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A novel nickel (II) complex based on a cyclam-cored generation-one dendrimeric salicylaldimine ligand and its application as a catalyst precursor in norbornene polymerization: Comparative study with some other first generation DAB-polypropyleneimine metallodendrimers

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ABSTRACT

A new cyclam based first generation metallodendrimer with nickel centres on the periphery as well as at the core was synthesized by reacting a novel tetrakis(salicylaldimine) cyclam ligand with nickel acetate. The trinuclear complex was evaluated as a catalyst precursor in the vinyl polymerization of norbornene using methylaluminoxane as co-catalyst. The activity of this cyclam-based complex was compared with that of first generation DAB-PPI-salicylaldimine and DAB-PPI-pyridine-imine complexes (DAB = diaminobutane, PPI = polypropyleneimine). The cyclam based complex was found to have superior activity than both the DAB-PPI analogues as well as analogous mononuclear complexes.

1. Introduction

Norbornene can typically be polymerized via three routes leading to different polymer structures. These routes are: (a) ring-opening metathesis polymerization (ROMP), (b) radical polymerization and (c) vinyl or addition polymerization of norbornene as shown in Fig. 1 [1].

The type of polynorbornene formed depends on the catalyst employed. Ring-opening metathesis polymerization (ROMP) is the most studied route to produce polynorbornene [2]. The unique properties of ROMP polynorbornene are due to the presence of the double bond within the polymer backbone. This makes cross-linking and vulcanization of the polymer possible [3].

In the radical polymerization of norbornene, the framework is rearranged to produce poly (2,7-bicyclo[2,2,1] hept-2-ene) oligomers [4]. The polymer obtained via this route has low molecular weights (molecular weight <1000 Da) and is usually obtained in low yields because of rearrangements and chain transfer reactions. The following activators typically initiate radical polymerization; azoisobutronitrile (AIBN) and *tert*-butyl perpivilate [5].

Vinyl or addition polymerization yields a 2,3-connected polymer, which occurs when the bicyclic structural unit remains intact and the double bond of the π-component is opened. Of the three types of polynorbornene, only the vinyl addition polymerization provides a completely saturated polymer with no rearranged norbornene units [6]. The vinyl polymerization of norbornene is usually activated by transition metal complexes such as palladium, chromium, cobalt, titanium, iridium, rhodium, copper, zinc and nickel [7].

Dendrimers are highly branched macromolecules which are monodispersed having well defined architectures. These macromolecules can be designed in such a way that they have discrete peripheral functionalities. The definitive structures and the associated chemical and physical properties result in dendrimers being explored in a wide range of applications. These include drug delivery [8], biosensors [9], MRI agents [10], light emitting diodes [11] and use as bio-conjugates [12]. The incorporation of metals into the dendrimer frame-work leads to the formation of metallodendrimers. These metal containing dendrimers have been employed as multinuclear catalyst precursors [13].

We previously reported the synthesis of dendritic nickel complexes derived from generation 1 (G1) and generation 2 (G2) dendrimeric salicylaldimine ligands based poly(propyleneimine) dendrimer scaffolds of the type, DAB-$(NH_2)_n$ ($n = 4$ or 8, DAB = diaminobutane). These catalysts were found to be active for norbornene polymerization giving polymers with moderate to high molecular weights and low polydispersity indices [14]. In this paper we now report on the evaluation of three nickel generation 1

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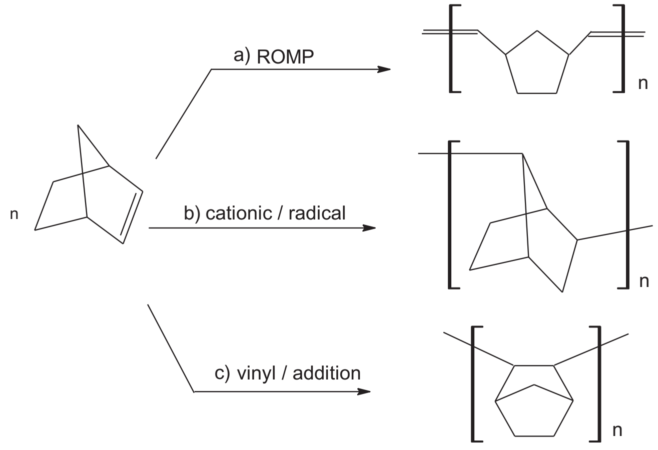


Fig. 1. Three different routes to polynorbornene formation [1].

metallodendrimer complexes based on dendrimeric Schiff base ligands as catalyst precursors in the vinyl addition polymerization of norbornene. Two of the complexes are based on diaminobutane-cored polypropylene imine (DAB-PPI) dendrimers while the third complex is based on a cyclam cored PPI dendrimer. Cyclam-based dendrimers is a relatively new concept, with not many examples reported in literature. However, those reported show favourable properties especially since the cyclam core is able to coordinate to metal centres. Both types of dendrimers were modified via Schiff base condensation reactions after which the functionalized dendrimers were complexed to nickel salts to form metallodendrimers. The DAB-based salicylaldimine complex, **C1** has been reported before [14] but the DAB-pyridinyl-imine complex **C3** and the cyclam based complex, **C2** are both novel.

