



Norbornene polymerization using multinuclear nickel catalysts based on a polypropyleneimine dendrimer scaffold

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ABSTRACT

Four multinuclear nickel complexes derived from generation 1 (G1) and generation 2 (G2) dendrimeric salicylaldimine ligands based poly(propyleneimine) dendrimer scaffolds of the type, DAB-(NH₂)_n (*n* = 4 or 8, DAB = diaminobutane) were evaluated as catalyst precursors in the polymerization of norbornene, using methylaluminoxane as co-catalyst. All four catalyst evaluated were found to be active for norbornene polymerization giving polymers with moderate to high molecular weights and low polydispersity indices. The polymerization results indicate that there is some sort of dendritic effect, in that the catalyst activity appears to be influenced by the dendrimer generation.

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1. Introduction

Dendrimers are spherically three-dimensional in nature and are typically characterized by a core unit emanating from which are branches that extend to peripheral units. These terminal units increase in number as generation number increases. Dendrimers are usually symmetrically branched and can contain a vast range of possible end groups. Tomalia and Newkome were amongst the first researchers to produce dendritic polymers during the eighties [1,2]. Subsequent to this a wide range of dendrimers have been prepared. Included amongst the more common dendrimers are the polypropyleneimine (PPI) dendrimers [1], the poly(amidoamine) (PAMAM) dendrimers [3] and the poly(benzylether) dendrimers [4]. Metal centres have also been incorporated into dendrimer frameworks and these materials are known as metallodendrimers. Some of the initial work on metallodendrimers was reported by Balzani et al. [5] and Newkome et al. [6]. Metals are commonly incorporated into the dendritic framework subsequent to the synthesis of the organic dendrimer. Metallodendrimers can also be constructed by systematically elaborating metal-containing dendrimer wedges (dendrons) and then subsequently anchoring these to a core molecule [7]. The metals can be located at various positions in the dendritic molecule which include termini, branching points or even the dendrimer core [8].

In recent times, it has been reported that dendrimers could be utilized in quite a diverse range of applications. Included amongst

these applications are the use as catalysts [9–12], biosensors [13,14], drug delivery agents [15–17], adhesives [18,19], magnetic resonance imaging (MRI) agents [20–22] and high performance polymers [23,24].

The use of metallodendrimers as catalyst precursors have increased in recent years. This has largely been due to the observation that in quite a few cases dendritic catalysts have shown enhanced performance when compared to mononuclear complexes [25,26].

Another advantage of catalysts based on metallodendrimers is the perceived ability of these systems to combine the best properties of homogeneous and heterogeneous catalysts in one system. Their stable macromolecular structure makes them suitable for facile isolation via ultra-filtration and hence providing the potential for catalyst recycling.

As stated earlier, recently there have been several reports detailing the application of metallodendrimers as catalysts. In a number of instances, some sort of dendritic effect has been observed. Van Leeuwen et al. [25] reported Ni catalyst systems for the oligomerization of ethylene in which the catalyst was embedded within a dendrimer template. The activity of the core-functionalized dendritic catalyst was compared to the activity of its parent complex and found to be far more active than its parent complex. De la Mata et al. [26] reported the use of titanium-containing carbosilane dendrimers as catalysts for the polymerization of ethylene. Using these metallodendrimers as catalyst precursors, polyethylene with high molecular weight and low polydispersity was produced. The dendritic nature of the catalyst also resulted in a higher degree of crystallinity in the polymers obtained. It

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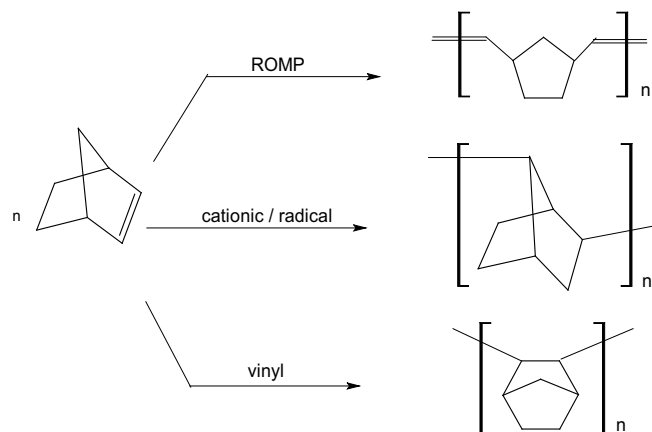


Fig. 1. Three different routes to polynorbornene.

was concluded that the electronic and steric effects induced by the different organometallic units on the phenolic capped dendrimeric ligands, have a big influence on the catalytic activity of the resultant dendrimeric complexes.

In this paper, we report on the evaluation of nickel complexes based on dendrimeric salicylaldehyde ligands as catalyst precursors in the vinyl addition polymerization of norbornene. Mononuclear Schiff base complexes are well known to be active catalysts for oligomerization and polymerization reactions [27]. There are

several ways in which norbornene can undergo polymerization. This include ring-opening metathesis polymerization (ROMP), cationic and radical polymerization and vinyl polymerization (Fig. 1). Each route leads to a different type of polynorbornene with different properties [28]. In this paper we will be focusing on vinyl-addition polymerization.

