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Vinylic Addition Poly(norbornene-*co*-alkenylnorbornenes) Synthesized with Benzylic Palladium Catalysts: Materials for Manifold Functionalization

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The incorporation of functional groups in the skeleton of vinylic addition polynorbornenes (VA-PNBs) is a difficult task due to the reluctant VA homo- and copolymerization of substituted norbornenes. We have found that copolymers of norbornene and alkenyl-norbornenes can be synthesized with good yields employing α-substituted benzylic complexes of palladium(II) as catalysts. The polymerization occurs exclusively through the endocyclic double bond and leaves the pendant double bond unaltered. Copolymers can be obtained with different compositions, richer in norbornene, and a different range of molecular weights depending on the catalyst used. The pendant double bond in these copolymers can be transformed by hydroboration or hydrosilylation reactions, leading to VA-PNBs with pendant polar groups not accessible either by direct polymerization or by post-polymerization functionalization reactions in an efficient way.

Introduction

The polymerization of bicyclo[2.2.1]hept-2-ene or norbornene (NB) by a vinylic addition route is, among the different polymerization pathways for this monomer,[1-3] the one that leads to high molecular weight polymers with a completely aliphatic backbone formed by intact bicyclic units (Equation 1).[2,4] This robust skeleton has high thermal and chemical stability, high Tg, and transparency, and it is suitable to behave as inert support in several applications.

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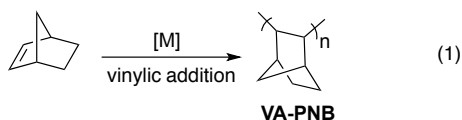
VA-PNB

The introduction of pendant functional groups in VA-polynorbornenes (VA-PNBs) is desirable and necessary to extend the range of their applications. For example, there is a lot of interest in the synthesis of VA-PNBs with silane groups because this type of polymers shows high gas permeability coefficients.[5] The incorporation of polar groups on these materials increases the adhesion on surfaces for their use as films and dielectrics in microelectronics.[6,7] The support of catalysts or reagents on VA-PNBs for sustainable organic synthesis needs a way to introduce an anchoring functional group.[8] The polymerization of substituted norbornenes would be a straightforward route to functionalized VA-PNBs. However, most catalysts that are active in the polymerization

of NB are much less active in the polymerization of norbornene derivatives, especially those norbornenes with polar groups.[9-12] This is in contrast to the high activity of ring opening metathesis catalysts toward the polymerization of substituted norbornenes, although the ROMP-PNB materials obtained are unsaturated and susceptible to degradation.[1] Efforts have been made to develop more active catalyst for the VA-polymerization of norbornene derivatives, mostly late transition metal catalysts less susceptible to deactivation by polar groups than the early transition metal complexes.[4,13,14] Nonetheless, the direct VA-polymerization of many substituted norbornenes is not efficient enough and the post-polymerization functionalization of suitable VA-PNBs is a more attractive alternative.

Few VA-polynorbornenes are amenable to the post-polymerization functionalization strategy. Since the chemical stability of the all-aliphatic backbone of VA-PNB does not allow a direct functionalization, it is necessary to introduce a reactive group in the starting polymer by polymerization of a suitable monomer. We described before the synthesis of ω-bromoalkyl VA-PNBs of different composition, by copolymerization of norbornene and 5-ω-bromoalkyl-2-norbornenes with a nickel catalyst, that can be functionalized by nucleophilic substitution of the bromine atom (Scheme 1, A).[15] This route is highly efficient for the introduction of many groups, including imidazolium,[16] or stannyl fragments.[17] However, the presence of strongly basic nucleophiles induced the HBr elimination and it is not possible, for example, to generate alcohol groups using a hydroxide salt (Scheme 1, B).

Other VA-PNBs that could be easily subjected to further functionalization would be those with pendant double bonds. If the polymerization of an alkenyl-substituted norbornene proceeds selectively through the endocyclic double bond, the
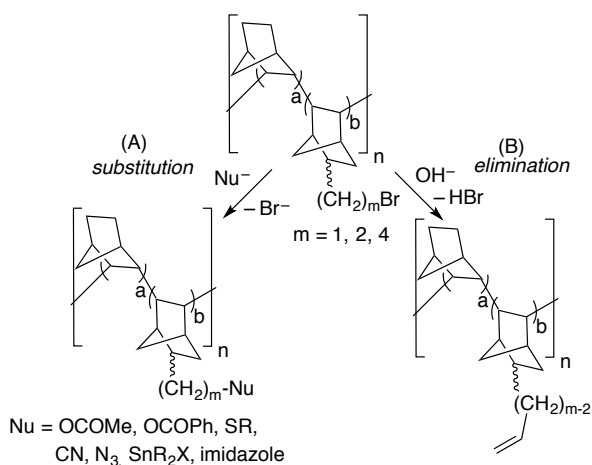
Scheme 1. Post-polymerization functionalization approach in a VA-PNB skeleton with ω-bromoalkyl groups: A) nucleophilic substitution, B) elimination with nucleophiles of high basicity

exocyclic pendant double bond is a versatile group for its transformation into other functional groups by addition reactions,[18-20] epoxidation,[19,21,22] cyclopropanation,[19] etc.[23,24] Particularly, alkenyl-monomers with a terminal unsaturation, such as the accessible and commercially available 5-vinyl-2-norbornene (VNB), are especially interesting. There are only a few efficient catalytic systems for the homopolymerization reaction of VNB because some intrinsic difficulties arise in this process.[25-27] Alkenyl-monomers are generally synthesized by a Diels-Alder reaction of cyclopentadiene and a linear diene so they are a mixture of endo and exo isomers. As for many other substituted norbornenes, the endo isomer (the major one) is the least reactive.[28-31] Besides, chemoselectivity issues appear with some catalysts and the exocyclic double bond is also involved in the polymerization process.[32] The copolymerization of vinyl norbornene and other terminal alkenyl norbornenes with norbornene to give copolymers of different composition and degree of functionalization has been seldom reported.[26,33,34]

