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A different polynorbornene backbone by combination of two polymer growth pathways: vinylic addition and ring opening *via* β -C elimination†

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A new polynorbornene skeleton has been found that contains bicyclic norbornane units and cyclohexenyl methyl linkages. The polymers have been synthesized using a nickel catalyst in the presence of a controlled amount of ligands with low or moderate coordination ability. The backbone structure is the result of a vinylic addition polymerization, *via* sequential insertions of norbornene into a Ni–C bond (bicyclic units) combined with an unusual ring opening of the norbornene structure by a β -C elimination (cyclohexenyl methyl units) to give a new Ni–C(alkyl) bond that continues the polymerization. The ring opening events are favored when the rate of propagation of the vinylic addition polymerization decreases, and this can be modulated by making the coordination of norbornene to the metal center less favorable using additional ligands.

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Introduction

Bicyclo[2.2.1]hept-2-ene or norbornene (NB) can be polymerized in several ways to give different polymer structures (Scheme 1).¹ Radical or cationic routes lead to low molecular weight polymers that show a 2,7-linkage of the bicyclic moieties (Scheme 1a). Norbornene and many norbornene derivatives are amenable to ring opening metathesis polymerization, which produces unsaturated polymeric structures (ROMP-PNB, Scheme 1b).² The vinylic addition polynorbornenes (VA-PNBs) result from a metal-catalyzed double bond insertion polymerization leading to an aliphatic backbone where the bicyclic units are preserved and show an *exo*-2,3-enchainment (Scheme 1c).³ Both ROMP-PNBs and VA-PNBs can be obtained as high molecular weight polymers with a wide range of applications and commercial availability.^{4,5} It has been shown that using suitable catalysts the ROMP route can be controlled to synthesize cyclic unsaturated polynorbornenes *via* what is called ring expansion metathesis polymerization or REMP.⁶

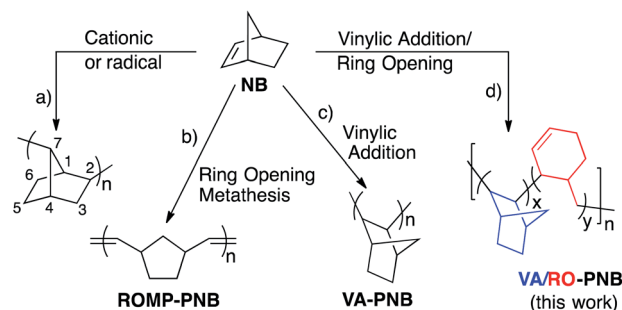
Few exceptions to these polymeric structures have been found and the reported examples combine two types of the known polymeric arrangements in Scheme 1a–c. For example, a few metal catalysts are capable of bringing about the ROMP and VA-polymerization of norbornene by switching during the process between a metal carbene species and a metal alkyl through an α -elimination–readdition process. The outcome is

a polymer structure that mixes 2,3-bicyclic moieties and ring opened olefinic units as shown in Scheme 2b.⁷ A norbornene oligomer was reported by Fink *et al.* that shows 2,3- and 2,7-enchainment bicyclic units. This structure is the result of a σ -bond metathesis between a Zr–C and a C(7)–H bond of the growing polymer chain in a VA-polymerization with a Zr metallocene (Scheme 2a).⁸

We report here a new type of polynorbornene structure (Scheme 1d) that includes in the polymer backbone both 2, 3-bicyclic and cyclohexenylmethyl fragments *via* vinylic addition polymerization and a ring opening of norbornene (NB) by β -C elimination, and therefore can be labeled as VA/RO-PNB.