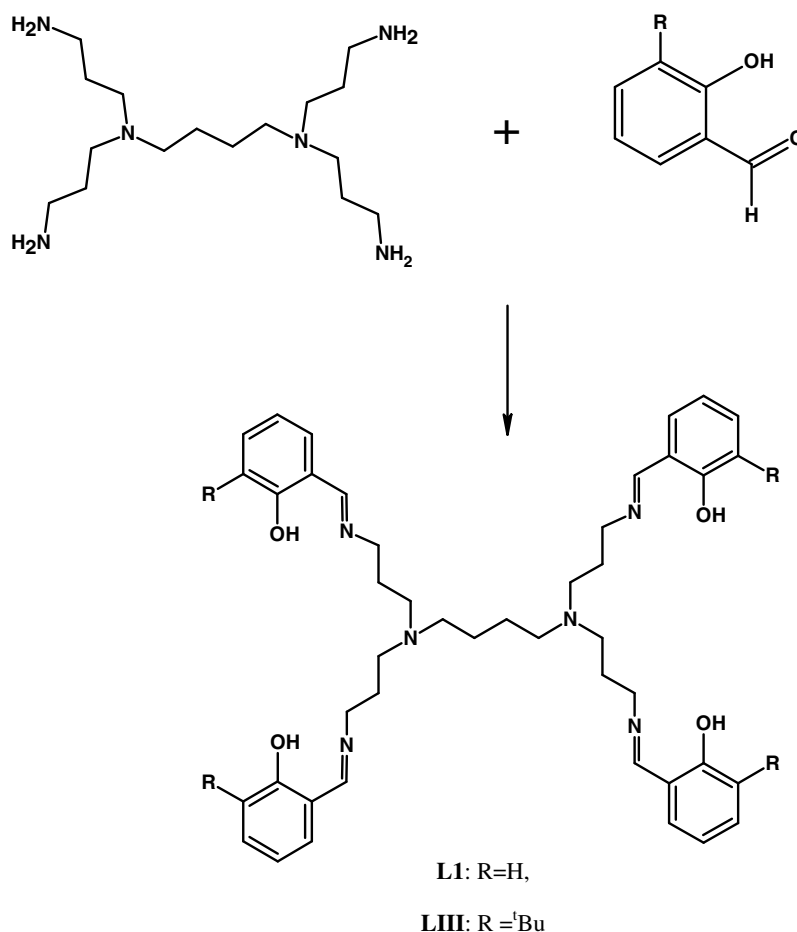
One of the objectives of our study was to investigate if different generations of dendrimeric salicylaldehyde complexes behave differently. We also investigated whether the substituents on the peripheral salicylaldehyde units impact on the catalytic behaviour of the complexes.

2. Results and discussion

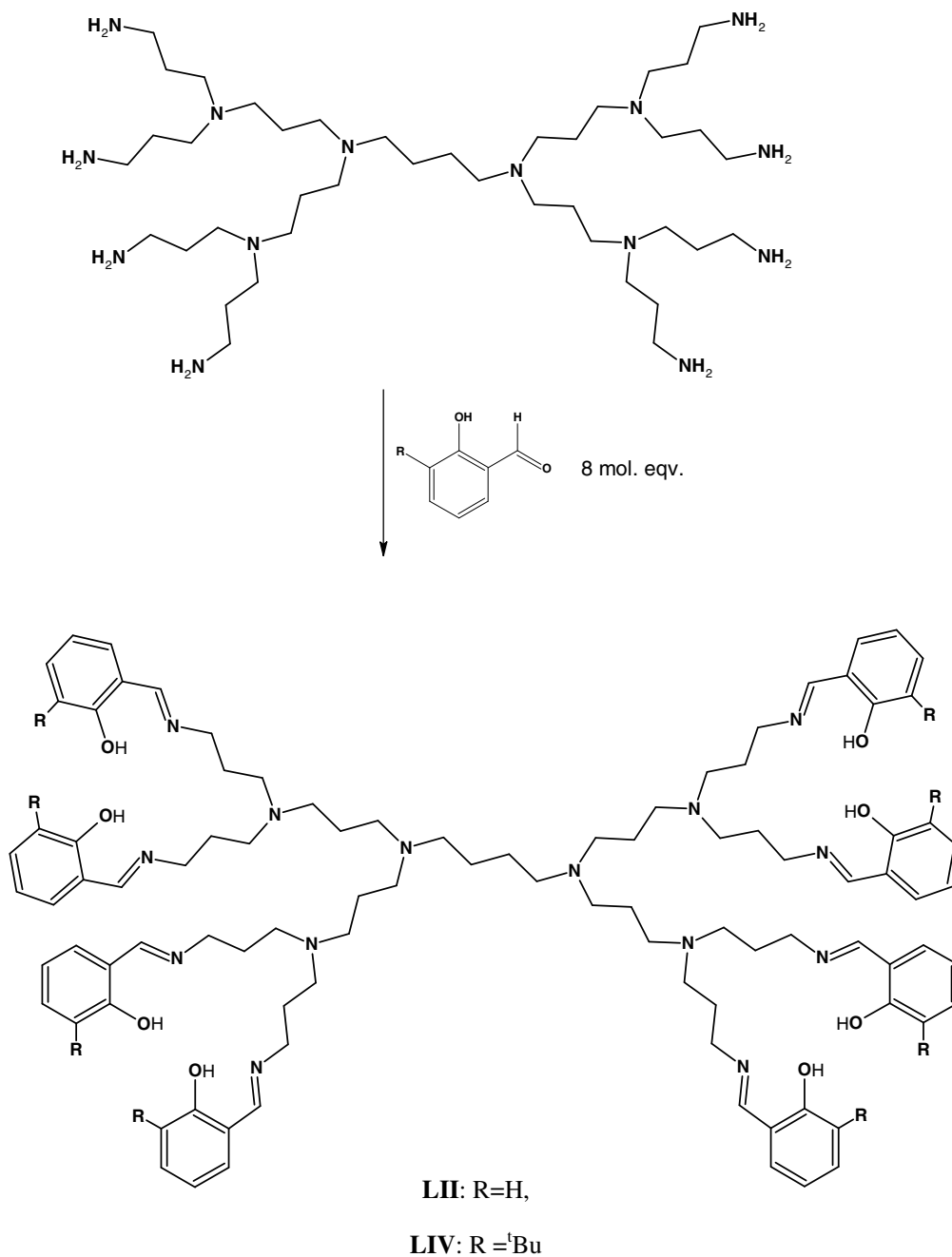
2.1. Ligand synthesis and characterization