Recently, we disclosed a highly efficient catalyst based on a η³-benzylic complex of palladium(II) for the VA-polymerization of VNB with excellent activities.[27] The easy transformation of the η³-benzyl moiety into the σ-benzyl coordinated form opens an available coordination site on the metal favoring the initiation of the polymerization by coordination-insertion of the norbornene monomer. Here, we describe the use of well-defined α-pentafluorophenyl-methyl benzylic complexes of palladium(II) that do not need any extra additive, as catalysts in the vinylic addition copolymerization of alkenyl-norbornenes and norbornene. The activity of the benzylic complexes in these VA-polymerizations is highly dependent on the auxiliary ligands coordinated to the palladium center, which is an advantage to obtain polymers with different composition and size. Also, we demonstrate that VA-polynorbornene-*co*-alkenylnorbornene polymers are easily functionalized by hydroboration or hydrosilylation reactions of the pendant double bond with excellent yields. This route leads to new VA-PNBs with polar groups not accessible by

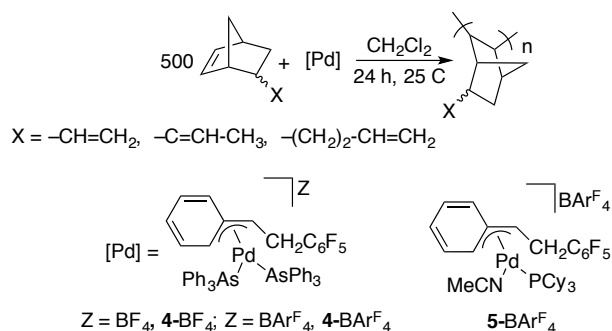nucleophilic substitution on the ω-bromoalkyl VA-PNBs (Scheme 1) or by direct polymerization of polar NB-derivatives.

Results and discussion

Homopolymerization experiments. We started exploring the activity in the homopolymerization of norbornene of several benzylic complexes of palladium(II) reported previously in our research group (Scheme 2).[35] We selected four complexes with different electrophilicity of the metal center (neutral or cationic) and with a different ligand environment. There are many catalysts for the polymerization of norbornene,[2] but this reaction provides a test for the selection of the best η³-benzylic palladium complex for the polymerization of more challenging norbornene derivatives. Complex **1**, a pentacoordinated neutral complex generated in situ as reported before,[35] gave no polymer after 24 h of reaction. In contrast, cationic complexes show some activity, which is determined by the coordination ability of the ligands. In the case of complex **2**, the chelating ligand has less tendency to generate a vacant coordination site so the yield in the polymerization is lower (25% yield) than that for its counterparts with monodentate ligands. Looking at the complexes with monodentate ligands **3** (40% yield) and **4**-BF₄ (95% yield), the complex with the more labile AsPh₃ (**4**-BF₄) gave the best result. Better yields in the polymerization of norbornene using complexes with more labile ligands has been observed before by Janiak et al. for [Pd(C₅H₅)(C₆F₅)L],[33] or by Espinet and Casares for the nickel complexes [Ni(C₆Cl₂F₃)₂L₂],[36] where L = SbPh₃, AsPh₃ and PPh₃. Therefore, complex **4**-BF₄, the one with a highly electrophilic palladium center and the labile ligand AsPh₃ is the best choice for a vinylic addition polymerization catalyst.
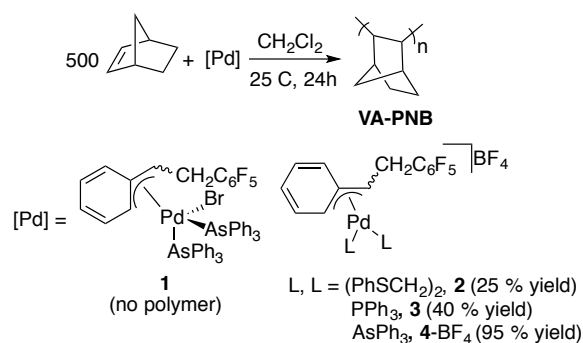
Scheme 2. Activity of η³-benzylic complexes of Pd(II) in the homopolymerization of NB.

We decided to test complex **4**-BF₄ in the polymerization of the more challenging 5-vinyl-2-norbornene (VNB) and 5-(but-1-en-4-yl)-2-norbornene (BNB). **4**-BF₄ is capable of polymerizing alkenyl-monomers giving polymers with low yields and molecular weights (entries 1 and 4, Table 1). We have found recently that the benzylic complex **5**-BArF₄, with just one coordinated bulky phosphine, is an excellent catalyst in the homopolymerization of VNB (entry 3, Table 1).[27] As expected, **5**-BArF₄ also gives VA-PBNB in excellent yields (entry

Table 1. Polymerization of alkenyl-norbornenes with catalysts **4**-BF$_4$, **4**-BAr$^F_4$ and **5**-BAr$^F_4$.[a]

$$500 \quad + \quad [Pd] \xrightarrow[\text{24 h, 25 C}]{\text{CH}_2\text{Cl}_2} \quad n$$

