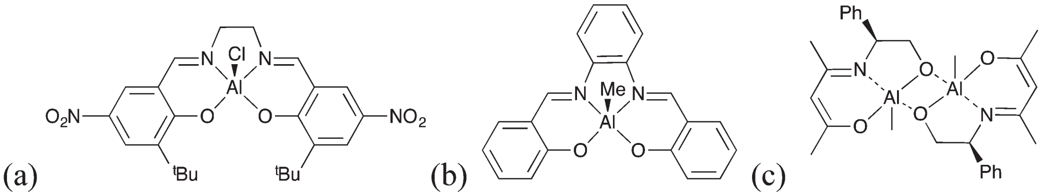


Fig. 5 (a) 'Most active' complex, (^{t}Bu)(NO_2)-salenAlCl, from Darensbourg study in 2005, (b) 'Most active' complex, (Salophen)AlMe, from Sugimoto study in 2005 (c) Chiral Al_2 β-ketoiminate complex, $\{(ONO)^{*Ph}AlMe\}_2$, from Sugimoto study in 2012.

This journal is © The Royal Society of Chemistry 2013

Published on 18 February 2013. Downloaded by Memorial University of Newfoundland on 21/11/2013 16:03:41.

co-catalyst variations in TOF of ±5 h^{-1} were observed and the optimum co-catalyst for each Al species had to be discovered on a trial and error basis. However, a trend was noticed for copolymerization reactions using neutral co-catalysts (*e.g.* DMAP). Higher TOF were achieved with a more strongly coordinating (more Lewis basic) co-catalyst. Furthermore, the degree of carbon dioxide incorporation was found to increase with the Lewis basicity of the co-catalyst. For example, (^{t}Bu)-(NO_2)-salenAlCl with DMAP achieved 28 h^{-1} TOF and 97% CO_2 incorporation, whilst with pyridine 8 h^{-1} TOF and 61% CO_2 incorporation was obtained. Such data give some insight into the reaction mechanism for Al-salen catalyzed copolymerization reactions. Namely, the carbon dioxide insertion process is significantly accelerated in the presence of a strongly electron donating ligand *trans* to the growing polymer chain, which is in complete agreement with the mechanism proposed by Chisholm and Zhou for the copolymerization of PO with carbon dioxide catalyzed by (TPP)AlCl described above.[39] Furthermore, backbiting reactions and formation of cyclic cyclohexene carbonate are prevented by the presence of this Lewis base. Unfortunately, no polymer molecular weight data or polymer end-group analyses were reported in this paper and therefore, conclusions regarding potential differences in termination and chain transfer processes cannot be made.

A detailed study on the selectivity in copolymerizations of CHO with carbon dioxide (polymer *vs.* cyclic) has been reported by Sugimoto and co-workers.[44] In this work, eight Al Schiff base complexes and a range of co-catalysts and reaction conditions were screened. The optimum co-catalyst in terms of polymer yields, control of polymerization (M_n and M_w/M_n), selectivity and % carbonate linkages was Et_4NOAc. The most active Al complex, (Salophen)AlMe, Fig. 5(b), contained a tetradentate salen type ligand with no substituents on the phenolate rings and a phenylene backbone. A related bidentate ligand complex, $(NO)_2AlCH_3$, was significantly less active (28% yield *cf.* 98% with (Salophen)AlMe) and was far less selective towards copolymerization (35% polymer *cf.* >95% with (Salophen)AlMe). This possibly indicates that a tetradentate ligand, which enforces a square-based pyramidal structure around the Al centre, is preferable to two bidentate ligands, which allow greater flexibility in the coordination environment about the Al centre. In addition to molecular weight data obtained *via* GPC, the resulting polycarbonate polymers were also characterized by MALDI-TOF MS. Surprisingly, Cl-terminated polymers were observed. As no chloride was present in the catalyst or co-catalyst, further studies were required to ascertain its origin. Control reactions analysed by ^{1}H NMR and GC showed that NEt_4Cl and methylene diacetate could form *via* reaction of NEt_4OAc with the solvent CH_2Cl_2 under reflux conditions. From MALDI-TOF MS and GPC data of polymers prepared in toluene (no Cl present), the authors found that two types of polymer chain existed within the product. Some chains had the expected end groups but bis-hydroxy terminated polymers were also observed and therefore, chain transfer from the presence of adventitious water was occurring. Mechanistically, a bifacial mechanism is proposed on the basis of the polymer end-groups. However, further kinetic studies are required to prove this definitively.