The synthesis of ligands **LI** and **LII** has previously been reported by Smith [29]. The same synthetic method was used to prepare the range of dendrimeric salicylaldehyde ligands, **LI–LIV** via Schiff base condensation of the diaminobutane tetra-amine dendrimer, (DAB- $(\text{NH}_2)_4$) with the appropriate aldehydes. This reaction is shown in Schemes 1 and 2.

To ensure complete reaction of all the peripheral amino groups of the dendrimer with the aldehyde, the reactions had to be carried out over an extended period of time. In all cases the crude product is initially isolated as a yellow oil. In the case of ligand **LI**, the product could be isolated from the oily residue as a yellow solid by recrystallization from a dichloromethane:hexane mixture. Ligand



Scheme 1.



Scheme 2.

LIII was purified by washing the crude oily product with water and isolating a yellow oil as the pure product.

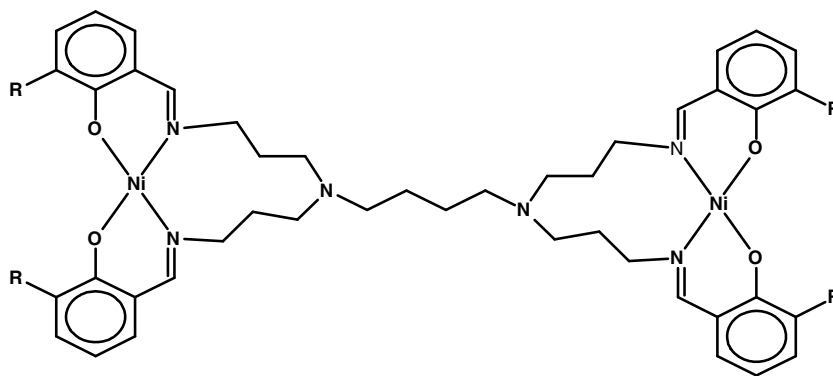
The second generation ligands **LII** and **LIV** were synthesized by reacting diaminobutane octa-amine [DAB-(NH₂)₈] with the appropriate aldehyde via a Schiff base condensation reaction. After attempting several different approaches it was ascertained that the best way for purifying **LII** was by exhaustive washing of the crude material with a large excess of water. The generation 2 substituted salicylaldimine ligand **LIV** was isolated using the same work-up method as for ligand **LIII**. **LIV** was obtained as pure yellow oil.

The IR spectra of ligands **LI–LIV** show peaks in the $\nu(\text{C}=\text{N})$ stretching frequency region indicating that the aldehydes had condensed with the amino groups on the periphery of the dendrimer to form the imine. The bands at 3400–3300 cm^{-1} are due to the O–H functionalities of the salicylaldimine units. The ¹H NMR spec-

tra of the salicylaldimine ligands (**LI–LIV**) all show the expected signals for the internal branches of the dendrimer, the proton attached to the imine group and the protons from the aryl rings. The proton NMR spectra of ligands **LIII** and **LIV** show a signal around δ 1 ppm indicating the presence of the mono ^tBu substituents on the aryl rings of the ligand at position 3. The complexes were also characterized by ¹³C NMR (see Section 3). In some cases not all the carbon resonances are resolved.