X = –CH=CH$_2$, –C=CH-CH$_3$, –(CH$_2$)$_2$-CH=CH$_2$

[Pd] =

Z = BF$_4$, **4**-BF$_4$; Z = BAr$^F_4$, **4**-BAr$^F_4$

5-BAr$^F_4$

Entry	Monomer	[Pd]	Yield (%)	M$_w$[b]	Đ
1	VNB	**4**-BF$_4$	17	7.2 x 10^3	1.2
2	VNB	**4**-BAr$^F_4$	34	3.46 x 10^4	1.4
3	VNB	**5**-BAr$^F_4$	99	4.9 x 10$^{5\,c}$	4.2
4	BNB	**4**-BF$_4$	23	1.73 x 10^4	1.5
5	BNB	**4**-BAr$^F_4$	87	3.05 x 10^4	7
6	BNB	**5**-BAr$^F_4$	83	4.5 x 10^4	3.1

a) The reactions were carried out using CH$_2$Cl$_2$ as solvent, [monomer]$_0$ = 1.2 M, 25 ˚C, 24 h, under N$_2$, molar ratio monomer:Pd = 500:1. b) M$_w$ (Da) and Đ (M$_w$/M$_n$) determined by GPC in CHCl$_3$ using polystyrene standards. c) The high M$_w$ observed indicates that only a fraction of the catalyst is involved in polymer growth (see reference 27).

6, Table 1). In our former studies with complex **5** we found that the nature of the counterion influences the propagation of the VA-polymerization of VNB without affecting the initiation step.[27] We synthesized **4**-BAr$^F_4$ and found that the bulkier low coordinating BAr$^F_4^-$ leads to a more active catalyst than the analogous **4**-BF$_4$. The change of counterion has a moderate effect in the homopolymerization of VNB (entries 1 and 2, Table 1) but it strongly increases the yield of the homopolymerization of BNB (entries 4 and 5, Table 1). Thus, the activity trend of these three complexes, i.e. **5**-BAr$^F_4$ > **4**-BAr$^F_4$ > **4**-BF$_4$, shows the importance of the presence of available coordination sites on palladium as well as a low coordinating counterion. None of these three catalysts are competent for the homopolymerization of substituted norbornenes with polar groups such as -COOH or -CH$_2$OH.

All homopolymers collected in Table 1 are soluble in common organic solvents and were characterized by IR, NMR and GPC. Higher molecular weights and dispersities are observed upon increase of the activity of the catalyst, which reflect a fast propagation and a relative slow initiation, with an overall poorly controlled polymerization. The analysis of the unreacted monomer after the homopolymerization of VNB with complex **4**-BF$_4$ (entry 1, Table 1) indicates a change in the ratio endo:exo. The initial ratio of the monomer is 80:20 but after the polymerization experiment the ratio changes to 86:14 (Figure S31, SI). This is indicative of a preference in the polymerization for the exo isomer.[28,29]

The structure of the alkenyl homopolymers shows that the polymerization occurs by insertion of the endocyclic double bond. The NMR analysis of the VA-PVNBs polymers showed the characteristic resonances of the pendant exocyclic double bond: resonances at 6.1-5.7 ppm (H^8) and 5.1-4.5 ppm (H^9) in the ^{1}H NMR (green rectangles, Figure 1) and 144-140.5 ppm (C^8) and 115.4-111.6 ppm (C^9) in the ^{13}C NMR. Also, the IR spectra show the exocyclic double bond, characterized by absorption bands at 1636 cm^{-1} (ν-C=C-) and at 970-905 cm^{-1} (δ-C=C-H). The absence of resonances around 20 ppm in the ^{13}C NMR conforms to the common cis-2,3-exo enchainment of VA-PNBs.[37] The exo and endo arrangements of alkenyl groups in the bicycle are visible in the ^{13}C NMR (Figures S29 and S35, SI). VA-PBNBs show similar NMR and IR patterns for the pendant double bond (see SI).

VA-PVNBs synthesized with complexes **4**-BF$_4$ and **4**-BAr$^F_4$ show an additional signal in the ^{13}C NMR at 13.8 ppm (methyl group region, Figure S29, SI) and in the ^{1}H NMR at 5.55-5.45 ppm (blue rectangle, Figure 1, a). This is consistent with the isomerization of the terminal double to the internal one as it was confirmed by the independent polymerization of the isomeric monomer 5-ethylidene-2-norbornene (ENB) to give a VA-PENB, which exhibits similar resonances (Figures S46 and S47, SI). The molar percentage of double bond isomerization can be calculated by integration in the ^{1}H NMR of the olefinic protons for the -C**H**=CH$_2$ signal (H^8) and -C=C**H**-CH$_3$ (H$^{8'}$). This molar percentage is 17% and 10% for the VA-PVNBs synthesized with **4**-BF$_4$ and **4**-BAr$^F_4$ respectively. The isomerization does not occur for the VA-PVNB synthesized with **5**-BAr$^F_4$ (Figure 1, b). The isomerization process is also operating in the synthesis of VA-PBNBs and two different resonances at 17 ppm and 13.1 ppm appear in the ^{13}C NMR spectra, tentatively assigned to a mixture of trans and cis-2-butenyl groups (Figure S40, SI). For VA-PBNBs synthesized with **4**-BF$_4$ and **4**-BAr$^F_4$ the molar percentage of isomerized double bond is 32% and 59%, respectively. The isomerization is almost complete (93%) in the VA-polymerization of BNB with catalyst **5**-BAr$^F_4$ (Figure S43, SI). α-Pentafluorophenyl-methyl benzylic complexes of palladium(II) are precursors of palladium hydrides and the isomerization of olefins with this type of catalysts has been demonstrated before.[38] We confirmed that
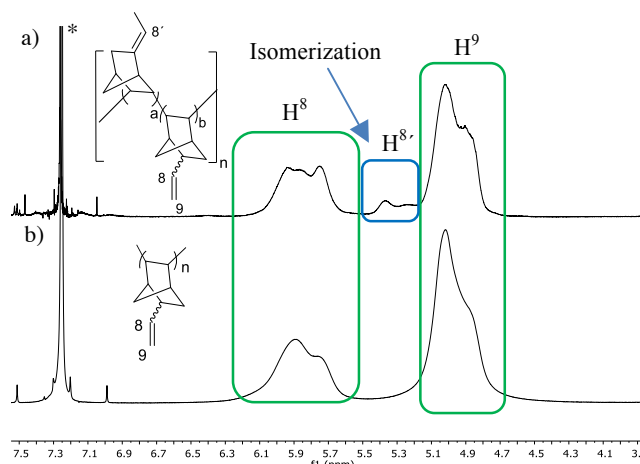
Fig. 1. ^{1}H NMR spectra in CDCl$_3$ of: a) VA-PVNB synthesized with catalyst **4**-BF$_4$; b) VA-PVNB synthesized with catalyst **5**-BAr$^F_4$. Only the olefinic part is shown. *CHCl$_3$.