It should be noted that the conditions of the reaction (temperature, pressure, concentration, solvent, co-catalyst) and the epoxide used have a profound effect on the outcome of these reactions.[33,43,45,46] Namely, Al-salen complexes typically afford PC from PO and carbon dioxide but produce alternating copolymers from carbon dioxide and CHO (with negligible to ~7% yield of cyclic carbonate by-products). This is in agreement with thermodynamic studies on such processes, as cyclic carbonate formation does not compete as significantly with chain growth for CHO copolymerizations compared with reactions involving PO.[47] A detailed computational study has been reported by Luinstra, Reiger and co-workers on M^{III}-salen complexes in the reactions of PO with carbon dioxide.[46] In the theoretical and experimental study, Al-salen species exclusively formed PC and not PPC whereas Cr-salen complexes could form PPC exclusively but typically gave a mixture of products dependent on the ligand, co-catalyst and reaction conditions. In this study, activation of the incoming epoxide group by a metal complex (not bearing the growing polymer chain) was proposed to play an important role in the polymerization process. This observation is similar to Lewis acid co-catalysed ROP of epoxides and copolymerizations catalysed by (TPP)AlCl and discussed above.[41,42] In studies aimed at structurally characterizing potential Al(salen) intermediates in the copolymerization process,[40] Chisholm and co-workers were able to obtain X-ray diffraction data on a ring-opened PO product: (*R,R*-salen)-AlOCHMe(*S*)CH_2Cl, Fig. 6. This compound was crystallized in neat *S*-PO and the Al centre remained 5-coordinate. The structural characterization of this product and a related 5-coordinate Al(salen) acetate complex (obtained from pyridine solution) perhaps imply that 6-coordinate Al(salen) species do not exist as intermediates in the reactions of epoxides with carbon dioxide and may lend weight to epoxide activation by a second metal centre during the reaction process. Of course, further studies would be needed to confirm this possibility.

Of particular note with regard to Al-Schiff base and related catalyst systems are recent results reported by Sugimoto and

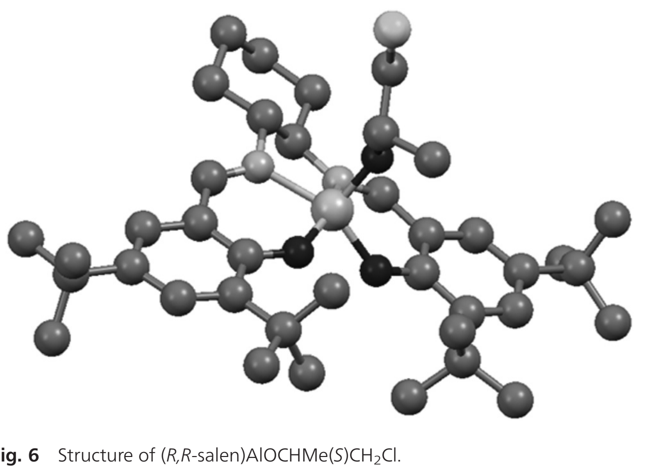


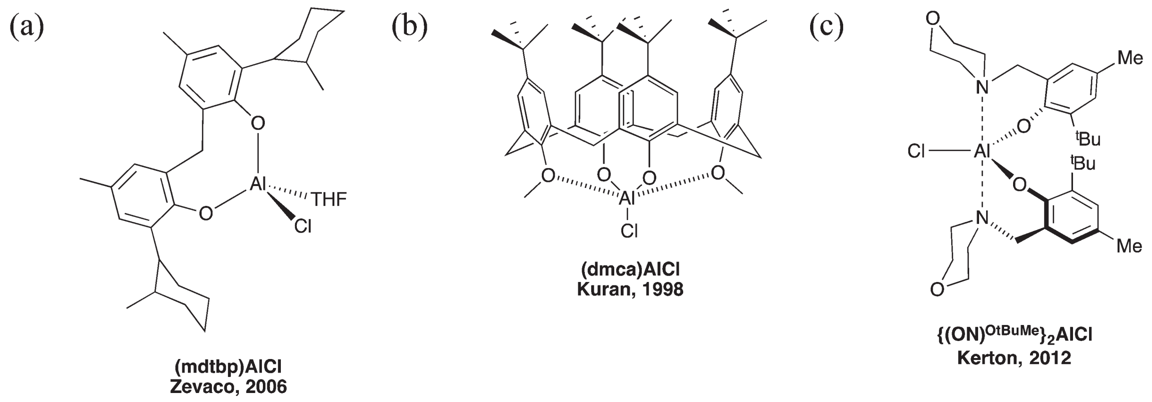
Fig. 6 Structure of (*R,R*-salen)AlOCHMe(*S*)CH_2Cl.

