Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

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

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5. Selected NMR and IR spectra for copolymers VA-PNB-*co*-VNB and VA-PNB-*co*-BNB.

6. Selected NMR and IR spectra for the functionalization post-polymerization of VA-PNB-*co*-VNB and VA-PNB-*co*-BNB copolymers

7. References

1. Experimental details

1.1- General Considerations

^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and ^{19}F NMR spectra were recorded on Bruker AV-400 or Agilent MR-500 spectrometers at the LTI-UVa Research Facilities. Chemical shifts (in δ units, ppm) were referenced to $SiMe_4$ (^1H and ^{13}C) and $CFCl_3$ (^{19}F). The spectroscopic data were recorded at 298 K unless otherwise noted. Homonuclear (^1H-COSY) and heteronuclear (^1H-^{13}C HSQC) experiments were used to help with the signal assignments. Size exclusion chromatography (SEC, also gel permeation chromatography, GPC) was carried out using a Waters SEC system on a three-column bed (Styragel 7.8x300 mm columns: 50-100000, 5000-500000 and 2000-4000000 Da) and a Waters 410 differential refractometer. SEC samples were run in $CHCl_3$ at 313 K and calibrated to polystyrene standards.

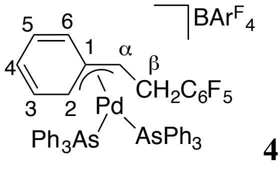
Solvents (CH_2Cl_2, hexane) were dried using a solvent purification system SPS PS-MD-5. $CDCl_3$ was dried using neutral activated aluminum oxide.

Norbornene, 5-vinyl-2-norbornene (mixture of isomers endo:exo = 80:20), 5-methanol-2-norbornene (mixture of isomers endo:exo = 80:20), 5-carboxylic acid-2-norbornene (mixture of isomers endo:exo = 80:20), 5-ethylidene-2-norbornene (mixture of isomers *E*:*Z* = 79:21), tricyclohexylphosphine and triphenylarsine are commercially available and were purchased from Merck-Aldrich, Alfa Aesar and Fluorochem. All commercial reagents and solvents were used as received unless otherwise indicated. The 5-(but-1-en-4-yl)-2-norbornene was synthesized by a Diels-Alder reaction between dicyclopentadiene and 1,6-hexadiene following a reported method and it is also a mixture of endo/exo isomers in a ratio 80:20.[1] A solution of norbornene in CH_2Cl_2 was used for all the polymerization experiments whose concentration was determined by ^1H NMR titration. The internal standard employed was $C_6H_3Br_3$. The platinum(0)-1,3-divinyl-1, 1, 3, 3-tetramethyldisiloxane complex (Karstedt catalyst) is commercial available and was purchased as a solution in xylene with an approximate amount of Pt of 2%. The tetramethylethylene chlorophosphite (PClpin) was synthesized using a reported method.[2] The $HBBr_2{\cdot}SMe$ is a commercial solution in CH_2Cl_2 with a molar concentration of 1 M. All polymerizations were carried out under N_2 by standard Schlenk techniques.

$[Pd_2(\mu\text{-}Br)_2(\eta^3\text{-}CHPhCH_2C_6F_5)_2]$,[3,4] $[Pd(\eta^3\text{-}CHPhCH_2C_6F_5)(PhSCH_2)_2](BF_4)$ (**2**),[5] $[Pd(\eta^3\text{-}CHPhCH_2C_6F_5)(PPh_3)_2](BF_4)$ (**3**),[5] $[Pd(\eta^3\text{-}CHPhCH_2C_6F_5)(AsPh_3)_2](BF_4)$ (**4**-BF_4),[5] $[Pd(\eta^3\text{-}CHPhCH_2C_6F_5)(NCMe)(PCy_3)](BAr^F_4)$ (**5**-BAr^F_4),[4] and $NaBAr^F_4$,[6] were prepared according to literature methods.