2. Experimental

2.1. General

All reactions were carried using standard Schlenk procedures under an inert atmosphere (nitrogen or argon) or in a nitrogen-filled glovebox. Solvents were dried by distillation prior to use and all other reagents were employed as obtained. NMR (^{1}H: 300 and 400 MHz; ^{13}C: 75 and 100 MHz) spectra were recorded on Varian VNMRS 300 MHz; Varian Unity Inova 400 MHz spectrometers and chemical shifts are reported in ppm, referenced to the residual protons of the deuterated solvents and tetramethylsilane (TMS) as internal standard.

ESI–MS (positive and negative modes) analyses were performed on either Waters API Quattro Micro or Waters API Q-TOF Ultima instruments by direct injection of sample (capillary voltage: 3.5 kV; cone voltage: 15 RF1:40; source: 100 °C; desolvation temp.: 400 °C; desolvation gas: 500 L/h; cone gas: 50 L/h). FT-IR analysis was performed on a Thermo Nicolet AVATAR 330 instrument, and was recorded as neat spectra (ATR) unless otherwise specified. Melting point determinations were performed on a Stuart Scientific SMP3 melting point apparatus and are reported as uncorrected. Elemental analyses were performed by the micro analytical laboratory at the University of Cape Town.

The complexes **C4** and **C5** were prepared using standard literature procedures [15].

2.2. Synthesis

2.2.1. Synthesis of **L1** and **L2**

L1 [16a] and **L2** [16b] were obtained using literature procedures. Characterization by ^{1}H NMR and IR spectroscopy confirms the identity of the compound.

2.2.2. Synthesis of **DL1**, DAB-PPI G1 salicylaldimine modified dendrimer

Ligand **DL1** was prepared as previously reported in the literature [14] and was obtained in a yield of 90%. m.p. 66–68 °C. IR (cm^{-1}): ν(O–H) 2924 (m); ν(C=N) 1632 (s); ν(C–O) 1284 (s); ^{13}C NMR in CDCl$_3$ (δ ppm): 25.1, 28.4, 51.5, 54.0, 57.4, 117.0, 118.4, 118.8, 131.1, 132.1, 161.3, 164.9. *Anal.* Calc. for $C_{44}H_{56}N_6O_4$: C, 72.10; H, 7.70; N, 11.47. Found: C, 71.90; H, 7.90; N, 11.49%. MS (MALDI-TOF) Calcd. ($C_{44}H_{56}N_6O_4$) [M]$^+$ at m/z = 733.

2.2.3. Synthesis of **DL2 cyclam-based** G1 salicylaldimine modified dendrimer

G1 cyclam-propyl dendrimer (0.31 g, 0.72 mmol) was added to dry toluene (10 ml) in a Schlenk tube, under nitrogen. Salicylaldehyde (0.35 ml, 2.9 mmol) was added to the solution. The mixture was allowed to stir for 72 h at room temperature. The solvent was evaporated on a rotary evaporator and a red oil was obtained. Dichloromethane (20 ml) was added to the oil and the solution washed with water (5 × 30 ml). The dichloromethane layer was dried over potassium carbonate after which the latter was filtered off. The filtrate was evaporated to give a red oil. Yield: 78%. IR (cm^{-1}): ν(O–H) 3058 (m); ν(C=N) 1662 (s); ν(C–O) 1276 (s). ^{1}H NMR in CDCl$_3$ (δ ppm) 1.59 (m, 4H, $NCH_2CH_2CH_2N$ in cyclam ring), 1.80 (br m, 8H, NCH_2CH_2, side arm), 2.42 (br t, 8H, NCH_2CH_2, side arm), 2.48–2.52 (m, 16H, $NCH_2CH_2CH_2N$ in cyclam ring), 3.58 (8H, t, $CH_2N{=}CH$), 6.93 (t, 4H, Ar), 7.02 (d, 4H, Ar), 7.21 (t, 4H, Ar), 7.56 (d, 4H, Ar), 7.56 (d, 4H, Ar), 8.33(s, 4H, $N{=}CH$) ^{13}C NMR in CDCl$_3$ (δ ppm): 29.91; 31.31; 48.05; 51.68; 117.84; 120.06; 133.94; 137.27; 141.14; 161.85; 169.09. *Anal.* Calc. for $C_{50}H_{68}N_8O_4$: C, 63.63; H, 7.30; N, 11.53. Found: C, 64.46; H, 7.35; N, 11.27%. ESI–MS Calc. ($C_{50}H_{68}N_8O_4$) [M+H]$^+$ at m/z = 846.