Published on 18 February 2013. Downloaded by Memorial University of Newfoundland on 21/11/2013 16:03:41.

co-workers where they employed a dual catalyst approach to achieve asymmetric copolymerizations of CHO with carbon dioxide.[48] Using (Salophen)AlMe (discussed above) relatively low amounts of asymmetric induction were achieved, however, bimetallic aluminium β-ketoiminate complexes could be used, Fig. 5(c) and very good stereoselectivity was obtained. As the bimetallic complexes catalyzed this reaction well, bidentate Lewis bases were used as co-catalysts as they could simultaneously coordinate with both Al centres within the catalyst. In order to increase reaction rates and allow reaction temperatures to be reduced, which would enhance stereoselectivity, Lewis acid co-catalysts (Me-Al(2,6-di-^{t}Bu-4-Me-phenolate)$_2$) were employed. These exciting results using a 3-component catalyst system will likely lead to further developments in this field in the future.

Other phenolate and alkoxide complexes

Sârbu and Beckman studied the reactivity of a series of Al alkoxide and phenoxide complexes for ROP of epoxides and copolymerization reactions with carbon dioxide.[49–51] In ROP of CHO, alcohols could be employed as chain transfer agents with no loss in catalytic activity,[50] and it was subsequently shown that iPrOH could be used as a chain transfer agent in the copolymerization of PO with carbon dioxide.[51] The most active of the alkoxide complexes studied in the copolymerization of CHO with carbon dioxide, $(CyO)_2AlCl$, produced 340 g of polymer per gram Al in a 24 h period,[49] and for the copolymerization of PO with carbon dioxide, $\{(C_6H_5)_3CO\}_2$-$AlOC_6H_{10}O^iPr$, produced 95 g polymer per gram Al in a 24 h period.[51] They employed ^{27}Al NMR to look at the structure of catalysts in solution (in the absence of carbon dioxide) and observed 5- and 6-coordinate species.[50] Due to the broad nature of ^{27}Al signals ($I = 5/2$),[52] it should be noted that there is no way to determine whether aggregated (dimetallic, trimetallic *etc.*) Al complexes are present in solution from this data alone. Therefore, further computational and experimental studies (*e.g.* kinetic data, MS data/end group analysis of polymer chains) would be needed to confirm the exact reaction mechanism for these complexes where more than one chain could grow at a particular Al centre. More recently, this research has been followed up by Zevaco, Dinjus and co-workers. They showed that commercially available aluminium tris(isopropoxide) could catalyze the copolymerization of CHO and carbon dioxide leading to a polymer with a 1 : 3 ratio of carbonate : ether linkages.[53] However, it should be noted that, in order to achieve a high degree of carbon dioxide insertion, a relatively high pressure (100 bar) was required. The group performed extensive *in situ* ^{27}Al NMR studies on reaction mixtures and concluded that the original tetrameric aluminium tris(isopropoxide) complex quickly breaks down to yield highly reactive 4-coordinate Al species, which undergo insertion reactions at all Al–OR bonds. Ultimately, as the reaction proceeds, the Al_4 complex breaks down to yield monometallic species, which are stabilized by intramolecular coordination of a carbonate group within the growing polymer chains. This results in the formation of a mixture of 4-, 5-, and 6-coordinate Al species within the reaction mixture. TOF for this system was very high, as up to 3 polymer chains could be growing per Al centre. This research group also studied the reactivity of several Al complexes bearing chelating bis(phenoxide) ligands and either labile ethyl or chloro ligands, Fig. 7(a).[54] The chloro complexes were generally more reactive than the ethyl containing species, as they yielded more polymer and that polymer contained a higher degree of carbonate linkages. Unfortunately, these relatively simple coordination complexes required high temperatures and pressures for reaction. This group also studied the effect of a range of commonly used co-catalysts (*e.g.* PPN$^+$Cl$^-$) on this reaction alongside their Al complexes but found that either selectivity switched to yield moderate quantities of cyclic cyclohexene carbonate or the system shut down altogether and no product was obtained. This contrasts significantly with Al-salen systems discussed above and may be due to the difference in structure between such complexes. The Al-salen catalysts contain Al in a square-based pyramidal environment whereas the bis(phenoxide) species contain Al in a tetrahedral environment, which might inhibit the involvement of the co-catalyst in the reaction mechanism, *i.e.* the constrained geometry enforced by the chelating bis(phenoxide)



(a) **(mdtbp)AlCl Zevaco, 2006**

(b) **(dmca)AlCl Kuran, 1998**

(c) **$\{(ON)^{OtBuMe}\}_2AlCl$ Kerton, 2012**

Fig. 7 Phenolate containing Al-chloride complexes active in copolymerization of CHO with carbon dioxide.