1.2- Synthesis of complex **4**-BAr^F_4

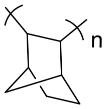
In a 100 mL Schlenk tube, $AsPh_3$ (0.107 g, 0.35 mmol) and $NaBAr^F_4$ (0.155 g, 0.175 mmol) were placed under N_2. The solids were dissolved in 5 mL of dry CH_2Cl_2 and the solution was cooled for 10 min in an acetone bath at 233 K. To this solution was added the dimeric complex $[Pd_2(\mu\text{-}Br)_2(\eta^3\text{-}CHPhCH_2C_6F_5)_2]$ (0.080 g, 0.0875 mmol) and the suspension was stirred for 30 min at 233 K. After this time, a suspension with a white solid in a yellow solution was formed. Activated carbon was added to the suspension and it was filtered via cannula. The yellow solution was evaporated to dryness generating a yellow solid. The solid was washed with dry hexane (2 x 10 mL) and it was dried under vacuum (0.25 g, 77.2% yield). ^1H NMR (500.13 MHz, δ, 233 K, CD_2Cl_2): 7.71 (s, 8H, H_{ortho} $BAr^F_4{}^-$), 7.52 (s, 4H, H_{para} $BAr^F_4{}^-$), 7.4-7.15 (m, 26H, H^5, H^4, $AsPh_3$), 7.01 (d, J = 7 Hz, 1H, H^2), 6.93 (d, J = 8 Hz, 1H, H^6), 6.80 (t, J = 7 Hz, 1H, H^3), 6.74 (m, 6H, $AsPh_3$), 4.25 (dd, J = 13 Hz, J = 4 Hz, 1H, H^α), 2.99 (t, J = 13 Hz, 1H, H^β), 2.5 (d, J = 13 Hz, 1H, $H^{\beta'}$). $^{13}C\{^1H\}$ NMR (125.758 MHz, δ, 233 K, CD_2Cl_2): 161.7 (m, $^1J_{C\text{-}^{11}B}$ = 54 Hz, C_{ipso} $BAr^F_4{}^-$), 144.2 (m, $^1J_{C\text{-}F}$ = 241.4 Hz, C_{ortho} C_6F_5), 139.7 (m, $^1J_{C\text{-}F}$ = 242.3 Hz, C_{para} C_6F_5), 137 (m, $^1J_{C\text{-}F}$ = 252.7 Hz, C_{meta} C_6F_5), 134.6 (C_{ortho}, $BAr^F_4{}^-$), 133.3 (C^5, C^3), 132.6-128.1 ($AsPh_3$; C^4), 128.6 (q, $^2J_{C\text{-}F}$ = 30.9 Hz, C_{meta} $BAr^F_4{}^-$), 124.4 (q, $^1J_{C\text{-}F}$ = 271.8 Hz, CF_3 BAr^F_4), 124.1 (C^6), 117.5 (C_{para}, $BAr^F_4{}^-$), 115.6 (C^1), 111.6 (t, $^2J_{C\text{-}F}$ = 21.5 Hz, C_{ipso} C_6F_5), 107 (C^2), 67.8 (C^α), 21.7 (C^β). ^{19}F NMR (376.498 MHz, δ, 233 K, CD_2Cl_2): -62.9 (s, CF_3 $BAr^F_4{}^-$), -143.15 (m, F_{ortho}), -155.9 (t, F_{para}), -162 (m, F_{meta}). Analysis calc. for $C_{82}H_{50}As_2BF_{29}Pd$ C, 53.14; H, 2.72; Found: C, 53.41; H, 2.75.



4-BAr^F_4

1.3- Homopolymerization experiments

General method for the polymerization of norbornene with isolated benzylic complexes (VA-PNB). In a Schlenk tube a solution of norbornene in CH_2Cl_2 (0.64 mL, 5 mmol; 7.84 M) was diluted with 3.5 mL of dry CH_2Cl_2 under N_2 ($[NB]_0$ = 1.2 M). Subsequently, the catalyst **4**-BF_4 (10.76 mg, 0.01 mmol) was added generating a yellow solution. After 15 min, a white precipitate appeared in the solution and the suspension was stirred for 24 h at 25 ºC. MeOH (15 mL) was added to the suspension and the mixture was stirred for 30 min at room temperature and filtered off. The white solid was washed with MeOH (2 x 20 mL) and air dried (0.45 g, 95.7% yield). IR (neat, cm^{-1}): 2943 (ν-CH asym.), 2866 (ν-CH sym.), 1449 (ν-VAPNBskeleton).



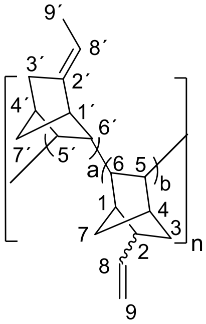
VA-PNB

The polymerizations of norbornene with catalysts **2** and **3** were performed following this general method (see main text).