2.2.4. Synthesis of **DL3** DAB-PPI G1 iminopyridyl modified dendrimer

DL3 was prepared employing the method previously reported by us [17]. The spectroscopic data of the product compares favourably with that reported.

2.2.5. Synthesis of **C1** DAB-PPI G1 salicylaldimine nickel metallodendrimer

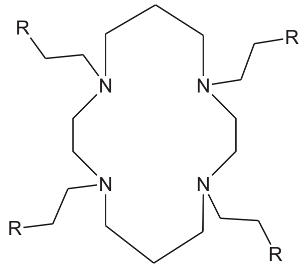
C1 was previously reported by us and was thus prepared using the method previously employed [14]. Characterization data obtained correspond well with that reported.

2.2.6. Synthesis of **C2**, cyclam-PPI G1 salicylaldimine nickel metallodendrimer

To the first generation cyclam-based salicylaldimine dendrimer ligand, **DL2** (0.125 g, 0.15 mmol) in ethanol (10 ml) in a round bottom flask was added nickel acetate tetrahydrate (0.11 g, 0.44 mmol) and the reaction mixture was allowed to stir under reflux for 24 h forming a lime green solution. The solvent was evaporated to give a lime green oily residue. The residue was recrystallized from dichloromethane (2 ml) and diethyl ether (10 ml) to afford **C2** as a lime green solid. Yield = 63%. m.p.: 260–263 °C. IR (cm^{-1}): ν(C=N) 1623 (s) and ν(C–O) 1319 (s). *Anal.* Calc. for $C_{54}H_{70}N_8Ni_3O_8\cdot 2.5CH_2Cl_2$: C, 50.67; H, 5.74; N, 8.29. Found: C, 50.19; H, 5.58; N, 8.16%. ESI–MS calc for ($C_{50}H_{64}N_8Ni_3O_4$) (cationic complex, [M+K]$^+$ at m/z = 1057.

2.2.7. Synthesis of **C3**, DAB-PPI G1 iminopyridyl nickel metallodendrimer

Ni(DME)Br$_2$ (0.18 g, 0.6 mmol) was added to a solution of **DL3** (0.10 g, 0.15 mmol) in dry ethanol (15 ml). An immediate colour change from orange to brown is observed, and all reagents dissolved to give a clear brown solution. The reaction mixture was refluxed for 24 h after which the solvent was evaporated to give a brown solid residue. Dichloromethane (5 ml) was added to the



L1: R = CN

L2: R = CH_2NH_2

Fig. 2. Tetracyanoethylcyclam ligands **L1** and its reduced analogue **L2** reported by Wainwright [16].

residue which was then triturated, leading to the formation of a brown precipitate. The solid was filtered and washed with CH_2Cl_2 (3 × 5 ml) to give **C3** as a brown solid. Yield = 85%. m.p.: 249–251 °C. IR (cm^{-1}): ν(C═N) at 1639 (s); ν(C═C) *pyr* at 1596 (s) and ν(C═N) *pyr* at 1567 (s). ESI–MS calc for ($C_{40}H_{52}Br_8N_{10}Ni_4$), $[M+2Na]^+$ at *m*/*z* = 1592. Due to the hygroscopic nature of the material we were unable to obtain suitable microanalysis.

2.3. Typical polymerization procedure

The amount of catalyst corresponding to 5 μmol of nickel was added to an appropriate amount of dry toluene in a Schlenk tube, under nitrogen. 5 ml (25 mmol) of a 5 M norbornene in toluene solution was added to the reaction vessel. The required amount of MAO (1.7 M, 10 %) was then added to the reaction mixture, to initiate the polymerization. The mixture was allowed to stir for 30 min at room temperature. The polymerization was stopped by adding the reaction solution to 200 ml of acidic methanol (95:5). A white solid precipitated out of solution. The polymer was filtered and then dried in the oven for 24 h. The norbornene:nickel ratio was 5000:1 and the total volume of the reaction mixture was 25 ml.

3. Results and discussion

3.1. Synthesis of generation 0.5 and generation 1 cyclam-cored polypropylene imine dendrimers, *L1* and *L2*

Wainwright [16] previously described the synthesis of *N*,*N*′,*N*″,*Ns*‴-tetrakis(2-cyanoethyl)-1,4,8,11-tetra-azacyclotetradecane which is referred to as the tetrakis(cyanoethyl)cyclam ligand, **L1** (Fig. 2), by reacting cyclam with excess acrylonitrile under reflux in the absence of solvent via a Michael addition reaction. Subsequent recrystalization of the oily residue leads to a white crystalline solid. We found that the optimum conditions to prepare this were simply the addition of the reagents employed, at room temperature, using methanol as a solvent. This gave an improved yield of the compound.