Results and discussion

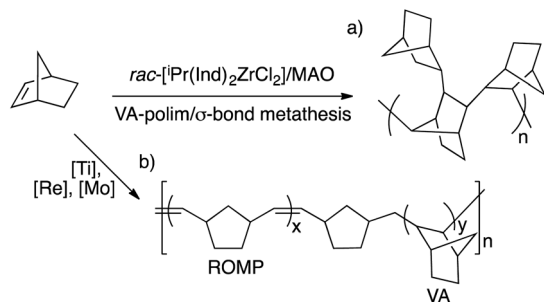
Complexes $[\text{Ni}(\text{R}_\text{F})_2\text{L}_2]$ ($\text{R}_\text{F} = \text{C}_6\text{F}_5$, $\text{C}_6\text{Cl}_2\text{F}_3$), where L is a labile ligand, are very efficient catalysts in the VA-polymerization of



Scheme 1 Types of norbornene polymerization.

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Scheme 2 Examples of two type of linkages in a polynorbornene.

norbornene.⁹ We have been using for some time $[\text{Ni}(\text{C}_6\text{F}_5)_2(\text{SbPh}_3)_2]$ (**1**) which is very active in the VA-polymerization of norbornene and some norbornene derivatives such as haloalkylnorbornenes,^{10b} generally much more reluctant to this type of polymerization, as well as in the copolymerization of functionalized norbornenes such as haloalkyl-,^{10b} alkenyl-,^{10c} and stannylated norbornenes,^{10a} with norbornene.^{4b} In the course of these studies, we observed that when the activity of the catalyst was low as, for example, in the copolymerization of substituted norbornenes with carbonyl groups, the polymers obtained in low yields showed an olefinic signal at about 5.7 ppm in the ^1H NMR.¹¹ We decided to look into the origin of this unsaturation and we started by carrying out the polymerization of norbornene with complexes $[\text{Ni}(\text{C}_6\text{F}_5)_2\text{L}_2]$ with ligands of different coordination ability and low NB : Ni mol ratios. Some of the polymers obtained showed the abovementioned unsaturation (Fig. 1a) and, as it is shown in Fig. 1, this signal is not consistent with the presence of ROMP units in the polymer (cf. spectra, Fig. 1a and c).

The chemical shifts in the ^1H and ^{13}C NMR are in agreement with an endocyclic cyclohexenyl double bond that could result from β -C elimination in a Ni-norbornyl complex during the polymerization as shown in eqn (1). β -C (or β -alkyl) elimination is not as common for group 10 metals as it is for early transition

metals.¹² However, examples of C-C cleavage by group 10 metal complexes can be found,¹³ and the process is gaining great importance in the context of norbornene-mediated palladium catalyzed regioselective reactions, that rely on a reversible norbornene insertion into a Pd-C bond.¹⁴ In the latter processes the norbornene cyclic structure remains intact and the type of ring opening of norbornene shown in eqn (1) is very scarce in the literature. Catellani *et al.* reported in 1983 the ring opening by β -C elimination of norbornene after two sequential insertions of norbornene into a Pd-Ar bond.¹⁵ Milstein also reported a similar process when studying the Heck reaction using norbornene.¹⁶ In the context of the Pd-catalyzed VA-polymerization of an ester derivative of norbornene, Rhodes *et al.* proposed the occurrence of the ring opening process in eqn (1) followed by β -H elimination to explain the chain termination observed.¹⁷ For Ni complexes, only the dimerization of norbornene mediated by an *in situ* generated nickel hydride has been reported and it leads to **4**, shown in Fig. 1b.¹⁸ As can be seen when comparing the spectra in Fig. 1a and b, the polymer unsaturation is consistent with the endocyclic double bond of a cyclohexenyl fragment similar to that in dimer **4** synthesized independently. In the polymerization, the cyclohexenyl methyl nickel complex (eqn (1)) undergoes a new monomer insertion instead of a β -H elimination and the exocyclic double bond is not formed.