2.2. Synthesis of complexes, C1–C4

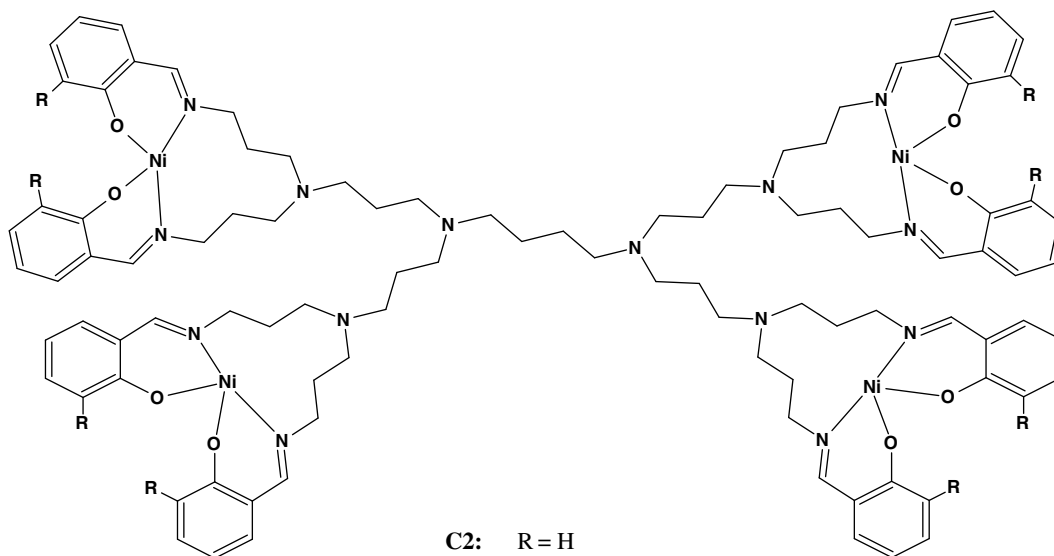
The nickel complexes (**C1–C4**) were prepared by reacting the ligands (**LI–LIV**) with nickel acetate tetrahydrate as the metal precursor. All complexes were isolated as green solids. Figs. 2 and 3 give the general structures of the generation 1 and the generation 2 dendrimeric nickel complexes, respectively.



C1: R = H

C3: R = ^tBu

Fig. 2. The structure of generation 1 nickel complexes, **C1** and **C3**.



C2: R = H

C4: R = ^tBu

Fig. 3. The structure of generation 2 salicylaldimine nickel complexes, **C2** and **C4**.

All the nickel complexes are paramagnetic and could thus not be characterized by NMR spectroscopy. However, other analytical techniques such as IR spectroscopy, mass spectrometry and elemental analysis confirmed the composition of the complexes. The IR spectra of the nickel complexes **C1–C4** show that the $\nu(\text{C}=\text{N})$ and $\nu(\text{C}-\text{O})$ stretching frequencies had shifted when compared to those of the free ligand. In the case of the $\nu(\text{C}=\text{N})$, the shift is from $\sim 1628\text{ cm}^{-1}$ (ligand) to $\sim 1632\text{ cm}^{-1}$ (complex) while in the case of the $\nu(\text{C}-\text{O})$ the shift is from $\sim 1280\text{ cm}^{-1}$ (ligand) to $\sim 1320\text{ cm}^{-1}$ (complex). The shift in the $\nu(\text{C}=\text{N})$ band indicates coordination of the azomethine nitrogen to the metal while the shifting of the $\nu(\text{C}-\text{O})$ band confirms M–O coordination. This is further confirmed by absence of the $\nu(\text{O}-\text{H})$ bands between 3400 and 3300 cm^{-1} seen in the ligand spectra but not in the complexes. The generation 1 complexes are thermally more stable than the generation 2 complexes as indicated by their decomposition temperatures.

2.3. Norbornene polymerization

2.3.1. Catalyst activity

The nickel complexes **C1–C4** were evaluated as catalysts in the vinyl polymerization of norbornene. Methylaluminoxane (MAO)

was used as an activator employing different MAO:Ni ratios. The amount of Ni used was $5\text{ }\mu\text{mol}$ in all polymerization reactions irrespective of whether the first or second generation precursor was used. Reaction time was 30 min at room temperature. The norbornene:nickel ratio employed was 5000:1 and the total volume of the reaction mixture was 25 ml. All catalysts evaluated showed activity at the various Al:Ni ratios. The results for the unsubstituted salicylaldimine complexes, **C1** and **C2** are shown in Table 1.

The generation 1 unsubstituted nickel complex (**C1**) shows optimum activity of $328\text{ kg PNB mol}^{-1}\text{ Ni h}^{-1}$ at an Al:Ni ratio of 4000:1 whereas the generation 2 unsubstituted nickel catalyst (**C2**) exhibits optimum activity of $792\text{ kg PNB mol}^{-1}\text{ Ni h}^{-1}$ at Al:Ni ratio of 4500:1. It is evident from these results that the generation 2 unsubstituted complex exhibits higher catalytic activity than the generation 1 unsubstituted complex over a wide range of Al:Ni ratios. These ratios are greater than those normally observed for similar mononuclear complexes reported previously [30]. The high activity of our dendritic system is possibly due to the increased local concentration of active sites within the dendrimer complex. Thus the same amount of metal is more widely distributed than is the case for mononuclear complexes. In our systems, we also

Table 1
Activity of complexes **C1** and **C2** for norbornene polymerization^a

Entry	Al:Ni	TOF ^b	
		C1 (G1)	C2 (G2)
1	500	21.6	60
2	1000	37.6	72
3	1500	92	76
4	2000	112	96
5	2500	128	148
6	3000	252	440
7	3500	260	480
8	4000	328	520
9	4500	292	792
10	5000	252	628

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

^b TOF: kg of polymer produced per mol of Ni per hour.

note that there is some sort of dendritic effect with regards to activity. The generation 2 catalyst, **C2** shows enhanced activity compared to the generation 1 catalyst, **C1**. This we believe is also related to the increased number of active sites in **C2** as opposed to **C1**. In addition the generation 2 catalyst (**C2**), due to its higher degree of branching might also be more effective in stabilizing the catalyst by preventing deactivation via metal agglomeration.