The FT-IR spectrum of **L1**, shows an intense band at 2244 cm^{-1} which is indicative of the ν(C≡N) stretching frequency. The ^1H NMR spectrum of **L1** shows two peaks at 1.67 and 2.48 ppm, which is due to the cyclam protons and another two peaks at 2.63 and 2.79 ppm for the cyanoethyl protons. **L1** was further characterized by ^{13}C NMR spectroscopy, ESI–mass spectrometry and elemental analysis.

We attempted several approaches to reduce the nitrile to the primary amine. This included the use of $LiAlH_4$, $NaBH_4$, H_2/Pd–C and KBH_4 but none of these gave complete reduction to the amine. We finally opted for a method involving the use of Na/toluene/ethanol as a reducing agent. This is based on a modification of a procedure reported in the literature [18]. The reduction process was monitored using IR spectroscopy by following the disappearance of the ν(C═N) band at 2244 cm^{-1} of the nitrile starting material with a concomitant appearance of the ν(N–H) band of the amine group of the product at 3352 cm^{-1}. The ^1H NMR spectrum of **L2**, also shows the appearance of a peak at δ3.59 ppm, due to the methylene protons of the carbon adjacent to the amino group.

3.2. Synthesis of Schiff base ligands

3.2.1. Preparation of DAB cored salicylaldimine ligand, *DL1*

Ligand **DL1** was synthesized as previously reported via Schiff base condensation of the G1-DAB-$(NH_2)_4$ dendrimer with salicylaldehyde [14]. The ligand was isolated as a yellow solid in high yield, 85%. **DL1** was characterized using IR and NMR spectroscopy and the data corresponds well with that reported previously.

3.2.2. Preparation and characterization of the generation 1 cyclam-based propyl-imine Schiff base ligands, *DL2*

The G1 cyclam-tetrakis(aminopropyl) dendrimer, **L2**, was reacted with salicylaldehyde to obtain the novel modified dendrimer ligand, **DL2** as shown in Fig. 3. The reaction time was 72 h, and the product was isolated as a red oil. The ν(C═N) band in the FT-IR spectrum for **DL2** is observed at 1662 cm^{-1} and the ν(C–O) stretching frequency at 1276 cm^{-1}. The ^{1} H NMR spectrum of the compound shows the signal for the imine proton at 8.33 ppm while in the ^{13}C NMR spectum, the imine carbon is observed at 161.85 ppm.

3.2.3. Preparation of DAB cored pyridinyl-imine ligand, *DL3*

This was prepared as described by Smith et al. [17]. The identity of the compound was confirmed by comparing its IR and ^1H NMR spectra with that previously reported by us.

3.3. Synthesis of DAB and cyclam-cored imine based nickel metallodendrimers

3.3.1. Synthesis and characterization of the generation 1 DAB salicylaldimine nickel metallodendrimer complex, *C1*

This complex was previously reported by us and we therefore prepared the complex in a similar manner [14]. The identity of the complex was confirmed by IR and UV spectroscopy and elemental analysis. The structure is shown below in Fig. 4.

3.3.2. Synthesis and characterization of the generation 1 cyclam salicylaldimine nickel metallodendrimer complex, *C2*

The G1 cyclam-propyl salicylaldimine dendrimer, **DL2**, was reacted with $Ni(OAc)_2{\cdot}4H_2O$ employing similar reaction conditions

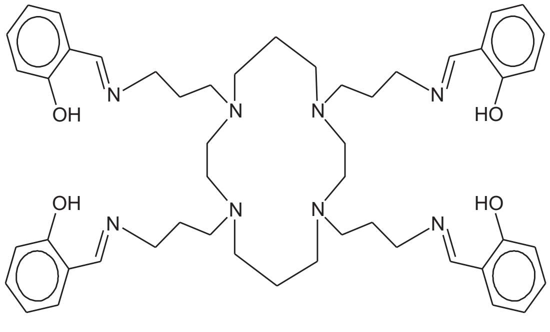


Fig. 3. Generation 1 cyclam-based propyl imine Schiff base ligand, **DL2**.

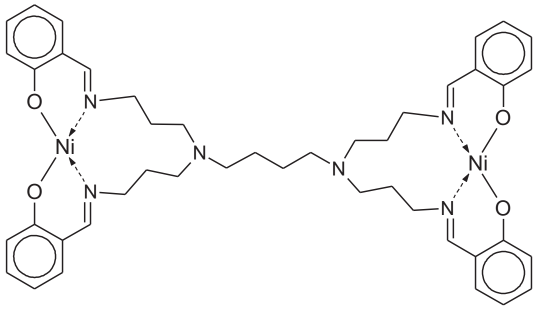


Fig. 4. The G1 DAB-core salicylaldimine modified nickel metallodendrimer, **C1**.