Polymerization of norbornene with complex 1 generated in situ. In a Schlenk tube the dimeric complex $[Pd_2(\mu\text{-}Br)_2(\eta^3\text{-}CHPhCH_2C_6F_5)_2]$ (4.6 mg, 0.005 mmol) was placed under N_2. The complex was suspended in 3.5 mL of dry CH_2Cl_2 and it was cooled for 10 min at 233 K. $AsPh_3$ (6.1 mg, 0.02 mmol) was added and the yellow suspension turned instantly to an orange solution. Subsequently, a solution of norbornene in CH_2Cl_2 (0.64 mL, 5 mmol; 7.84 M) was added ($[NB]_0$ = 1.2 M). The solution was allowed to warm to room temperature and it was stirred for 24 h at 25 ºC. After this time, 20 mL of MeOH were added but neither polymer nor oligomers were isolated.

Polymerization of 5-vinyl-2-norbornene with catalyst 4-BF$_4$ (VA-PVNB). In a Schlenk tube, 5-vinyl-2-norbornene (0.71 mL, 5 mmol) was diluted in 3.4 mL of dry CH_2Cl_2 under N_2 ($[VNB]_0$ = 1.2 M). Subsequently, the catalyst **4**-BF_4 was added (10.76 mg, 0.01 mmol) and the yellow solution was stirred for 24 h at 25 ºC. MeOH (15 mL) was added to the solution inducing the precipitation of the polymer. The suspension was stirred for 30 min at room temperature and it was filtered off. The white solid was washed with MeOH (2 x 20 mL) and Et_2O (2 x 5 mL) and then air dried (0.07 g, 16.6%

yield). ^{1}H NMR (500.13 MHz, δ, $CDCl_3$): 6.1-5.6 (b, H^8), 5.5-5.15 (b, $H^{8'}$), 5.2-4.7 (b, H^9), 2.8-0.7 ($H^{9'}$, H^7, $H^{7'}$, H^6, $H^{6'}$, $H^{5'}$, H^5, H^4, $H^{4'}$, H^3, $H^{3'}$, H^2, H^1, $H^{1'}$). $^{13}C\{^1H\}$ (125.66 MHz, δ, $CDCl_3$): 150-145 ($C^{2'}$), 146-145 (*exo* C^8), 143-141 (*endo* C^8), 115-113 (*endo* C^9), 112-111 (*exo* C^9), 111-108 ($C^{8'}$), 58-30 (C^7, $C^{7'}$ C^6, $C^{6'}$, C^5, $C^{5'}$, C^4, $C^{4'}$, C^3, $C^{3'}$, C^2, C^1, $C^{1'}$), 14 ($C^{9'}$). ^{19}F NMR (470.592 MHz, δ, $CDCl_3$): -142 (b, F_{ortho} VA-PVNB-C_6F_5), -157.9 (b, F_{para} VA-PVNB-C_6F_5), -163 (b, F_{meta} VA-PVNB-C_6F_5). IR (neat, cm^{-1}): 2938 (ν-CH asym.), 2873 (ν-CH sym.), 1636 (ν-C=C-), 1449 (ν-VAPNB skeleton), 962, 906 (δ-C=C-H). $M_w = 7.2 \times 10^3$ Da, Đ (M_w/M_n) = 1.09. The molar percentage of isomerized double bond (17%) was calculated by ^{1}H NMR spectroscopy.

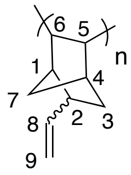


VA-PVNB

The same experimental procedure was employed for the polymerization with catalyst **4**-BAr^F$_4$ giving a similar VA-PVNB (0.055 g, 34% yield). $M_w = 3.46 \times 10^4$ Da, Đ (M_w /M_n) = 1.37. (entry 2, Table 1, main text). The molar percentage of isomerized double bond (10%) was calculated by ^{1}H NMR spectroscopy.