the isomerization of the pendant terminal double bond to the internal olefin can take place in VA-PBNB in the presence of **4**-BF$_4$: the double bond undergoes complete isomerization after 30 min at room temperature (SI, section 1.4; Figures S49 and S50). Thus, either the added catalyst or Pd-H species formedupon termination of the polymerization can induce the isomerization, which is more important for the more accessible butenyl moiety in the polymer.[39]

There are two possible pathways for the initiation of this polymerization, shown in Scheme 3. In path a) the insertion of the norbornene monomer occurs into the Pd-C bond of the Pd-benzyl moiety. On the other hand, in path b) the polymerization starts by insertion of the endocyclic double bond into the Pd-H bond of a putative intermediate [PdHL$_n$]$^+$, generated by β-hydrogen elimination. We have found that path a in Scheme 3 is preferred. The analysis by ^{19}F NMR of the reaction mixture in a homopolymerization reaction of VNB with **4**-BF$_4$ shows that 90% of the benzylic group, -CHPhCH$_2$C$_6$F$_5$, is anchored to the polymer skeleton (insertion into the Pd-C$^\alpha$ bond) and only 10% of trans-PhCH=CH$_2$C$_6$F$_5$ (**6**) is generated (maximum insertion into the Pd-H bond (Figure S8, SI). The amount of **6** formed changes slightly with the initial [NB]:[**4**-BF$_4$] ratio used but, at high concentration of norbornene (or high mol ratio [NB]:[**4**-BF$_4$], closer to the conditions of the polymerization), the amount of Pd-H is very low so the initiation step through insertion of the monomer into the Pd-CHPhCH$_2$C$_6$F$_5$ bond is preferred (Figure S7, SI). The mechanism for the initiation step with catalyst **5**-BAr$^F_4$ was studied previously in the homopolymerization of VNB and it also conforms to pathway a, Scheme 3.[27] The propagation of the polymerization is faster for the monophoshino species generated from **5**-BAr$^F_4$, [Pd(alkyl)(PCy$_3$)Lm]BAr$^F_4$, than for the diarsine species derived from **4**-BF$_4$, [Pd(alkyl)(AsPh$_3$)$_2$L]BF$_4$, where L = VNB and alkyl = growing polymer. This leads to high molecular weight VA-PVNB in high yields when **5**-BAr$^F_4$ is used.
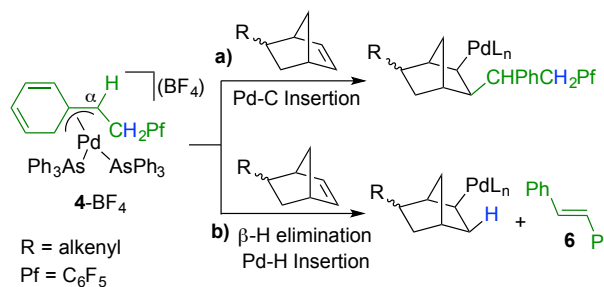
Scheme 3. Possible pathways for the initiation of the VA-polymerization of alkenyl-NBs in the presence of **4**-BF$_4$ (a, preferred).

Copolymerization reactions. Copolymerization reactions of substituted norbornenes and norbornene are more interesting in terms of functionalization as the amount of functional group in the backbone of the polymer can be roughly controlled by the initial molar ratio of the monomers in the feed. We tested the activity of complexes **4**-BF$_4$, **4**-BAr$^F_4$ and **5**-BAr$^F_4$ in the copolymerization of norbornene with substituted norbornenes with polar groups and pendant double bonds. The copolymers VA-PNB-*co*-NBCOOH and VA-PNB-*co*-NBCH$_2$OH synthesized from equimolar amounts of NB and the substituted monomer with catalyst **4**-BF$_4$ were isolated in low yields (34% and 14% respectively) and they are insoluble in common organic solvents. Even complex **5**-BAr$^F_4$, the most active catalyst for the VA-polymerization of VNB leads to VA-PNB-*co*-NBCH$_2$OH in low yields (37%). The IR spectra confirmed the presence of carboxylic groups anchored to the skeleton of VA-PNB-*co*-NBCOOH (1750 cm^{-1}, ν(C=O), Figure S67, SI) and hydroxyl groups for VA-PNB-*co*-NBCH$_2$OH (3450 cm^{-1} ν(OH) and 1046 cm^{-1} ν(C-O), Figures S68 and S69, SI).