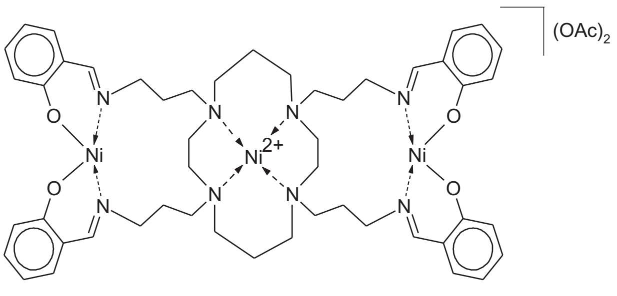
to those used for the synthesis of **C1** to give the cyclam-based salicylaldimine nickel complex **C2** as shown in Fig. 5.

The synthesized G1 cyclam-based salicylaldimine metallodendrimer, **C2**, is similar to the G1 DAB-based salicylaldimine metallodendrimer complex, **C1**, with two metal centres on the dendrimer periphery. However, the cyclam metallodendrimers also has an extra nickel centre coordinated to the cyclam core. This was confirmed by ICP-OES, which gave a nickel content corresponding to three nickel centres per mole of ligand. The complex is cationic with two acetate groups as counter ions. The complex was isolated as a lime green solid in a yield of 63%. The most significant bands monitored by FT-IR is the shift in the ν(C=N) and the ν(C–O) stretching frequencies, which indicates that metal coordination between the nickel and the dendrimer ligand had occurred. The ν(C=N) band shifted from 1662 to 1623 cm^{-1} and the ν(C–O) band from 1276 to 1319 cm^{-1}. The magnetic moment for **C2** was found to be 3.19 BM. The magnetic moment of **C2** is slightly higher than its G1 DAB analogue, **C1**, which has a magnetic moment of 2.95 BM. These values are within the range normally obtained for tetrahedral Ni(II) systems [19].

The ESI mass spectrum (positive ion mode) for **C2** shows a high mass peak at m/z = 1057 which can be assigned to a potassium adduct of the molecular ion of the cationic species. A peak assigned to the pure ligand is also observed at m/z = 846.

The UV–Vis spectrum of the G1 cyclam ligand, **DL2**, in the solution phase is similar to that of the DAB salicylaldimine ligand, showing three absorption bands. Two of the bands *viz.* at 260 nm and 225 nm are similar for both the DAB salicylaldimine and the cyclam salicylaldimine ligands. The third band however differs and occurs at 330 nm in the spectrum for the DAB ligand while in the cyclam ligand spectrum it occurs at 320 nm. These bands are assigned to $\pi \rightarrow \pi^*$ transitions of the aromatic units to the ligands.

The UV–Vis spectrum of the G1 cyclam complex, **C2**, shows four absorption bands. The two bands observed at 260 and 225 nm are similar to what is observed in the spectrum of the ligand and can be assigned to $\pi \rightarrow \pi^*$ transitions. On complexation of the peripheral salicylaldimine groups to the metal ion, the UV–Vis spectrum of the cyclam based salicylaldimine nickel complex shows a third band around 340 nm (complex spectrum) which is assigned to a metal-to-ligand charge transfer (MLCT) transition. The weak fourth band at 400 nm is assigned to forbidden d–d transitions, Ni(II) coordinated to an unsubstituted cyclam core usually absorbs at around 445 nm as reported by Hancock and co-workers [20]. When comparing the UV–Vis spectrum of the G1 DAB salicylaldimine nickel complex, **C1**, and the G1 cyclam salicylaldimine nickel complex, **C2**, we observe that the latter has an extra band in its spectrum at 400 nm, and this is thought to be due to the complexation of the nickel to the cyclam core.



C2

Fig. 5. The G1 cyclam-based salicylaldimine modified nickel metallodendrimer, **C2**.

3.3.3. Synthesis and characterization of the generation 1 DAB iminopyridyl nickel metallodendrimer complex, C3

The G1-DAB iminopyridyl nickel complex, **C3** which is also novel, (Fig. 6) was synthesized by reacting the iminopyridyl modified dendritic ligand, **DL3**, with Ni(DME)Br$_2$ as a metal precursor. The reaction conditions were similar to those used for the synthesis of **C1**–**C2**. The reaction of ligand, **DL3** with Ni(DME)Br$_2$, resulted in a brown solid being isolated as product (yield, 85%). The iminopyridyl complex appears to be hygroscopic and consequently had to be stored in a nitrogen purged glove-box. This is in contrast to the salicylaldimine complexes which are quite air stable, as well as stable in solution. A major difference between the salicylaldimine complexes, **C1**–**C2** and the iminopyridyl complex **C3**, is that the latter has double the amount of nickel centres at the periphery compared to the former. Thus the G1 iminopyridyl complex, **C3**, has four nickel centres whereas the G1 salicylaldimine complex, **C1**, has only 2 nickel centres.