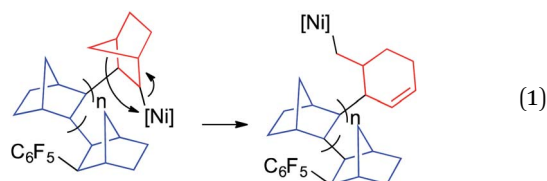


Table 1 shows the polymerization experiments with complexes **1**–**3**. The polymerization of norbornene requires

Table 1 Formation of VA-PNB or VA/RO-PNB with catalysts **1**, **2** and **3**

Entry	[Ni]	m	[NB] ₀ ^a	NB _{VA} /NB _{RO} ^b	% NB _{RO} ^c	Yield	M _w ^d	D ^d
1	1	75	0.34	No NB _{RO}	0%	90%	162090	4.4
2	1	75	0.061	67/1	1.5%	75%	49065	1.9
3	2	75	0.34	No NB _{RO}	0%	95%	138411	4.2
4	2	75	0.061	14.3/1	6.5%	67%	14071	2.3
5	2	225	0.061	No NB _{RO}	0%	74%	87947	1.9
6	3	75	0.34	—	—	—	—	—

^a Initial molar concentration of norbornene (NB). ^b The mol ratio NB_{VA}/NB_{RO} was calculated by comparison of the integral of the ^1H NMR signals (olefinic vs. aliphatic) of the polymer (see ESI). ^c The mol% of NB_{RO} was calculated from the mol ratio NB_{VA}/NB_{RO}. ^d M_w (Da) and D (M_w/M_n) determined by GPC in CHCl₃ using polystyrene standards.

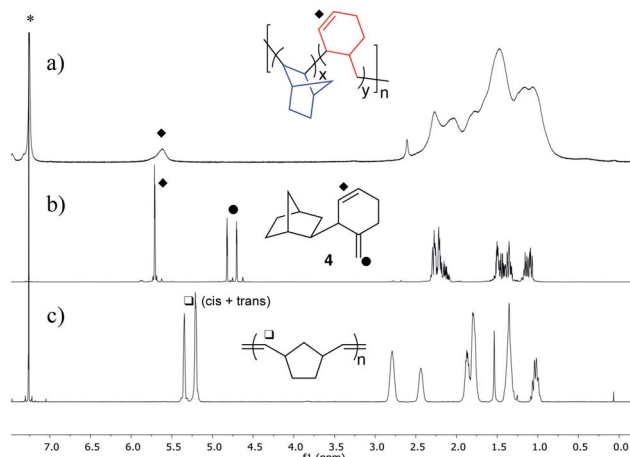


Fig. 1 ^1H NMR (CDCl_3) of: (a) VA/RO-PNB (NB_{VA}/NB_{RO} = 7.6/1). (b) dimer **4**; (c) ROMP-PNB. *Signal corresponding to the residual solvent.

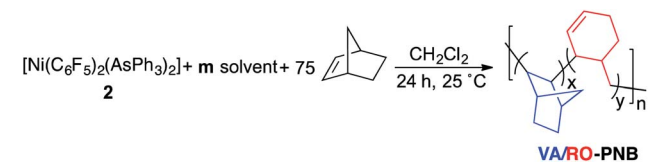
a weakly coordinating ligand, *i.e.* SbPh_3 or AsPh_3 . The more donating PPh_3 renders the complex inactive (*cf.* entries 1, 3 and 6, Table 1). The presence of ring-opened norbornene units (NB_{RO}) was observed when the reactions were carried out at low initial concentration of monomer (entries 2 and 4, Table 1). This effect is more important for the more coordinating AsPh_3 *vs.* SbPh_3 (*cf.* entries 2 and 4, Table 1). The amount of cyclohexenylmethyl units (or ring-opened norbornene, NB_{RO}) can be calculated by comparison of the intensity of the olefinic signal at about 5.7 ppm with the aliphatic region in the ^1H NMR spectra of the polymers (for details see page S4, ESI†). The composition of the polymers is given in the tables as the ratio of bicyclic units (NB_{VA}) to ring-opened units (NB_{RO}) as well as the percentage of NB_{RO} in the polymers. Table 1 (entry 5) also shows that a decrease in the catalyst amount, using the same initial NB concentration, disfavors the ring opening process. The use of a lower concentration of the nickel complex implies that the concentration of free ligand L, dissociated during the polymerization, is also lower. Therefore, all these results show that the formation of NB_{RO} units is favored by a low initial monomer (NB) concentration and the presence of free AsPh_3 , dissociated from the nickel complex.