On the other hand, good to excellent yields were achieved for the copolymerization of NB and VNB (VA-PNB-*co*-VNB, entries 1-4 Table 2) and

Table 2. Copolymerization of alkenyl-norbornenes with norbornene in the presence of catalyst **4**-BF$_4$, **4**-BAr$^F_4$ and **5**-BAr$^F_4$.[a]

Entry	Monomer	[Pd]	Yield (%)[b]	a/b[c]	mmol FNB/gr[d]	M_w[e]	Đ
1	NB + VNB	**4**-BF$_4$	63	1.8	3.5	5.6×10^4	2.4
2	NB + VNB	**4**-BAr$^F_4$	73	1.7	3.6	---	---
3[f]	NB + VNB	**4**-BAr$^F_4$	79	1.5	3.8	4.8×10^4	2.4
4	NB + VNB	**5**-BAr$^F_4$	99	1.0	4.7	4.1×10^5	3.3
5	NB + BNB	**4**-BF$_4$	57	2.1	2.9	2.99×10^4	1.8
6	NB + BNB	**5**-BAr$^F_4$	82	1.4	3.6	1.98×10^5	5.1

a) Reaction conditions: CH$_2$Cl$_2$, 25 ˚C, 24 h, under N$_2$, [VNB]$_0$ = [NB]$_0$ = 1.2 M. b) Yields are referred to the total monomer mass. c) a/b was determined by integration in the ^{1}H NMR (see section 1.6, SI). d) mmol of functionalized monomer/g pol. calculated from the ratio a/b (see section 1.6, SI). e) M_w (Da) and Đ (M_w/M_n) determined by GPC in CHCl$_3$ using polystyrene standards. f) [VNB]$_0$ = [NB]$_0$ = 2.1 M.

NB and BNB (VA-PNB-*co*-BNB, entries 5 and 6, Table 2).

The composition of the copolymers was determined by comparison of the integral values of the olefinic and aliphatic regions in the ^{1}H NMR of soluble polymers (see section 1.6.1, SI). For insoluble polymer the composition was determined by IR spectroscopy (see section 1.6.2, SI) The GPC chromatograms show unimodal distributions indicating the presence of one copolymer and not a mixture of two homopolymers (see SI). The structure of the alkenyl-copolymers is analogous to that of the homopolymers: a cis-2,3-exo insertion of the endocyclic double bond with the presence of the two endo and exo arrangements of the pendant alkenyl-substituent. The isomerization of the terminal double bond is not observed in the VA-PNB-*co*-VNBs copolymers. However, although less important than in the homopolymerization experiments, the internal double bond is still visible in the VA-PNB-*co*-BNB copolymers synthesized with **4**-BF$_4$ (13% of the total pendant unsaturation, Figure S61, SI). The isomerization process occurs in large extent when catalyst **5**-BAr$^F_4$ is employed (77% of internal double bond, Figure S65, SI).

The triphenylarsine complexes **4**-BAr$^F_4$ and **4**-BF$_4$ provide copolymers with similar molecular weights (around 50 kDa) and compositions (a/b = 1.5-1.8) as shown in entries 1-3, Table 2. In contrast, the more active monophosphine complex **5**-BAr$^F_4$ afforded a VA-PNB-*co*-VNB polymer in high yield and much higher M_w (entry 4, Table 2), in the same way observed for the homopolymerization reactions. Therefore, both types of complexes allow to obtain copolymers with different properties and the behavior of **4**-BF$_4$ and **5**-BAr$^F_4$ was further analyzed using the commercially available 5-vinyl-2-norbornene (VNB).

The incorporation of the VNB monomer in the copolymers can be roughly controlled by the monomer mol ratio in the feed, as shown in Table 3 for the copolymerization of NB and VNB with **4**-BF$_4$ (entries 4-6, Table 3). The NB content in the copolymer is always higher than that expected from the initial molar ratio in the monomer feed, showing the higher reactivity of NB.

Table 3. Copolymerization of NB and VNB with catalyst **4**-BF$_4$.[a]

Entry	NB:VNB: **4**-BF$_4$[b]	Yield (%)[c]	a/b[d,e]	mmol VNB/gr[e]	M_w[f]	Đ[f]
1	500:500:1	63	1.8	3.5	5.6×10^4	2.4
2[g]	500:500:1	63	2.1	3.1	4.1×10^4	2.7
3[h]	500:500:1	73	1.8	3.5	9.1×10^4	2.0
4	500:1000:1	54	1.4	4.0	3.06×10^4	3.4
5[i]	1000:500:1	80	3.9	2.1	---	---
6	1000:1000:1	64	2.1	3.1	6.4×10^4	2.1
7	2000:2000:1	43	2.3	3.0	---	---

a) Reaction conditions: CH$_2$Cl$_2$, [VNB]$_0$ = 1.2 M, 25 ˚C, 24 h, under N$_2$. b) Initial mol ratio in the feed. c) Yields are referred to the total monomer mass. d) a/b is the mol ratio NB/VNB in the copolymer. e) Composition determined by integration of ^{1}H NMR signals or by IR spectroscopy for the insoluble polymers (see SI). f) M_w (Da) and Đ (M_w/M_n) determined by GPC in CHCl$_3$ using polystyrene standards. g) [VNB]$_0$ = [NB]$_0$ = 2.1 M. h) 45 ˚C. i) Insoluble copolymers.