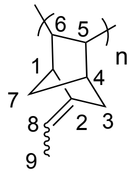
Polymerization of 5-vinyl-2-norbornene with catalyst 5-BAr^F$_4$ (VA-PVNB). Complex **5**-BAr^F$_4$ (5.5 mg, 3.52×10^{-3} mmol) was placed in a Schlenk tube under N_2. It was dissolved in 1.2 mL of dry CH_2Cl_2 and immediately the VNB was added (0.25 mL; 1.76 mmol) ($[VNB]_0$ = 1.2 M). The intense yellow solution was stirred for 24 h at 25 ºC acquiring a viscous aspect after 1 hour. Then, 10 mL of $CHCl_3$ were added to the viscous mixture and it was stirred for 10 min at room temperature. The polymer was precipitated adding 20 mL of MeOH. The solid was filtered off and washed with MeOH (2 x 15 mL) and Et_2O (2 x 5 mL). Finally, the white solid was air dried (0.19 g, 99% yield). ^{1}H NMR (500.13 MHz, δ, $CDCl_3$): 6.1-5.6 (b, H^8), 5.25-4.6 (b, H^9), 3-0.5 (b, H^7, H^6, H^5, H^4, H^3, H^2, H^1). $^{13}C\{^1H\}$ (125.66 MHz, δ, $CDCl_3$): 145-144 (*exo* C^8), 144-140 (*endo* C^8), 116-114 (*endo* C^9), 114-112.5 (*exo* C^9), 55-30 (C^7, C^6, C^5, C^4, C^3, C^2, C^1). ^{19}F

NMR (470.592 MHz, δ, $CDCl_3$): -141.9-143 (b, F_{ortho}, VA-PVNB-C_6F_5), -157.5-158.3 (b, F_{para}, VA-PVNB-C_6F_5), -162.9-163.9 (b, F_{meta}, VA-PVNB-C_6F_5). IR (neat, cm^{-1}): 2939 (ν-CH asym.), 2911 (ν-CH sym.), 1637 (ν-C=C-), 1453 (ν-VAPNBskeleton), 962, 905 (δ-C=C-H). $M_w = 4.9 \times 10^5$ Da; Đ (M_w/M_n) = 4.2. (Cf. entry 3, Table 2 main text). No double bond isomerization was detected by ^1H NMR.



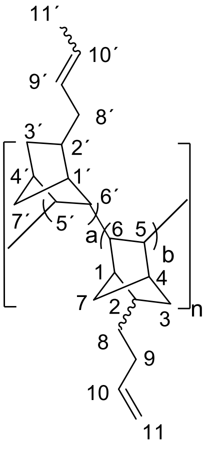
VA-PVNB

Polymerization of 5-ethylidene-2-norbornene with catalyst 4-BF_4 (VA-PENB). In a Schlenk tube, 5-ethylidene-2-norbornene (0.67 mL, 5 mmol) was dissolved in 3.5 mL of dry CH_2Cl_2 under N_2 ($[ENB]_0$ = 1.2 M) Subsequently, the catalyst **4**-BF_4 was added (10.76 mg, 0.01 mmol) and the yellow solution was stirred for 24 h at 25 ºC. MeOH (15 mL) was added to the solution inducing the precipitation of the polymer. The suspension was stirred for 30 min at room temperature and it was filtered off. The white solid was washed with MeOH (2 x 20 mL) and Et_2O (2 x 5 mL) and then air dried (0.19 g, 32% yield). ^1H NMR (500.13 MHz, δ, $CDCl_3$): 5.5-4.8 (b, H^8), 3.5-0.8 (b, H^9 H^7, H^6, H^5, H^4, H^3, H^1). $^{13}C\{^1H\}$ NMR (125.66 MHz, δ, $CDCl_3$): 150-141 (C^2), 117-107 (C^8), 59-32 (C^7, C^6, C^5, C^4, C^3, C^1), 14 (C^9). ^{19}F NMR (470.592 MHz, δ, $CDCl_3$): -140-144 (b, F_{ortho} VA-PVNB-C_6F_5), -157.9 (b, F_{para} VA-PVNB-C_6F_5), -163 (b, F_{meta} VA-PVNB-C_6F_5). IR (neat, cm^{-1}): 2938 (ν-CH asym.), 2913 (ν-CH sym.), 1690 (ν-C=C-), 1434 (ν-VAPNBskeleton), 808 (δ-C=C-H). $M_w = 1.64 \times 10^4$ Da. Đ (M_w/M_n) = 1.57.