From the IR spectrum, we observe a shift in the ν(C=N) stretching frequency from around 1647 to 1639 cm^{-1} when comparing the ligand and complex spectra. The pyridine ring ν(C=N) stretching frequency also shifted from around 1586 cm^{-1} to around 1596 cm^{-1} for complex, **C3**. The magnetic moment of this nickel iminopyridyl metallodendrimer also gives information regarding the geometry of the complex. The magnetic moment of the iminopyridyl complex, **C3** is in a similar region to that of the salicylaldimine complexes, being 3.64 BM. This is within the range of magnetic moments expected for a Ni(II) centre with tetrahedral geometry. This value is higher than those for **C1** and **C2** indicating that the latter two complexes possibly have a more distorted tetrahedral geometry.

The iminopyridyl complex is less thermally stable than the salicylaldimine complexes, **C1**–**C2**. It is also fairly sensitive to moisture.

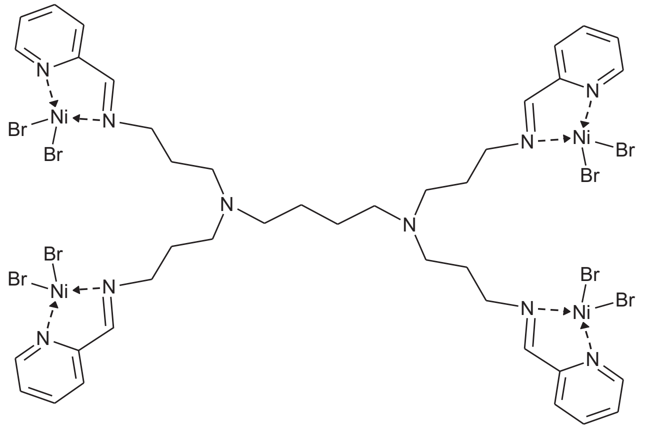


Fig. 6. Structure of DAB G1 iminopyridyl nickel metallodendrimer, **C3**.

Table 1
Norbornene polymerization activity for the various catalyst precursors.[a]

Al/Ni	G1 DAB- Sal TOF[b] **C1**	G1 Cyclam–Sal TOF[b] **C2**	G1-DAB Py-Im TOF[b] **C3**	Sal-model TOF[b] **C4**	Im-model TOF[b] **C5**
1000	3.76×10^5	0	0.74×10^5	0.75×10^5	0.82×10^5
2000	1.12×10^5	1.98×10^5	$3.\ 00 \times 10^5$	**2.59×10^5**	**2.83×10^5**
3000	2.52×10^5	**4.68×10^5**	3.29×10^5	2.26×10^5	2.50×10^5
4000	**3.28×10^5**	3.96×10^5	**3.60×10^5**	1.86×10^5	2.09×10^5
5000	2.52×10^5	2.04×10^5	2.37×10^5	–	–

The bold figures indicate the optimum activity for each of the catalysts.

[a] *Reaction conditions:* catalyst: 5 μmol Ni; time: 30 min, solvent: toluene; total volume: 25 ml; temperature: room temperature; monomer: Ni = 5000.

[b] TOF: g of polymer produced per mol of Ni per hour.

The ESI mass spectrum for **C3** shows a high mass peak at $m/z = 1592$ which can be assigned to an adduct of the parent ion containing two sodium units.

In addition to the multinuclear complexes prepared we also synthesized the known mononuclear complexes, **C4** and **C5**. This involved the reaction of the Schiff base ligand with either the monofunctional salicyaldimine ligand (for **C4**) or the monofunctional pydinyl-imine ligand (for **C5**).

3.4. Norbornene polymerization

*3.4.1. Evaluation of generation 1 DAB and cyclam cored nickel metallodendrimers, **C1**–**C3**, as norbornene polymerization pre-catalysts*

In this paper we compare the behaviour of the three generation 1 (G1) metallodendrimers **C1**–**C3** as catalysts precursors in the polymerization of norbornene. The catalysts were activated using methylaluminoxane as co-catalyst. A range of Al:Ni ratios were evaluated in an effort to obtain the optimum activity. It should be noted that in all cases the amount of Ni in the reaction mixture was kept constant irrespective of the precatalyst employed. The activity results are summarized in Table 1. When comparing the activities of the three multinuclear systems it is evident that the cyclam cored system is the most active of the three multinuclear catalysts tested followed by the DAB-pyridine-imine system. The polymerization was conducted using a range of Al:Ni ratios. The cyclam based catalyst, **C2,** shows an optimum activity of 4.68×10^5 g PNB/$\mathrm{mol_{Ni}}$/h which is much higher than that of the DAB-PPI based catalysts, **C1** (3.28×10^5 g PNB/$\mathrm{mol_{Ni}}$/h) and **C3** ((3.60×10^5 g PNB/$\mathrm{mol_{Ni}}$/h). These activities compare well with those reported for other Ni salicyaldimine complexes [21].