Even when an initial mol ratio of monomers is NB:VNB = 1:2, NB is present in higher amount than VNB (entry 4, Table 3). An initial monomer mol ratio NB:VNB ≥ 2:1 leads to insoluble copolymers (entry 5, Table 3). A low amount of functionalization (i.e. low VNB content) can be achieved and an insoluble VA-PNB-*co*-VNB with a composition a/b = 21.5 was prepared on a large scale (7.8 g) with 71.5% yield (section 1.5, SI). There is a significant decrease in the yield when using an amount of catalyst **4**-BF$_4$ below 0.05 mol% (cf. entries 6 and 7, Table 3). A raise in the reaction temperature increases slightly the yield of the polymerization and has an effect in the molecular weight of the polymer (entries 1 and 3, Table 3). The initial concentration of the monomer has little influence in the yield of the polymerization (entries 1 and 2, Table 3).

The more active **5**-BAr$^F_4$ allows to synthesize VA-PNB-*co*-VNBs using a much lower amount of catalyst (Table 4). A moderate yield (49%) was obtained using a 0.001 mol % of **5**-BAr$^F_4$ at 25 ˚C (entry 1, Table 4). However, changing the reaction temperature to 45 ˚C it is possible to synthesize copolymers with high molecular weights, in the range 1.2-1.9x10^6 Da, in good yields. Below 0.001% mol of catalyst at 45 ˚C, the yield in the polymerization decreases greatly (entry 6, Table 4). As mentioned above for **4**-BF$_4$, the change in the initial molar ratio of monomers leads to copolymers with different composition (entries 2, 4 and 5, Table 4).

Table 4. Copolymerization of NB and VNB with catalyst **5**-BAr$^F_4$.[a]

Entry	NB:VNB: **5**-BAr$^F_4$[b]	Yield (%)[c]	a/b[d]	mmol VNB/g[d]	M_w[e]	Đ[e]
1[f]	50000:50000:1	49	3.1	2.4	1.66×10^6	2.6
2	50000:50000:1	63	1.8	3.5	1.62×10^6	3.4
3[g]	50000:50000:1	74	1.9	3.3	1.70×10^6	3.8
4	50000:100000:1	45	1.05	4.6	1.74×10^6	3.7
5	100000:50000:1	82	2.4	2.9	1.23×10^6	3.7
6	100000:100000:1	41	2.6	2.7	1.89×10^6	3.2

a) Reaction conditions: CH$_2$Cl$_2$, [VNB]$_0$ = 2.1 M, 45 ˚C, 3 h, under N$_2$. b) Initial mol ratio in the feed. c) Yields are referred to the total monomer mass. d) Composition determined by integration of ^{1}H NMR (see SI). e) M_w (Da) and Đ (M_w/M_n) determined by GPC in CHCl$_3$ using polystyrene standards. f) 25 ˚C. g) [VNB]$_0$ = [NB]$_0$ = 1.2 M.

The reactivity ratios of NB and VNB in the copolymerization with **4**-BF$_4$ and **5**-BAr$^F_4$ were determined (see section 1.7, SI). Using the Fineman-Ross method the values r_{NB} = 2.49 and r_{VNB} = 0.22 for complex **4**-BF$_4$ and r_{NB} = 2.26 and r_{VNB} = 0.06 for **5**-BAr$^F_4$ were obtained.[40] In both cases the reactivity ratio for NB is always higher than that for VNB, so the copolymers are richer in norbornene as shown in Tables 2-4. The values deviate from those of ideal random copolymers and a composition drift in the VA-PNB-*co*-VNB backbone is expected.[41] We performed several copolymerization experiments using the same initial composition of the monomer feed (molar ratio 1:1) and quenching the process at different reaction times (section 1.8, SI). Figure 2a shows the

higher amount of NB in the VA-PNB-*co*-VNBs prepared with complex **4**-BF$_4$, at the initial stages of the polymerization and the gradual increase of the amount of VNB in the copolymer with the yield. This shows that there is a composition drift along the chain. A similar behavior is found for VA-PNB-*co*-VNBs synthesized with **5**-BArF$_4$ (Figure S6, a, SI). Neither the copolymerization of NB and VNB with **4**-BF$_4$ nor with **5**-BArF$_4$ are living polymerizations. For **4**-BF$_4$ a plot of the M$_n$ vs the yield shows a nonlinear increase of M$_n$ (Figure 2, b), whereas linearity is a necessary condition for a living polymerization. An almost linear increase is observed at low yields but, as the reaction progresses, the growth of the polymer slows down and termination processes start to be dominating. For **5**-BArF$_4$, a plot closer to linearity is observed showing that the polymer growth is more efficient in this case (Figure S6, b, SI).
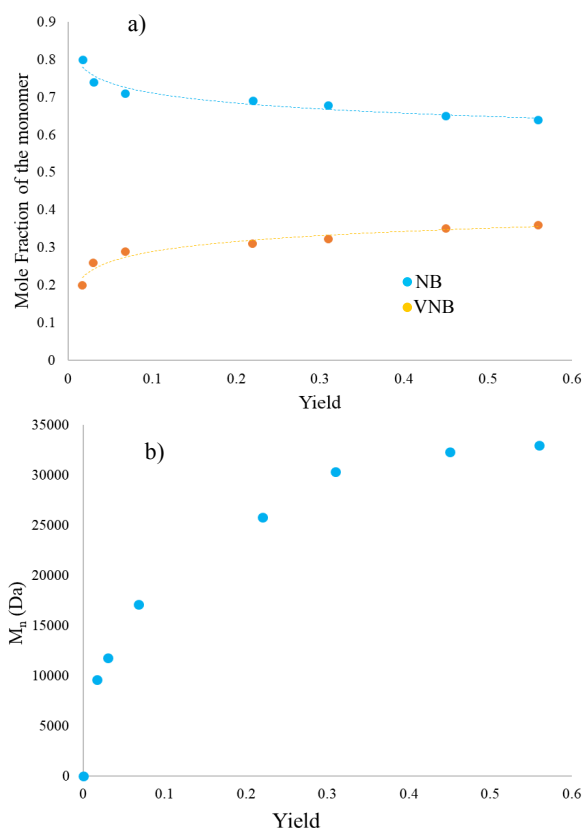