This journal is © The Royal Society of Chemistry 2013

Published on 18 February 2013. Downloaded by Memorial University of Newfoundland on 21/11/2013 16:03:41.

ligand does not allow the groups bound to Al to rearrange and allow the co-catalyst to coordinate *trans* to the nucleophilic (Cl or Et) group.

In 1998, Kuran and co-workers described the reactivity of an Al calixarene complex, Fig. 7(b), in ROP of PO and CHO, and also in copolymerizations with carbon dioxide.[55] Low levels of carbon dioxide incorporation were observed and long reaction times were required. For the ROP reaction of PO, a bimetallic mechanism was proposed and therefore, a bimetallic process might also be operative in the copolymerization reactions. Structurally, (dmca)AlCl contains Al in a distorted trigonal bipyramidal environment, however, data were of low quality and therefore, accurate bond lengths and angles could not be determined.[56] Recently, we have reported an amine-phenolate Al complex that is active for copolymerization of CHO with carbon dioxide, Fig. 7(c).[20] Similarly to Zevaco and co-workers, we found that the reactivity of this catalyst shut down and neither polymer nor cyclic carbonate formed in the presence of the commonly used co-catalyst PPN^+Cl^-. This catalyst shows promise for further optimization as moderate levels of carbon dioxide incorporation were achieved (higher than the other phenolate complexes discussed in this section), a relatively high molecular weight polymer obtained (it is the highest value reported in Table 1) and TON values are comparable with many of the other Al-catalyst systems reported to date (Table 1). However, the polydispersity of the polymer is broad and further development of this system including reaction optimization, mechanistic studies and characterization of the polymer (*e.g.* end group analyses) are needed. It should be noted that this complex is also active for ROP of ε-caprolactone, which suggests terpolymerization to yield a polyester-carbonate block terpolymer might be possible.

Conclusion

In summary, due to the diamagnetic nature of Al complexes, porphyrin and salen derivatives of this metal have been studied extensively for copolymerization reactions of epoxides with carbon dioxide. TOF are significantly less than state of the art catalysts containing Cr or Mg. However, the ability of Al complexes to polymerize a wide range of monomers and their ability to perform chain transfer reactions and immortal polymerizations means that there is significant scope for producing tailor-made polymers using Al catalysts. Very exciting results concerned with asymmetric copolymerization of CHO with carbon dioxide have been reported in the past year.[48] Such results were only possible by building on the mechanistic understanding for these reactions, which has been built up over the past 15 years. There are a wealth of opportunities available in terms of studying carbon dioxide utilization using this cheap metal, for example oxetane has been copolymerized with carbon dioxide using Cr complexes,[57] and as far as we are aware this has not been studied using Al complexes. Furthermore, as described in this perspective, Al can be used as a Lewis acid 'activator' in reactions of epoxides including copolymerizations with carbon dioxide. Therefore, potentially di-aluminium complexes could be prepared, which would allow the Al to play both reactivity roles from within a single compound (with one Al centre for polymer growth and one for activation of the incoming monomer). In this regard, hetero-metallic catalysts containing Al-salen cations and $[Co(CO)_4]^-$ anions have been studied for carbonylation of epoxides (to yield anyhydrides).[58,59] Clearly, there is scope for preparing other systems for cooperative catalysis employing Al as a metal centre. In addition to Al, other heavier p-block metals have recently found use in carbon dioxide utilization.[60,61] A terphenyl indium complex has been reported to undergo reactions with ethylene glycol and carbon dioxide.[60] Unfortunately, efforts to liberate the ethylene carbonate product were not successful but further studies aimed at such goals are worthwhile. An air-stable sulfur bridged organobismuth complex has been studied and found to be active for cyclic carbonate formation from a range of epoxides and carbon dioxide.[61] Just as s-block metals have demonstrated excellent activity in recent years for copolymerizations of epoxides with carbon dioxide, perhaps it is time to give Al another look.