The polymers were characterized by NMR (see below and ESI for details†) and they show unimodal distributions in GPC, indicating that they are not mixtures of two types of polymers. A higher amount of NB_{RO} units is associated with a lower yield of the polymerization as well as a lower M_w for the polymer (Table 1), therefore a less efficient polymer growth. Thus, we tested the polymerization in the presence of small amounts of compounds that have shown to hamper the VA-polymerization of norbornene when used as solvents.^{9b,19} These are coordinating solvents, such as ketones, acetonitrile or amides. Table 2 shows

that polymers with up to 12% of NB_{RO} units can be obtained in good or moderate yields using a controlled amount of ketones (acetone or acetophenone) as additives in a polymerization of norbornene with complex 2 (entries 1–5, Table 2). The more coordinating DMA can also be used but a smaller amount is required (entries 8–11, Table 2). The presence of MeCN halts the polymerization. The experiments with the ketones show that there is a direct correlation between the amount of additive and the percentage of NB_{RO} units (entries 2–4, Table 2). Also, a larger amount of NB_{RO} is observed when the coordinating ability of the additive increases (*cf.* entries 2 and 5, Table 2).²⁰ The effect of the temperature in the polymerization was tested in the small range allowed by the significant catalyst decomposition ($T > 45^\circ\text{C}$) and the very low conversion at 0°C . The relative amount of ring opened units (% NB_{RO}) decreases when lowering the reaction temperature (entries 6 and 7, Table 2). The data in Table 2 show that the VA/RO-PNBs have molecular weights in the range $1\text{--}3 \times 10^4$ Da and T_g s between $150\text{--}230^\circ\text{C}$. As the percentage of NB_{RO} units increases, a trend toward lower M_w s (entries 2–4, Table 2) and lower T_g s is observed (*cf.* entries 1 and 5, Table 2, for polymers with similar size). The thermogravimetric analysis shows the decomposition of the polymers at about 430°C with no significant differences between VA/RO-PNBs with different percentage of NB_{RO} units (Fig. S32, ESI†).

In order to learn about the distribution of NB_{RO} units in the polymer, experiments were carried out in the conditions of entry 5, Table 2, quenching the polymerization at different reaction times, *i.e.* at different conversions (Table S1, ESI†). Fig. 2a, shows that at short reaction times, the % of NB_{RO} units is low but it increases with time, as the conversion increases and norbornene is consumed. This is consistent with the results in Table 1 (entries 3 and 4) and the experiments shown in Fig. 2b,

Table 2 Formation of VA/RO-PNBs with catalyst 2 in the presence of coordinating solvents



Entry	$[\text{NB}]_0^a$	m solvent	$\text{NB}_{\text{VA}}/\text{NB}_{\text{RO}}^b$	% NB_{RO}^c	Yield	M_w^d	D^d	T_g^e ($^\circ\text{C}$)
1	0.34	160 Me_2CO	15.7/1	6.0%	70%	18769	2.4	227
2	0.061	160 Me_2CO	12.1/1	7.6%	65%	14302	2.2	
3	0.061	320 Me_2CO	9.4/1	9.6%	63%	11770	2.6	169
4	0.061	640 Me_2CO	8.5/1	10.5%	50%	10900	2.3	164
5	0.061	160 PhMeCO	7.6/1	11.6%	64%	17391	1.5	159
6 ^f	0.061	160 PhMeCO	8.1/1	10.9%	50%	12141	2.0	
7 ^g	0.061	160 PhMeCO	16.1/1	5.8%	43%	19297	1.8	
8	0.061	20 DMA	7.0/1	12.5%	34%	12570	1.4	
9	0.34	20 DMA	13.9/1	6.7%	74%	33605	1.6	
10	0.34	40 DMA	8.4/1	10.6%	55%	22366	1.7	
11	0.061	160 DMA	—	—	0%	—	—	
12	0.34	20 MeCN	—	—	0%	—	—	