Fig. 2. a) Plot of the cumulative mol fraction in the VA-PNB-*co*-VNB polymer synthesized with **4**-BF$_4$ vs the yield (blue and orange dots represent the mol fraction of NB and VNB respectively). b) Plot of the M$_n$ vs the yield. Reaction conditions: mol ratio NB:VNB:**4**-BF$_4$ = 500:500:1, [NB]$_0$ = [VNB]$_0$ = 1.2 M, CH$_2$Cl$_2$, 25 ˚C, under N$_2$ (see SI, section 1.8.2 for details).

Functionalization post-polymerization. The copolymers VA-PNB-*co*-VNB and VA-PNB-*co*-BNB with pendant terminal double bonds shown in Tables 2-4 are good starting materials for the synthesis of new functionalized VA-polynorbornenes. We tested two useful reactions: the hydroboration and the hydrosilylation of olefins. The borylated or silylated polymers synthesized in this way are versatile materials that can be transformed into other functional polymers. All the new polymers are insoluble in common organic solvents, so they were characterized by IR spectroscopy and solid state CP-MAS

NMR. The dramatic changes in the solubility of these VA-PNBs upon functionalization is known and it was reported before for other functional groups, such as imidazolium fragments, by our research group.[16,17,42] In addition to the structural changes introduced by the new substituent, a modification of the conformational behavior of the rigid bicyclic units in the polymer backbone during the hydroboration/oxidation or hydrosilylation processes could also contribute to this change in solubility behavior.[43]

VA-PNB-*co*-VNB polymers are easily hydroborated in mild conditions in the presence of BHBr$_2$·SMe$_2$ (Scheme 4). The polymeric boronic acid VA-PNB-*co*-NB(CH$_2$)$_2$B(OH)$_2$ can be isolated by hydroboration of a VA-PNB-*co*-VNB followed by hydrolysis upon addition of water. The IR spectrum shows the complete disappearance of the characteristic absorptions for the pendant double bond (the most significant at 906 cm^{-1}, δ-C=C-H) and the formation of new bands assigned to the boronic acid (3382 cm^{-1}, ν(OH); 1632 cm^{-1}, δ(OH); 1348 cm^{-1}, ν(B-O); Figure S70, SI). On the other hand, VA-hydroxyl polynorbornenes can be synthesized by addition of a mixture of H$_2$O$_2$/NaOH$_{(aq)}$, after the hydroboration. The solid state ^{13}C NMR of the hydroxyl polymer VA-PNB-*co*-NB(CH$_2$)$_2$OH shows the disappearance of the olefinic resonances around 145 and 120 ppm (Figure S72, SI). Also, typical bands for hydroxyl groups (3354 cm^{-1} ν(OH) and 1047 cm^{-1} ν(C-O)) are visible in the IR spectrum. The high molecular weight copolymers of VA-PNB-*co*-VNB synthesized with catalyst **5**-BArF$_4$ can also be hydroborated/oxidized successfully and polymers with hydroxyl groups anchored to the VA-backbone were synthesized in high yields.

The hydroxyl group in VA-PNB-*co*-NBCH$_2$CH$_2$OH can be easily transformed into new functional groups as shown in Scheme 4. Swern oxidation using a mixture of oxalyl chloride, DMSO and NEt$_3$ leads to the formation of aldehyde groups. Significant absorption bands appear in the IR spectrum for the aldehyde anchored in the VA-backbone: 2706 cm^{-1}, ν(C-H) comb and 1722 cm^{-1}, ν(C=O) (Figure S78, SI). On the other hand, carboxylic groups can be synthesized with excellent conversion employing pyridinium dichromate (PDC) in DMF.
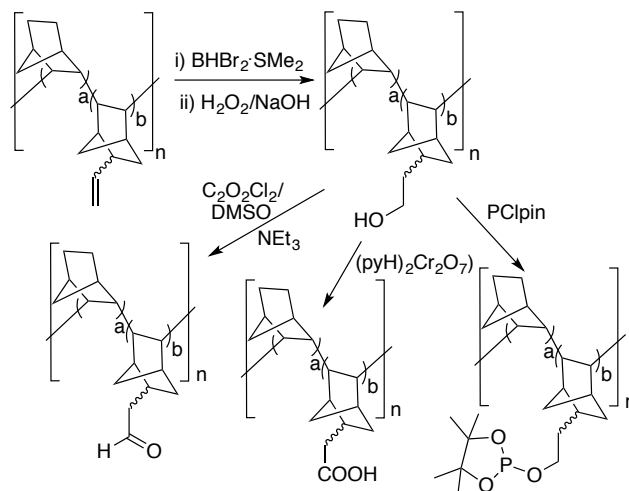
Scheme 4. Post-polymerization functionalization of VA-PNB-*co*-VNB by hydroboration/oxidation to generate the VA-hydroxyl-polymer and reactions thereof.