VA-PENB

Polymerization of 5-(but-1-en-4-yl)-2-norbornene with catalyst 4-BF_4 (VA-PBNB). In a Schlenk tube, 5-(but-1-en-4-yl)-2-norbornene (0.37 g, 2.5 mmol) was diluted in 1.6 mL of dry CH_2Cl_2 under N_2 ($[BNB]_0$ = 1.2 M). The catalyst **4**-BF_4 was added (5.38 mg, 0.005 mmol) and the yellow mixture was stirred for 24 h at 25 ºC. MeOH (15 mL) was added to the solution inducing the precipitation of the polymer. The suspension was stirred for 30 min at room temperature and it was filtered off. The white solid was washed with MeOH (2 x 20 mL) and Et_2O (2 x 5 mL) and then air dried (0.086 g, 23.2% yield). ^{1}H NMR (500.13 MHz, δ, $CDCl_3$): 5.9-5.7 (b, H^{10}), 5.6-5.3 (b, $H^{10'}$, $H^{9'}$), 5.1-4.9 (b, H^{11}), 3-0.5 (b, $H^{11'}$, H^{9}, H^{8}, $H^{8'}$, H^{7}, $H^{7'}$, H^{6}, $H^{6'}$, H^{5}, $H^{5'}$, H^{4}, $H^{4'}$, H^{3}, $H^{3'}$, H^{2}, $H^{2'}$, H^{1}, $H^{1'}$). $^{13}C\{^{1}H\}$ (125.66 MHz, δ, $CDCl_3$): 140-138.5 (C^{10}), 133-124 ($C^{10'}$, $C^{9'}$), 115-113 (C^{11}), 60-30 (C^{9}, C^{8}, $C^{8'}$, C^{7}, $C^{7'}$, C^{6}, $C^{6'}$, C^{5}, $C^{5'}$, C^{4}, $C^{4'}$, C^{3}, $C^{3'}$, C^{2}, $C^{2'}$, C^{1}, $C^{1'}$), 17 (*trans* $C^{11'}$), 13.1 (*cis* $C^{11'}$). ^{19}F NMR (470.592 MHz, δ, $CDCl_3$): -142-144.5 (b, F_{ortho} VA-PVNB-C_6F_5), -157 (b, F_{para} VA-PVNB-C_6F_5), -163 (b, F_{meta} VA-PVNB-C_6F_5). IR (neat, cm^{-1}): 2929 (ν-CH asym.), 2873 (ν-CH sym.), 1640 (ν-C=C-), 1449 (ν-VAPNBskeleton), 964, 908 (δ-C=C-H). $M_w = 1.73 \times 10^4$ Da, Đ (M_w/M_n) = 1.53. The molar percentage of isomerized double bond (32%) was calculated by ^{1}H NMR spectroscopy.



VA-PBNB

The same experimental procedure was employed for catalyst **4**-BAr^F_4 giving a similar VA-PBNB (0.186 g, 87% yield). $M_w = 3.05 \times 10^4$ Da, Đ (M_w/M_n) = 7 (entry 5, Table 1, main text). The molar percentage of isomerized double bond (59%) was calculated by ^{1}H NMR spectroscopy.

Polymerization of 5-(but-1-en-4-yl)-2-norbornene with catalyst 5-BAr^F_4 (VA-PBNB). In a Schlenk tube, catalyst **5**-BAr^F_4 (3.7 mg, 0.00236 mmol) was placed under N_2. It was dissolved in 0.75 mL of dry CH_2Cl_2 and immediately, 5-(but-1-en-4-yl)-2-norbornene (0.17 g, 1.15 mmol) was added ($[BNB]_0$ = 1.2 M). The yellow mixture was stirred for 24 h at 25 ºC acquiring a viscous aspect after 1 hour. Then, 10 mL of $CHCl_3$ were added to the viscous mixture and it was stirred for 10 min at room temperature. The polymer was precipitated adding 20 mL of MeOH. The solid was filtered off and washed with MeOH (2 x 15 mL) and Et_2O (2 x 10 mL). Finally, the white solid was air dried (0.14 g, 83% yield). $M_w = 4.5 \times 10^4$ Da. Đ (M_w/M_n) = 3.1 (entry 6, Table 1, main text). Most of the terminal exocyclic double bonds are isomerized to the internal olefin (molar percentage analyzed by ^{1}H NMR spectroscopy: 93%), showing a structure related to the polymer described in section 1.4.

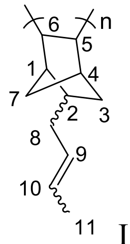
Polymerization of 5-carboxylic acid-2-norbornene with catalyst 4-BF_4. In a Schlenk tube, 5-carboxylic acid-2-norbornene (0.61 mL, 5 mmol) was dissolved in 3.6 mL of dry CH_2Cl_2 under N_2 ($[NBCOOH]_0$ = 1.2 M). Subsequently, the catalyst **4**-BF_4 was added (10.76 mg, 0.01 mmol) and the yellow solution was stirred for 24 h at 25 ºC. MeOH (20 mL) was added to the solution to induce the precipitation of the polymer but no polymer was isolated.