^a Initial molar concentration. ^b The mol ratio $\text{NB}_{\text{VA}}/\text{NB}_{\text{RO}}$ was calculated by comparison of the integral of the ^1H NMR signals (olefinic *vs.* aliphatic) of the polymer (see ESI). ^c The molar% was calculated from the mol ratio $\text{NB}_{\text{VA}}/\text{NB}_{\text{RO}}$. ^d M_w (Da) and D (M_w/M_n) determined by GPC in CHCl_3 using polystyrene standards. ^e Determined by DSC. ^f $T = 45^\circ\text{C}$; some catalyst decomposition was observed. ^g $T = 12.5^\circ\text{C}$.



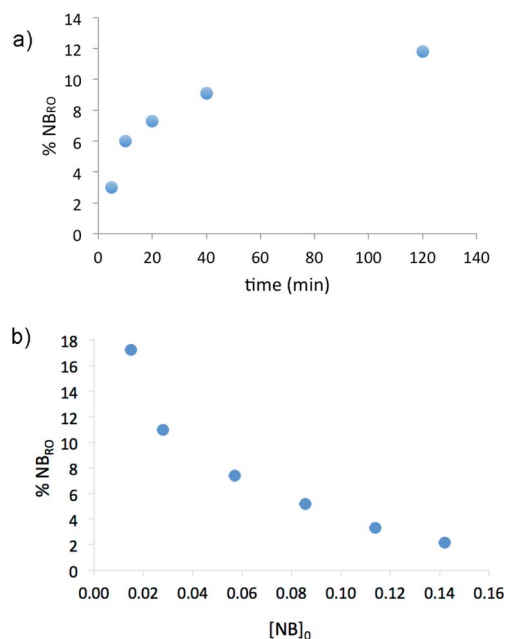


Fig. 2 Plot of the amount of ring opened units (% of NB_{RO}) vs. the polymerization reaction time (a) or the initial norbornene concentration (b).

where low initial NB concentrations favor the ring opening for polymerizations quenched at the same reaction time (Table S2, ESI†). As the reaction progresses the NB concentration also decreases leading to a higher relative ratio of NB_{RO}.

A short polymer was synthesized in order to gather some information about the end-groups of the materials. Using a lower NB : Ni mol ratio in the presence of acetophenone (NB : Ni : PhCOMe = 5 : 1 : 15) a polymer with $M_w = 2270$ Da was prepared, which contains pentafluorophenyl groups as clearly shown in its ^{19}F NMR spectrum (Fig. S8, ESI†). This indicates that the polymerization initiates by insertion of a norbornene into a Ni-C₆F₅ bond, as it has been observed for this type of complexes before.⁹ The ^1H NMR spectrum of this polymer also shows a signal corresponding to the CH-C₆F₅ group at 3.25 ppm, as well as two singlets at about 4.7 ppm characteristic of a terminal exocyclic methylenecyclohexenyl