Acknowledgements

We thank NSERC, the Canada Foundation for Innovation, the Provincial Government of Newfoundland and Labrador, and Memorial University for financial support.

References

1 M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann and F. E. Kuehn, *Angew. Chem., Int. Ed.*, 2011, **50**, 8510–8537.

2 N. MacDowell, N. Florin, A. Buchard, J. Hallett, A. Galindo, G. Jackson, C. S. Adjiman, C. K. Williams, N. Shah and P. Fennell, *Energy Environ. Sci.*, 2010, **3**, 1645–1669.

3 R. Martin and A. W. Kleij, *ChemSusChem*, 2011, **4**, 1259–1263.

4 E. A. Quadrelli, G. Centi, J.-L. Duplan and S. Perathoner, *ChemSusChem*, 2011, **4**, 1194–1215.

5 G. W. Coates and D. R. Moore, *Angew. Chem., Int. Ed.*, 2004, **43**, 6618–6639.

6 D. J. Darensbourg, *Chem. Rev.*, 2007, **107**, 2388–2410.

7 D. J. Darensbourg, *Inorg. Chem.*, 2010, **49**, 10765–10780.

8 D. J. Darensbourg and S. J. Wilson, *Green Chem.*, 2012, **14**, 2665–2671.

9 M. R. Kember, A. Buchard and C. K. Williams, *Chem. Commun.*, 2011, **47**, 141–163.

10 S. Klaus, M. W. Lehenmeier, C. E. Anderson and B. Rieger, *Coord. Chem. Rev.*, 2011, **255**, 1460–1479.

11 X.-B. Lu, W.-M. Ren and G.-P. Wu, *Acc. Chem. Res.*, 2012, **45**, 1721–1735.

12 Y. Xiao, Z. Wang and K. Ding, *Macromolecules*, 2006, **39**, 128–137.

Published on 18 February 2013. Downloaded by Memorial University of Newfoundland on 21/11/2013 16:03:41.

13 M. R. Kember and C. K. Williams, *J. Am. Chem. Soc.*, 2012, **134**, 15676–15679.

14 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.

15 M. Bouyahyi, T. Roisnel and J.-F. Carpentier, *Organometallics*, 2012, **31**, 1458–1466.

16 M. Bouyhayi, Y. Sarazin, O. L. Casagrande and J.-F. Carpentier, *Appl. Organomet. Chem.*, 2012, **26**, 681–688.

17 D. J. Darensbourg and O. Karroonnirun, *Organometallics*, 2010, **29**, 5627–5634.

18 D. J. Darensbourg, O. Karroonnirun and S. J. Wilson, *Inorg. Chem.*, 2011, **50**, 6775–6787.

19 H. Du, A. H. Velders, P. J. Dijkstra, J. Sun, Z. Zhong, X. Chen and J. Feijen, *Chem.–Eur. J.*, 2009, **15**, 9836–9845.

20 N. Ikpo, S. M. Barbon, M. W. Drover, L. N. Dawe and F. M. Kerton, *Organometallics*, 2012, **31**, 8145–8158.

21 M. Lamberti, I. D'Auria, M. Mazzeo, S. Milione, V. Bertolasi and D. Pappalardo, *Organometallics*, 2012, **31**, 5551–5560.

22 B. Lian, H. Ma, T. P. Spaniol and J. Okuda, *Dalton Trans.*, 2009, 9033–9042.

23 K. Phomphrai, P. Chumsaeng, P. Sangtrirutnugul, P. Kongsaeree and M. Pohmakotr, *Dalton Trans.*, 2010, **39**, 1865–1871.

24 A. D. Schwarz, Z. Chu and P. Mountford, *Organometallics*, 2010, **29**, 1246–1260.

25 M.-H. Thibault and F.-G. Fontaine, *Dalton Trans.*, 2010, **39**, 5688–5697.

26 E. L. Whitelaw, G. Loraine, M. F. Mahon and M. D. Jones, *Dalton Trans.*, 2011, **40**, 11469–11473.

27 D. J. Darensbourg, P. Ganguly and D. Billodeaux, *Macromolecules*, 2005, **38**, 5406–5410.

28 F. Hild, L. Brelot and S. Dagorne, *Organometallics*, 2011, **30**, 5457–5462.

29 S. Dagorne, M. Bouyahyi, J. Vergnaud and J.-F. Carpentier, *Organometallics*, 2010, **29**, 1865–1868.

30 W. Braune and J. Okuda, *Angew. Chem., Int. Ed.*, 2003, **42**, 64–68.

31 J.-T. Issenhuth, J. Pluvinage, R. Welter, S. Bellemin-Laponnaz and S. Dagorne, *Eur. J. Inorg. Chem.*, 2009, 4701–4709.