It was found that the generation 2 catalyst needs more MAO to reach the optimum activity when compared to its generation 1 analogue. It is thought that the tertiary amine groups within the internal framework of the dendrimer complexes can potentially act as Lewis base sites. Thus MAO, which is a Lewis acid, first coordinates to these N atoms before activating the metal centres. Only once all the internal tertiary amines have interacted with MAO, does activation of the metal centres take place. It is well known that N-donor molecules form adducts with Lewis acidic aluminium complexes [31,32].

A similar reactivity trend is observed for the norbornene polymerization results obtained using the ^tBu substituted complexes **C3** and **C4** as shown in Table 2. The same reaction conditions were applied for these complexes as for the unsubstituted complexes. Once again both catalysts show optimum activity at relatively high Al:Ni ratios. The generation 1 ^tBu substituted nickel complex (**C3**) shows an optimum activity of 512 kg PNB mol⁻¹Ni h⁻¹ at a Al:Ni ratio of 3500:1, whereas the generation 2 ^tBu substituted nickel

Table 2
Activity of complexes **C3** and **C4** for norbornene polymerization^a

Entry	Al:Ni	TOF ^b	
		C3 (G1)	C4 (G2)
1	500	168	200
2	1000	188	228
3	1500	196	256
4	2000	224	300
5	2500	240	372
6	3000	264	516
7	3500	512	540
8	4000	500	640
9	4500	448	628
10	5000	440	588

^a Reaction conditions: catalyst: 5 μmol Ni; time: 30 min; solvent: toluene; total volume: 25 ml; temperature: room temperature; Monomer:Ni = 5000.

^b TOF: kg of polymer produced per mol of Ni per hour.

catalyst (**C4**) exhibits optimum activity of 640 kg PNB mol⁻¹ Ni h⁻¹ at a Al:Ni ratio of 4000:1. As is the case for the unsubstituted complexes, the second generation complex, **C4** is a more active catalyst than its first generation analogue (**C3**) but as was the case for the unsubstituted nickel catalysts, the generation 2 substituted catalyst requires more MAO than the generation 1 substituted catalyst to reach optimum activity.

When the activities of the unsubstituted nickel complexes (**C1** and **C2**) are compared to those of the ^tBu substituted nickel complexes (**C3** and **C4**), the G1 ^tBu substituted complex exhibits a higher activity than the G1 unsubstituted complex. However, the G2 ^tBu complex is less active as a catalyst than the G2 unsubstituted nickel complex.

2.3.2. Characterization of polynorbornene produced

The ¹H NMR spectra of the polymeric products were recorded in trichlorobenzene spiked with C₆D₆ at 160 °C. Fig. 4 is an example of a proton NMR spectrum of one of the obtained norbornene polymers. All other polymers show similar NMR spectra. From the ¹H NMR spectrum it can be noted that no trace of the C=C bond is present which is usually indicative of polynorbornene formed by ring opening metathesis polymerization (ROMP). In addition, since the product is not a low mass oligomer which it would have been in the case of cationic or radical polymerization, we can deduce that the product is typical of vinyl addition norbornene polymeri-

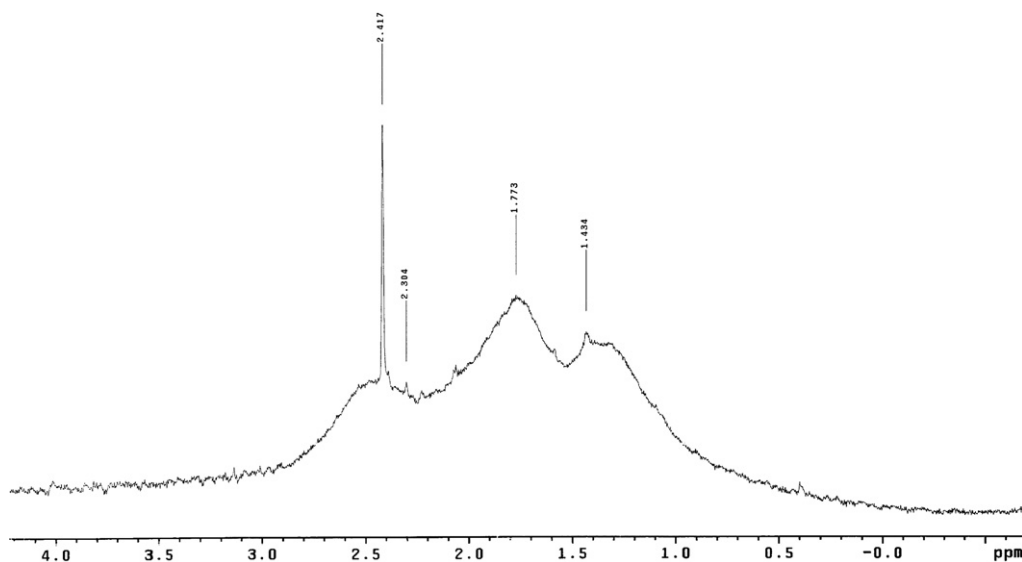


Fig. 4. ¹H NMR spectrum of obtained polynorbornene.

Table 3
GPC results for polynorbornene^a

Catalyst	Al:Ni = 1500		Al:Ni = 3000		Optimum ^b Al:Ni	
	$M_w \times 10^5$	PDI	$M_w \times 10^5$	PDI	$M_w \times 10^5$	PDI
C1	6.39	2.60	5.12	2.51	7.66	2.02
C2	6.68	2.31	7.38	2.07	7.20	2.31
C3	5.46	3.10	7.32	2.08	7.16	2.24
C4	6.39	2.46	5.12	2.26	7.66	2.04

^a Measured at 160 °C in trichlorobenzene as solvent.