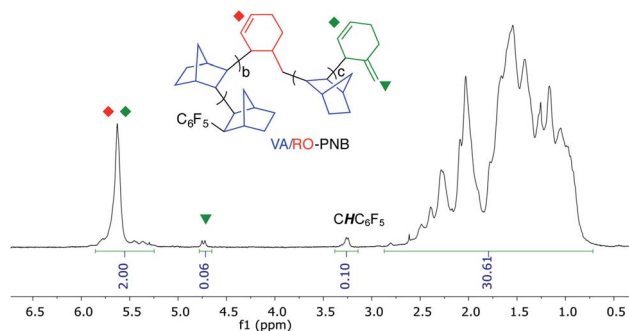
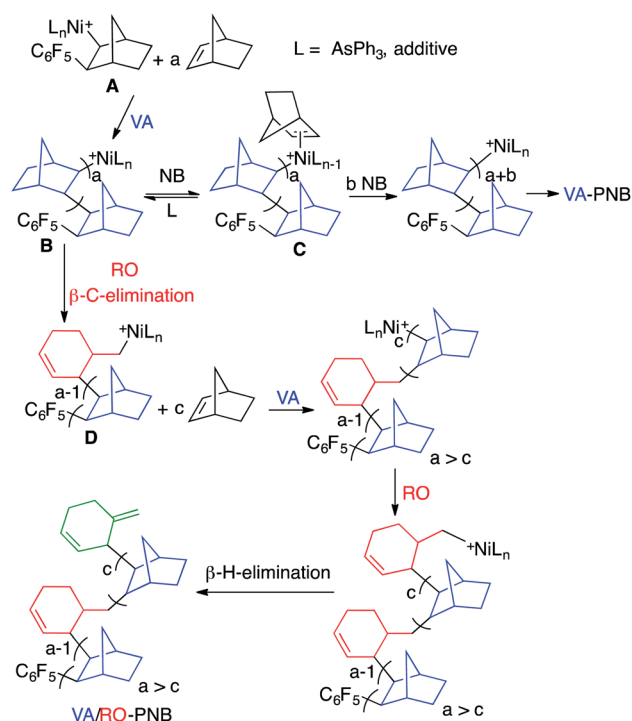


Fig. 3 ^1H NMR (CDCl₃) of a short VA/RO-PNB (NB_{VA}/NB_{RO} = 2.3/1, M_w = 2270 Da).

double bond (Fig. 3, S23 and S24, ESI†). This fragment is the result of a β -H elimination in a cyclohexenylmethyl nickel growing polymer chain and it is a termination pathway for the polymerization. However, when comparing the integral value of the CH-C₆F₅ (chain initiation) in Fig. 3 and the C=CH₂ resonances (chain termination) it is clear that the terminal olefinic signal is less intense than expected, and therefore the β -H elimination route is important but not the only termination pathway. We could not identify any other end-group that could shed light into it.† In these polymerizations the metal stays attached to the growing chain long enough to be trapped by a carbonylation process, indicating that the termination step is slow.²¹ We quenched a polymerization under the same conditions used for the synthesis of the polymer mentioned above, by bubbling CO through the solution and adding NaOMe in MeOH. The obtained polymer showed characteristic -COOMe resonance in the ^1H NMR (3.68 ppm, Fig. S11, ESI†) and a carbonyl resonance at 174 ppm as a cross peak in a long range ^1H - ^{13}C HMBC NMR experiment. This ester group was also found when a VA-polymerization (conditions of Table 1, entry 1, 15 min) was quenched in the same way (Fig. S16, ESI†).

According to all these data a plausible polymerization scheme can be drawn as depicted in Scheme 3. The polymerization initiates by insertion of norbornene into a Ni-C₆F₅ bond, as supported by the presence of pentafluorophenyl groups in the polymer. The initiation is slower than the propagation of the polymerization as shown by the high molecular weight of the polymers obtained when compared to the amount of catalyst used. For example, most of the polymerizations were carried out with a mol ratio Ni : NB = 1 : 75; if every Ni atom starts



Scheme 3 Formation of VA/RO-PNB.

a polymer chain the maximum M_w of the polymer should be 7062 Da (*i.e.* $75 \times M_{WNB}$, $M_{WNB} = 94.16$). In all cases the M_w found is higher than expected, so only a fraction of the Ni catalyst, which undergoes the slower initiation, is responsible for the polymer growth.