32 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.

33 M. North, R. Pasquale and C. Young, *Green Chem.*, 2010, **12**, 1514–1539.

34 N. Takeda and S. Inoue, *Makromol. Chem.*, 1978, **179**, 1377–1381.

35 T. Aida and S. Inoue, *Macromolecules*, 1982, **15**, 682–684.

36 T. Aida, M. Ishikawa and S. Inoue, *Macromolecules*, 1986, **19**, 8–13.

37 C. Chatterjee and M. H. Chisholm, *Inorg. Chem.*, 2011, **50**, 4481–4492.

38 J. H. Jung, M. Ree and T. Chang, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, **37**, 3329–3336.

39 M. H. Chisholm and Z. Zhou, *J. Am. Chem. Soc.*, 2004, **126**, 11030–11039.

40 P. Chen, M. H. Chisholm, J. C. Gallucci, X. Zhang and Z. Zhou, *Inorg. Chem.*, 2005, **44**, 2588–2595.

41 Y.-S. Qin, X.-H. Wang, X.-J. Zhao and F.-S. Wang, *Chin. J. Polym. Sci.*, 2008, **26**, 241–247.

42 M. Akatsuka, T. Aida and S. Inoue, *Macromolecules*, 1994, **27**, 2820–2825.

43 D. J. Darensbourg and D. R. Billodeaux, *Inorg. Chem.*, 2005, **44**, 1433–1442.

44 H. Sugimoto, H. Ohtsuka and S. Inoue, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 4172–4186.

45 D. Tian, B. Liu, Q. Gan, H. Li and D. J. Darensbourg, *ACS Catal.*, 2012, **2**, 2029–2035.

46 G. A. Luinstra, G. R. Haas, F. Molnar, V. Bernhart, R. Eberhardt and B. Rieger, *Chem.–Eur. J.*, 2005, **11**, 6298–6314.

47 D. J. Darensbourg, J. C. Yarbrough, C. Ortiz and C. C. Fang, *J. Am. Chem. Soc.*, 2003, **125**, 7586–7591.

48 K. Nishioka, H. Goto and H. Sugimoto, *Macromolecules*, 2012, **45**, 8172–8192.

49 T. Sârbu and E. J. Beckman, *Macromolecules*, 1999, **32**, 6904–6912.

50 T. Sârbu and E. J. Beckman, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 1999, **40**, 903–904.

51 T. Sârbu, T. J. Styranec and E. J. Beckman, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 2000, **41**, 137–138.

52 J. J. Delpuech, Chapter 6, in *NMR of Newly Accessible Nuclei*, ed. P. Laszlo, Academic Press, New York, 1983.

53 T. A. Zevaco, A. Janssen, J. Sypien and E. Dinjus, *Green Chem.*, 2005, **7**, 659–666.

54 T. A. Zevaco, J. Sypien, A. Janssen, O. Walter and E. Dinjus, *Catal. Today*, 2006, **115**, 151–161.

55 W. Kuran, T. Listos, M. Abramczyk and A. Dawidek, *J. Macromol. Sci., Pure Appl. Chem.*, 1998, **A35**, 427–437.

56 M. G. Gradiner, G. A. Koutsantonis, S. M. Lawrence, P. J. Nichols and C. L. Raston, *Chem. Commun.*, 1996, 2035–2036.

57 D. J. Darensbourg and A. I. Moncada, *Macromolecules*, 2010, **43**, 5996–6003.

58 T. L. Church, Y. D. Y. L. Getzler and G. W. Coates, *J. Am. Chem. Soc.*, 2006, **128**, 10125–10133.

59 J. M. Rowley, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2007, **129**, 4948–4960.

60 S. U. Ahmad, J. Beckmann and A. Duthie, *Organometallics*, 2012, **31**, 3802–3805.

61 R. Qiu, Z. Meng, S. Yin, X. Song, N. Tan, Y. Zhou, K. Yu, X. Xu, S. Luo, C.-T. Au and W.-Y. Wong, *ChemPlusChem*, 2012, **77**, 404–410.

This journal is © The Royal Society of Chemistry 2013