The presence of the absorption band corresponding to the carboxylic group at 1711 cm^{-1} (ν(C=O)) indicates the transformation of the OH group to COOH (Figure S79, SI). This methodology allows a more efficient synthesis of VA-polynorbornenes with polar carbonyl groups, in contrast to the bad results obtained in the direct copolymerization of NB and polar co-monomers. Other synthetic routes can be employed for the incorporation of functional groups and an example is the introduction of an organophosphite moiety by reaction of VA-PNB-*co*-NB(CH$_2$)$_2$OH with tetramethylethylene chlorophosphite (Scheme 4). The ^{31}P CP-MAS NMR clearly shows a signal at 148 ppm typical of phosphite compounds (Figure S77, SI) and the presence of the P-O band (963 cm^{-1}) in the IR spectrum is also significative.[44]

The hydrosilylation of olefins allows to functionalize double bonds with silane groups that are, in turn, versatile synthetic fragments.[45] Well-established metal-catalyzed methods are available, in particular using platinum catalysts. Because of the high efficiency (very low amounts of Pt(0) are necessary) and commercial availability, we selected the Karstedt catalyst for the hydrosilylation reaction on our copolymers. In this case, we tested the copolymer with the longer chain, VA-PNB-*co*-BNB, synthesized with catalyst **4**-BF$_4$ that induces little isomerization of the terminal double bond (see above). The hydrosilylation of the pendant double bond of a VA-PNB-*co*-BNB in the presence of an excess of SiHClMe$_2$ and Karstedt catalyst gives VA-PNB-*co*-NB(CH$_2$)$_4$SiClMe$_2$, which was isolated with very good yield (Scheme 5). The IR spectrum of this polymer shows the disappearance of the absorption bands for the double bond (ν(C=C) at 1640 cm^{-1} and δ(C=C-H) at 963 and 907 cm^{-1}) and the appearance of new absorption bands for the ν(Si-C) (846 cm^{-1}, 809 cm^{-1} and 789 cm^{-1}) and ν(Si-Cl) (475 cm^{-1}) confirming the presence of the silane groups (Figure S80, SI).[46] A small amount of hydrolysis of the Si-Cl bond is observed (Si-O band at 1047 cm^{-1} in the IR spectrum). The Si-Cl moiety anchored to the polymer can be transformed into new Si-R (allyl for example) or Si-H bonds (Scheme 5), the latter being amenable to further hydrosilylation reactions.
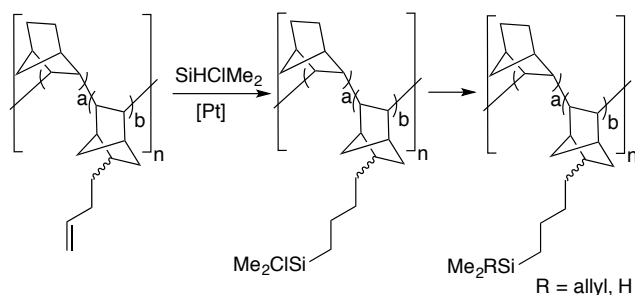
Scheme 5. Post-polymerization functionalization of VA-PNB-*co*-BNB by hydrosilylation.

Conclusions

Benzylic complexes of palladium of formula [Pd(η^3-CHPhCH$_2$C$_6$F$_5$)LL']BY$_4$ are excellent catalysts for the vinylic addition homopolymerization of alkenylnorbornenes and their copolymerization with norbornene. The nature of the auxiliary ligands is very important in determining the rate of polymer growth and therefore the size of the resulting VA-polynorbornene. Copolymers with molecular weights in the range 50-90 kDa can be obtained when L = L' = AsPh$_3$ (complexes **4**). However, the more active benzylic complex where L = PCy$_3$, L' = NCMe (**5**) generates very high molecular weight polynorbornenes (1.2-1.7 MDa) with just 10 mol ppm of catalyst. The copolymers obtained are always richer in NB and show a composition drift with a higher incorporation of the less reactive VNB as the polymerization progresses.

The isomerization of the terminal double bonds of the VA-polynorbornenes with pendant alkenyl groups to the internal alkene has been observed. This process is more important in the homopolymerization reactions and for the polymerization of butenylnorbornene (BNB). No isomerization occurs in the copolymerization of NB and VNB, and VA-PNB-*co*-VNBs bear terminal double bonds exclusively. VA-PNB-*co*-BNBs with just a small amount of internal double bonds can be prepared. Independent experiments show that this isomerization occurs on the polymers, catalyzed by palladium species.

The pendant double bonds in VA-PNB-*co*-VNB polymers can be hydroborated successfully under mild conditions and then transformed into polar functional groups (hydroxyl, carboxylate, etc.). Hydrosilylation of these copolymers can also be achieved. Therefore the synthesis of VA-PNB-*co*-alkenylNBs and their postpolymerization functionalization is the most efficient method to synthesize functionalized VA-PNBs with a range of compositions and sizes, which cannot be obtained by direct polymerization of the corresponding norbornenes with polar substituents.

Author contributions

I.P.O. conducted the investigation under A. C. A. supervision. All authors contributed to the conceptualization of the project, the writing of the manuscript as well as the review and editing process.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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