The equilibrium between intermediates **B** and **C** determines the pathway for the polymer growth. 2,3-Insertion of NB (NB_{VA} units) is favored by a high concentration of intermediate **C** and this occurs when L is labile and the amount of free ligand is low (*i.e.* no additive added) as well as when there is a high concentration of NB. If the equilibrium is shifted to intermediate **B** the insertion is disfavored and the β -C elimination with concomitant ring opening occurs (NB_{RO} units).

This scenario is favored for more coordinating L, higher L concentration and low NB concentration. The latter inevitably occurs as the polymerization progresses and the relative number of NB_{RO} events increases accordingly as we have observed (Fig. 2a). At the end of the polymerization the probability of β -C elimination *vs.* a new NB insertion is highest so this pathway is a viable termination in the VA-polymerization of norbornene with group 10 metal complexes.¹⁷ We have carried out the monitorization of a polymerization reaction in the conditions described above for the synthesis of a low molecular weight VA/RO-PNB (mol ratio NB : Ni : PhCOMe = 5 : 1 : 15). The kinetic experimental data conforms to the scenario described above as shown by microkinetic modeling using the COPASI software.²² All the details can be found in the ESI (Section 1.10†).

An increase in the percentage of NB_{RO} units was observed upon increasing the polymerization temperature (entries 6 and 7, Table 2) and this could be rationalized considering the entropic effects affecting the VA and RO routes. The ring opening (β -C elimination) is a unimolecular process and it is reasonable to assume that it will have a small entropy of activation. In contrast the formation of **C** is a ligand substitution reaction, which in an associative scenario would imply a more ordered transition state (negative entropic term). Thus, an increase in temperature would disfavor the VA route while little affecting the ring opening and therefore increasing the relative amount of NB_{RO} units.

The β -H elimination in the Ni-cyclohexenylmethyl complex **D** is not very fast and the insertion of a new norbornene molecule in the primary Ni-alkyl bond competes efficiently leading to the incorporation of the ring-opened moiety in the polymer. Because of the sluggish β -H elimination and comparably faster olefin insertion,²³ nickel complexes are more convenient to obtain these type of VA/RO-PNBs than palladium complexes. Eventually, at the end of the polymerization the formation of an exocyclic double bond by β -H elimination to give a methylene cyclohexene end group can occur, as we have observed.

Conclusions

A new type of polynorbornene backbone has been found that results from a typical vinylic addition polymerization, leading to bicyclic norbornyl units (NB_{VA}) combined with an unusual ring

opening *via* a β -C elimination, which forms cyclohexenylmethyl units (NB_{RO}). This mixed VA/RO-PNB skeleton appears when the coordination of the monomer to the Ni center used as catalyst is disfavored by lowering the norbornene concentration or by using competing ligands of moderated coordination ability. These results show that the β - γ -C-C cleavage of a nickel bound norbornyl group is facile whereas the β -H elimination in the primary Ni-cyclohexenylmethyl moiety formed is not too fast and further olefin insertions into the Ni-alkyl bond occur. This leads to the incorporation of the ring-opened norbornene fragments into the polymer, and to a new VA/RO-polynorbornene structure.

The C-C cleavage in the norbornyl-M fragment is more prevalent at the end of the polymerization and therefore this is a probable termination pathway in the conventional vinylic addition polymerization of norbornene or norbornene derivatives where some of the common termination pathways, such as a direct β -H elimination, are not possible.²¹

Data availability

Data supporting this article have been uploaded as ESI.†

Author contributions

I. P. O. conducted the investigation under A. C. A. supervision. A. C. A. wrote the manuscript and I. P. O. prepared the ESI.† All authors contributed to the conceptualization of the project and the review and editing of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

‡ A termination by involvement of the MeOH used to quench the polymerization could be plausible, *via* methoxy coordination, β -H elimination to give a Ni-H, and reductive elimination. We carried out several experiment using CD_3OD but could not detect the incorporation of deuterium in the polymer. A chain transfer to the monomer *via* sigma bond metathesis has also been suggested and this aliphatic termination would not be detected in the polymer.

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