^b Al:Ni ratio at which the highest activity was observed.

zation. This spectrum resembles that reported by Bao et al. who also produced polynorbornene via vinyl polymerization [33].

Polynorbornene samples obtained from reactions using catalysts **C1–C4** at the various optimum Al:Ni ratios as well as those produced at the Al:Ni ratios of 1500 and 3000 were analyzed by high temperature GPC. The GPC results are tabulated in Table 3. The PDIs for the polymers obtained from reactions using catalysts **C1–C4**, ranges from 2.02 to 3.10. This represents a relatively uniform molecular weight distribution and the results compare favourably when compared to PDI values of polynorbornenes reported in the literature. For example, Sun et al. synthesized salicylaldiminato nickel complexes as catalysts for norbornene polymerization via vinyl addition. The PDIs obtained from their polynorbornene ranged from 2.95 to 6.86 for various Al:Ni ratios [28]. In another paper by the same authors but using different nickel complexes, they reported polynorbornenes with PDI values ranging from 3.17 to 4.99 for Al:Ni ratios ranging between 500 and 2500. In all cases, the molecular weight distributions for our polymers are narrower than those reported for polynorbornene produced using similar types of nickel catalysts. When comparing the substituted nickel complexes to the unsubstituted nickel complexes, we observe that in some cases the unsubstituted complexes produce polymers with lower PDI values than the substituted complexes.

The molecular weights of the polymers obtained range from 5.12×10^5 to 7.66×10^5 g mol⁻¹ indicating fairly long polymer chains. Also, at optimum ratios the molecular weights of the polynorbornene range from 7.16×10^5 to 7.66×10^5 g mol⁻¹ and are quite similar for the four catalysts. From this we can conclude that our dendrimer catalysts produce similar chain lengths of polynorbornene irrespective of the dendrimer generation or the nature of substituents on the aryl rings of the complexes.

3. Experimental

3.1. Materials and methods

All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques. Toluene was dried by refluxing over sodium/benzophenone ketyl. The polypropyleneimine dendrimers with diaminobutane cores, DAB-(NH₂)₄ and DAB-(NH₂)₈ were obtained from Symochem, Netherlands, and used as received. Nickel acetate tetrahydrate, salicylaldehyde and its 3-*tert*-butyl substituted analogue were purchased from Sigma-Aldrich and were used without any further purification. Methylaluminoxane (MAO), 10% solution in toluene, was also obtained from Sigma-Aldrich. Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 PC FT-IR spectrophotometer, using KBr pellets or as nujol mulls on NaCl plates. ¹H NMR (200 MHz) and ¹³C NMR (50.3 MHz) spectra were recorded on a Varian XR200 spectrometer, using tetramethylsilane as an internal standard. ESI mass spectra were recorded on a Waters API Q-TOF Ultima instrument in V-mode. The source temperature was 100 °C and the desolvation temperature was 350 °C. The capillary voltage used was 3.5 kV.

Microanalysis was done at the University of Cape Town. Melting points were recorded on a Leitz Microscope Hot Stage 350.

3.2. Synthesis of generation 1 unsubstituted ligand (**LI**)

DAB-(NH₂)₄ (0.5 g, 1.6 mmol) was added to dry toluene (10 ml) in a Schlenk tube, under nitrogen. Salicylaldehyde (0.77 ml, 6.3 mmol) was added to the solution. The mixture was allowed to stir at room temperature for 72 h. The solvent was evaporated on a rotary evaporator leaving a yellow oily residue. Dichloromethane (10 ml) was added to the oil, after which hexane (20 ml) was added. This mixture was allowed to stand for 72 h at -4 °C. The yellow precipitate obtained was filtered off via vacuum filtration and washed with cold hexane. Yield 1.06 g (90%); m.p. 66–68 °C. Anal. Calc. for C₄₄H₅₆N₆O₄: C, 72.10; H, 7.70; N, 11.47. Found: C, 71.90; H, 7.90; N, 11.49%. IR (NaCl, cm⁻¹): ν(O-H) 2924; ν(C=N) 1632; ν(C-O) 1284; ¹H NMR (CDCl₃): δ 1.42 (br m, 4H, -NCH₂CH₂ core), 1.87 (m, 8H, -NCH₂CH₂branches), 2.42 (t, 4H, -NCH₂ core), 2.57 (br t, 8H, -NCH₂branches), 3.67 (t, 8H, C=NCH₂), 6.88 (m, 4H, Ar); 7.19–7.35 (m, 12H, Ar); 8.32 (s, 4H, N=C-H). ¹³C NMR (CDCl₃): δ 25.1, 28.4, 51.5, 54.0, 57.4, 117.0, 118.4, 118.8, 131.1, 132.1, 161.3, 164.9. Positive ion ESI-MS, m/z: 733 (M⁺).