The optimum activity for both DAB cored systems was found to be at an Al:Ni ratio of 4000:1 while that for the cyclam cored system, **C2,** was 3000:1. It thought that the reason for **C1** and **C3** requiring a higher amount of Al co-catalysts is that the MAO being Lewis acidic first coordinates to the tertiary amine functionalities within the frame-work of the DAB based dendrimers. We have seen similar behaviour in other catalytic processes using other PPI dendrimers [14,22]. These tertiary amines are absent in the cyclam cored dendrimer. The latter is thus not able to form an acid-base adduct with the aluminium alkyl co-catalyst. The enhanced activity of the catalyst based on the cyclam cored dendrimer, **C2**, is most likely due to the fact that in this case we are dealing with a cationic species. It should be noted that the central metal centre is coordinated by the tetradentate cyclam frame-work which is neutral. The net result is that the overall complex is cationic. The cationic centre is thought to also reduce the electron density of the outer nickel centres which are bonded to the salicylaldimine units. This therefore makes the metal centres to be highly electrophilic which in turn will promote monomer coordination ultimately leading to a more effective catalyst. The enhanced activity of the pyridine-imine system relative to the salicylaldimine catalyst, **C1** could be due to the fact that the nickel centres in the imino-pyridyl catalyst are more accessible than is the case for the salicylaldimine catalysts. This should facilitate the interaction of the substrate with the active centres of the catalyst.

It should however be noted that when carrying out the comparative study between the DAB and the cyclam nickel precursors, the total nickel concentration was maintained at 5 μmol.

The norbornene polymerization activities of the multinuclear complexes were also compared to that of two mononuclear model compounds, **C4** and **C5** (Figs. 7 and 8). Both the mononuclear complexes displayed optimum activity at an Al:Ni ratio of 2000:1. This was at an Al:Ni ratio lower than that for all three multinuclear complexes. As indicated above the complexes based on dendritic ligands have internal tertiary amine functionalities which may interact with the Lewis acidic aluminium co-catalyst. Despite requiring higher levels of co-catalyst to reach optimum activity, all three multinuclear catalysts, **C1**–**C3**, show enhanced activity relative to the two model compounds. Thus a positive dendritic enhancement is observed for all three complexes.

3.4.2. Characterization of polynorbornene produced

The polymers obtained in the reactions described in the previous section, are not soluble at room temperature in common organic solvents such as dichloromethane, THF, chloroform and methanol. This is characteristic of vinyl norbornene polymers. These types of polymers are reported in literature to be soluble

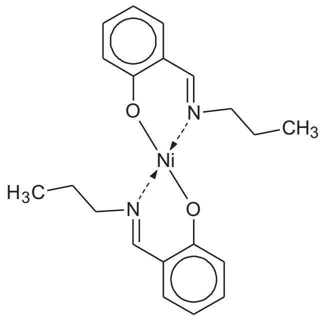


Fig. 7. Structure of mononuclear model complex, **C4**.

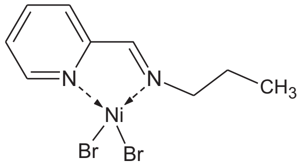


Fig. 8. Structure of mononuclear imino-pyridyl model complex, **C5**.

Table 2
GPC data for the polymers obtained using catalysts **C1**–**C5**.[a]

Al:Ni ratio	**C1**		**C2**		**C3**		**C4**		**C5**	
	$M_w \times 10^5$ (Da)	PDI	$M_w \times 10^5$ (Da)	PDI	$M_w \times 10^5$ (Da)	PDI	$M_w \times 10^5$ (Da)	PDI	$M_w \times 10^5$ (Da)	PDI
1000	6.39	2.60	–	–	–	–	4.08	2.87	5.12	3.12
2000	7.66	2.02	10.3	2.80	11.17	2.00	4.90	3.05	5.17	2.00
3000	5.12	2.51	7.61	2.30	9.56	2.12	4.42	2.92	4.56	2.12
4000	7.12	2.2	9.66	2.10	10.84	2.23	4.84	2.83	5.34	2.23
5000	8.34	2.02	11.07	2.00	11.36	2.01	–	–	–	–

[a] Measured at 160 °C against polystyrene standards.

in warm cyclohexane, chlorobenzene and trichlorobenzene, and this was also the case for our polymers.

3.4.2.1. FT-IR spectroscopy of isolated polymers. The polymers obtained were characterized by FT-IR spectroscopy. The IR spectra revealed no traces of any C=C double bonds, which often appear in the region of 1620–1680 cm^{-1}. This eliminates the possibility of ROMP polynorbornene. The ROMP polynorbornene would still have the double bond intact in the polymer backbone. As mentioned previously, complexes of nickel tend to polymerize norbornene by the vinyl addition mechanism. The IR spectrum shows strong ν(C–H) absorption bands around 2943 cm^{-1}. Medium intensity bands are also observed around 1452 and 1373 cm^{-1} clearly indicative of a saturated hydrocarbon species.