3.3. Synthesis of generation 2 unsubstituted ligand (**LI**)

DAB-(NH₂)₈ (1.6 g, 5.4 mmol) was dissolved in dry toluene (10 ml) in a Schlenk tube, under nitrogen. Salicylaldehyde (2.4 ml, 16.4 mmol) was added to the solution. The mixture was allowed to stir at room temperature for 72 h. The solvent was evaporated on a rotary evaporator leaving a yellow oil. The product was dissolved in dichloromethane (20 ml) and then washed with water (5 × 30 ml). The dichloromethane layer was dried over magnesium sulphate after which the mixture was filtered by gravity. The filtrate was taken to dryness producing a yellow oil. Yield 2.7 g (80%). Anal. Calc. for C₉₆H₁₂₈N₁₄O₈: C, 71.90; H, 8.03; N, 12.21. Found: C, 71.87; H, 8.28; N, 11.86%. IR (NaCl, cm⁻¹): ν(O-H) 3058; ν(C=N) 1664; ν(C-O) 1279. ¹H NMR (CDCl₃): δ 1.31 (br m, 4H, -NCH₂CH₂ core), 2.45 (t, 4H, -NCH₂ core), 1.61 (br t, 8H, NCH₂CH₂CH₂, 1st branch), 1.90 (br t, 8H, CH₂CH₂N, 1st branch), 2.32 (br t, 8H, NCH₂CH₂CH₂, 1st branch), 2.39 (br t, 16H, NCH₂CH₂CH₂), 2.61 (m, 16H, NCH₂CH₂CH₂, 2nd branch), 3.61 (t, 16H, C=NCH₂, 2nd branch), 6.86 (m, 8H, Ar); 7.37–7.53 (m, 24H, Ar); 8.31 (s, 8H, N=C-H). ¹³C NMR (CDCl₃): δ 24.1, 24.8, 30.1, 52.1, 52.2, 116.9, 118.4, 118.7, 131.1, 131.9, 134.5, 161.2, 164.8. Positive ion ESI-MS, m/z: 1606 (M⁺).

3.4. Synthesis of the generation 1, ^tBu substituted ligand (**LI**)

LI was prepared in a similar manner as to **LI**, the only exception being that 3-*tert*-butyl-2-hydroxybenzaldehyde was used in place of salicylaldehyde. The mole ratio of aldehyde to DAB-(NH₂)₄ was 4:1. The work-up of the product was the same as for **LI**. A yellow oil was obtained in a yield of 85%. Anal. Calc. for C₆₀H₈₈N₆O₄: C, 70.29; H, 8.70; N, 8.06. Found: C, 70.84; H, 8.93; N, 8.05%. IR (NaCl, cm⁻¹): ν(O-H) 2958; ν(C=N) 1637; ν(C-O) 1265. ¹H NMR (CDCl₃): δ 1.41 (d, 36H, CH₃), 1.44 (br m, 4H, -NCH₂CH₂ core), 2.44 (t, 4H, -NCH₂ core), 2.53 (br t, 8H, -NCH₂branches), 1.90 (m, 8H, -NCH₂CH₂ branches), 3.61 (t, 8H, C=NCH₂), 6.82 (m, 4H, Ar); 7.16–7.29 (m, 12H, Ar); 8.32 (s, 4H, N=C-H). ¹³C NMR (CDCl₃): δ 24.9, 28.2, 29.2, 34.8, 51.2, 53.8, 57.1, 117.6, 118.5, 129.5, 137.2, 160.5, 165.6. Positive ESI-MS, m/z: 958 (M+H)⁺.

3.5. Synthesis of the generation 2, ^tBu substituted ligand (**LI**)

The synthesis and the work up of ligand, **LI** was similar to that of **LI**, using an 8:1 mol ratio of 3-*tert*-butyl-2-hydroxybenzaldehyde

hyde: DAB-(NH₂)₈. The product was obtained as a yellow oil, yield 83%. Anal. Calc. for C₁₂₈H₁₉₂N₁₄O₈: C, 74.81; H, 9.42; N, 9.54. Found: C, 74.50; H, 8.94; N, 9.83%. IR (NaCl, cm⁻¹): ν(O–H) 2906; ν(C=N) 1618; ν(C–O) 1224. ¹H NMR (CDCl₃): δ 1.42 (d, 72H, CH₃), δ 1.45 (br m, 4H, –NCH₂CH₂ core), 1.56 (br t, 8H, NCH₂CH₂CH₂, 1st branch), 1.81 (br t, 8H, CH₂CH₂N, 1st branch), 2.36 (br t, 8H, NCH₂CH₂CH₂, 1st branch), 2.41 (br t, 16H, NCH₂CH₂CH₂), 2.51 (t, 4H, –NCH₂ core), 2.78 (m, 16H, NCH₂CH₂CH₂, 2nd branch), 3.58 (t, 16H, C=NCH₂, 2nd branch), 6.86 (m, 8H, Ar); 7.23–7.53 (m, 24H, Ar); 8.30 (s, 8H, N=C–H). ¹³C NMR (CDCl₃): δ 24.2, 24.9, 29.2, 30.0, 35.0, 53.1, 53.2, 60.8, 117.6, 117.0, 118.1, 129.9, 130.5, 134.9, 159.85, 165.4. Positive ion ESI–MS, *m/z*: 1028 (M)²⁺ (doubly charged ion).

3.6. Synthesis of generation 1 unsubstituted nickel complex (C1)

LI (0.5 g, 0.68 mmol) was dissolved in ethanol (10 ml) in a round bottom flask, under nitrogen. Nickel acetate tetrahydrate (0.34 g, 1.4 mmol) was then added to the solution and the reaction mixture was refluxed for 24 h. During this time a green precipitate formed. This was filtered off by vacuum filtration and washed extensively with cold ethanol to yield a green solid. Yield 0.49 g (85%); m.p. 275–278 (dec); °C; Anal. Calc. for C₄₄H₅₂N₆Ni₂O₄ · 0.25 H₂O: C, 62.12; H, 6.14; N, 9.87. Found: C, 62.15; H, 6.15; N, 9.9%. IR (NaCl, cm⁻¹): ν(C=N) 1628; ν(C–O) 1324. Positive ESI–MS, *m/z*: 848, (M+H)⁺.

3.7. Synthesis of generation 2 unsubstituted nickel complex (C2)

LI (0.35 g, 2.3 mmol) was dissolved in ethanol (10 ml) in a round bottom flask, under nitrogen. Nickel acetate tetrahydrate (0.23 g, 0.92 mmol) was added to the solution and the reaction mixture refluxed under nitrogen for 24 h. The solvent was evaporated via rotary evaporation yielding a green residue. The residue was dissolved in dichloromethane (15 ml) and the solution was filtered by gravity filtration. The solvent was removed from the filtrate producing a green solid which was washed with hexane (3 × 5 ml). The product was dried under vacuum, yielding a bright green solid. Yield 0.32 g (80%); m.p. 210–215 °C (dec); Anal. Calc. for C₉₆H₁₂₀N₁₄Ni₄O₈ · 2CH₂Cl₂: C, 58.77; H, 6.24; N, 9.79. Found: C, 58.04; H, 6.25; N, 9.38%. IR (NaCl, cm⁻¹): ν(C=N) 1632; ν(C–O) 1344. Positive ion ESI–MS, *m/z*, 1833 (M⁺).

3.8. Synthesis of generation 1 ^tBu substituted nickel complex (C3)

C3 was prepared in a similar manner to **C2** using 2 mol equivalents of nickel acetate tetrahydrate. The product was obtained as a green solid, yield 75%; m.p. 281–283 °C (dec). Anal. Calc. for C₆₀H₈₄N₆Ni₂O₄: C, 67.30; H, 7.91; N, 7.85. Found: C, 67.18; H, 7.80; N, 7.43%. IR (NaCl, cm⁻¹): ν(C=N) 1640; ν(C–O) 1310. Positive ion ESI–MS, *m/z*, 1072 (M+H)⁺.

3.9. Synthesis of generation 2 ^tBu substituted nickel complex (C4)

LIV was reacted with 4 equiv. of nickel acetate tetrahydrate under the same reaction conditions as for **C3** producing a green solid in a yield of 82%; m.p. 191–195 °C (dec). Anal. Calc. for C₁₂₈H₁₈₄N₁₄Ni₄O₈ · CH₂Cl₂: C, 65.47; H, 7.92; N, 8.29. Found: C, 65.61; H, 8.04; N, 8.30%. IR (NaCl, cm⁻¹): ν(C=N) 1630; ν(C–O) 1316. Positive ion ESI–MS, *m/z*, 2281 (M)⁺.

3.10. Catalytic reactions

3.10.1. Materials for norbornene polymerization

All work involving moisture and air sensitive compounds such as methylaluminoxane (MAO) was carried out using standard

Schlenk techniques. GPC analysis of the polynorbornene (PNB) was done at SASTECH R&D using trichlorobenzene as a solvent at 160 °C and polystyrene as standards. Toluene was dried by refluxing over sodium/benzophenone. Norbornene was obtained from Sigma–Aldrich and dried over calcium hydride before being distilled. A 5 M norbornene stock solution in toluene was prepared and used for all reactions. Methylaluminoxane (MAO), a 10% solution in toluene, was obtained from Sigma–Aldrich and used without any further purification.

3.10.2. Typical polymerization procedure

The appropriate amount of catalyst corresponding to 5 μmol of nickel was added to the required amount of dry toluene in a Schlenk tube, under nitrogen. Five milliliters (25 mmol) of a 5 M norbornene in toluene solution was added to the reaction vessel. The required amount of MAO was then injected into the reaction solution to initiate the polymerization. The total volume of the reaction mixture was maintained at 25 ml for all reactions. The reaction was allowed to continue for 30 min at room temperature after which it was stopped by adding the reaction mixture to 200 ml of acidic methanol (95:5). A white solid precipitated from solution. The polymer product was dried at 60 °C in a vacuum oven for 24 h.

4. Conclusion

Complexes **C1–C4** are all active as catalysts for the vinyl polymerization of norbornene. When comparing the effect of dendrimer generation on activity, the generation 2 catalysts were found to be more active than the generation 1 catalysts. Comparison between substituted and unsubstituted catalysts shows that although the generation 1 unsubstituted catalyst exhibits higher activity than the generation 1 substituted catalyst, the steric hindrance caused by the substituents on the aryl rings of substituted generation 2 complex **C4** makes it less active as catalyst than the unsubstituted generation 2 complex **C2**. Catalytic activities also rely on the ratio of Al:Ni ratio employed. The GPC results indicate that the type of polynorbornene formed with regard to chain length, is similar regardless of the catalyst employed. Thus the dendrimer generation as well as the substituents on the aryl ring of the ligand has an affect on the activity of the complexes but not on the chain length or polydispersity of the polynorbornene obtained.

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