3.4.2.2. ^{1}H NMR spectroscopy of isolated polymers. The polymers obtained are soluble in warm cyclohexane or warm trichlorobenzene. The proton NMR spectra were recorded in trichlorobenzene spiked with C_6D_6 at 50 °C. The sample preparation involves heating the polymer in a 9:1 mixture of trichlorobenzene and deuterated benzene at 110 °C. After cooling, a viscous liquid was observed, for which a proton NMR spectrum could be obtained at 50 °C. From the ^{1}H NMR the signals for the HC=CH protons around 5.1 ppm are absent in the spectrum. The presence of the C=C bond usually indicates the formation of polynorbornene by ring opening metathesis polymerization (ROMP). Therefore we can conclude that either vinyl addition polymerization or radical polymerization is occurring. This spectrum also resembles that reported by Yang et al. who produced polynorbornene via the vinyl polymerization mechanism [23].

3.4.2.3. TGA and DSC of polymers prepared. The polymers obtained were also studied via thermal analysis. The TGA plot and its derivative show that the polymers obtained are very stable up to 450 °C. There's an initial weight loss of 5% from 25 to 425 °C, and then a 90% weight loss from 425 to 475 °C. Complete decomposition occurs after 600 °C. The DTGA plot shows an average decomposition temperature of around 450 °C. The TGA curve is similar to that reported by Wang et al. for other polynorbornene samples prepared via addition polymerization [24].

The DSC curve for our polynorbornene does not show an endothermic peak upon heating to 400 °C. Vinyl norbornene polymers are known to decompose before melting. The polynorbornene obtained using titanium catalysts, reported by Mi et al., exhibited glass transition temperatures (T_g) in range of 330–400 °C, and decomposes without melting [25].

3.4.2.4. Gel permeation chromatography (GPC). Gel permeation chromatography was conducted on the polymers obtained from the catalytic polymerization using 1,2,4-trichlorobenzene as solvent at 160 °C. GPC data are summarized in Table 2. All the catalysts systems employed gave moderate to high molecular weight polymers with molecular weights ranging from 5.12×10^5 to 11.36×10^5 Da. For all three catalyst systems there is an overall increase in molecular weight with increasing amount of co-catalyst employed. The polymers obtained using the pyridinyl-imine precatalyst generally have higher molecular weights compared to those polymers obtained from the DAB and cyclam cored dendritic salicylaldimine catalysts. The molecular weights obtained with these dendritic catalysts are much higher than those obtained using mononuclear salicylaldimine Ni complexes [21].

All polymers obtained exhibit extremely good polydispersity indices ranging between 2.01 and 2.80. This indicates that the molecular weights are reasonably uniform which points to the uniform nature of the catalytically active sites. We are thus dealing with "single site" catalysts. The PDI values compare favourably with those reported for other polynorbornene systems produced via addition polymerization and in many cases we have PDI's which are superior [21,26]. Once again the pyridinyl-imine catalysts, **C3** performs slightly better than the other two analogues in terms of the molecular weight distribution. It is also observed that in all cases the PDI values tend to decrease slightly with increasing Al:Ni ratios employed during the polymerization processes. It thus appears that lower polydispersity indices are obtained for the higher molecular weight polymers. This is slightly unusual since one would expect that the longer chain growth the more the likelihood of chain transfer processes occurring.

From the GPC data it can be seen that a similar type of polynorbornene is formed irrespective of the catalyst precursor used. All the polymers obtained had molecular weights far exceeding the 1000 Da limit usually observed for polynorbornene produced via free radical polymerization. In addition the ^{1}H NMR spectra of the polymers show no indication of unsaturated carbons in the polymer backbone thus ruling out a ROMP process. It can thus be concluded that norbornene polymerization using the dendritic catalysts proceeds via a vinyl addition mechanism.

4. Conclusion

NMR and IR spectra of the obtained polynorbornene show that no ROMP occurs in the polymerization processes but that the reaction proceeds via a 2,3-vinyl addition mechanism. The molecular weights of the obtained polynorbornenes are relatively high, ranging from 10^5 to 10^6 g/mol. This means that the polymerization is not a typical cationic or radical polymerization, which usually results in low molecular weights (molecular weight <1000 g/mol) and low yields because of rearrangements and chain transfer reactions. We can thus conclude that these types of nickel metallodendrimer catalysts polymerize norbornene through the vinyl-addition mechanism.

Three different types of Ni catalysts were tested, (a) the DAB G1–G3 salicylaldimine complexes, (b) the DAB G1 iminopyridyl complex and (c) the cyclam G1 salicylaldimine complex.

The cyclam cored salicylaldimine complex, **C2** shows the highest overall activity of the three catalysts tested. Its optimum activity occurs at an Al:Ni ratio of 3000:1 whereas the optimum activity for the other two catalysts is a higher Al:Ni ration (4000:1). All three catalysts exhibit relatively well controlled polymerization with all the polymers obtained exhibiting polydispersity indices less than 3 with most being around 2.20.

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