A similar procedure was employed for the polymerization of 5-methanol-2-norbornene with **4**-BF_4 and 5-carboxylic acid-2-norbornene and 5-methanol-2-norbornene with catalyst **5**-BAr^F_4. No polymer was isolated in any of these polymerizations.

1.4- Isomerization post-polymerization of a VA-PBNB with complex **4**-BF_4

In an NMR tube, a VA-PBNB polymer synthesized with catalyst **4-**BF_4 (28 mg, 0.157 mmol; 5.6 mmol -C=C-/gr; 37% of double bond isomerized) was dissolved in 0.6 mL of dry $CDCl_3$. To the solution was added the catalyst **4-**BF_4 (21 mg, 0.0196 mmol) and the reaction was followed by ^{1}H NMR spectroscopy. After 30 min of reaction, the orange solution was transfer to a 50 mL bottom flask and 5 mL of MeOH were added. The white solid was filtered off, washed with MeOH (2 x 5 mL) and air dried for 6 h (0.025 g, 90% yield). ^{1}H NMR (500.13 MHz, δ, $CDCl_3$): 5.6-5.1 (b, H^{10}, H^9), 3.3-0.5 (b, H^{11}, H^8, H^7, H^6, H^5, H^4, H^3, H^2, H^1). $^{13}C\{^1H\}$ (125.66 MHz, δ, $CDCl_3$): 135-123 (C^{10}, C^9), 56-27 (C^8, C^7, C^6, C^5, C^4, C^3, C^2, C^1), 17.1 (*trans*-C^{11}), 13.1 (*cis*-C^{11}). IR (neat, cm^{-1}):

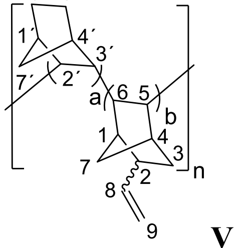
2929 (ν-CH asym.), 2884 (ν-CH sym.), 1640 (ν-C=C-), 1449 (ν-VAPNBskeleton), 963, 907 (δ-C=C-H).



Isomerized **VA-PBNB**

1.5.- General Procedure for the copolymerization experiments

Copolymerization of VNB and NB with catalyst 4-BF_4 (VA-PNB-*co*-VNB, mol ratio NB:VNB:Pd = 500:500:1; a/b = 1.8, entry 1, Table 2, main text). A solution of norbornene in CH_2Cl_2 (0.63 mL, 5 mmol; 7.84 M), 5-vinyl-2-norbornene (0.71 mL, 5 mmol) and 2.8 mL of dry CH_2Cl_2 were placed in a Schlenk tube under N_2 ($[VNB]_0$ = 1.2 M, $[NB]_0$ = 1.2 M). Finally, the catalyst **4**-BF_4 (10.73 mg, 0.01 mmol) was added. After 1 h, a white precipitate appeared and the suspension was stirred for 24 h at 25 ºC. MeOH (15 mL) was added to the suspension, the mixture was stirred for 30 min at room temperature and it was filtered off. The white solid was washed with MeOH (2 x 20 mL) and Et_2O (2 x 5 mL) and then air dried (0.68 g, 63.5% yield). ^1H NMR (500.13 MHz, δ, $CDCl_3$): 6.07-5.63 (b, H^8), 5.16-4.77 (b, H^9), 2.80-0.76 (b, H^7, $H^{7'}$, H^6, $H^{6'}$, H^5, $H^{5'}$, H^4, $H^{4'}$, H^3, $H^{3'}$, H^2, $H^{2'}$, H^1, $H^{1'}$). $^{13}C\{^1H\}$ (125.66 MHz, δ, $CDCl_3$): 146-145 (*exo* C^8), 143-141 (*endo* C^8), 115-113 (*endo* C^9), 112.5-111 (*exo* C^9), 60-21 (C^7, $C^{7'}$, C^6, $C^{6'}$, C^5, $C^{5'}$, C^4, $C^{4'}$, C^3, $C^{3'}$, C^2, $C^{2'}$, C^1, $C^{1'}$). ^{19}F NMR (470.592 MHz, δ, $CDCl_3$): -142 to -144 (b, F_{ortho} VA-pol-C_6F_5), -157.7 (b, F_{para} VA-pol-C_6F_5), -163.5 (b, F_{meta} VA-pol-C_6F_5). IR (neat, cm^{-1}): 2943 (ν-CH asym.), 2867 (ν-CH sym.), 1635 (ν-C=C-), 1451 (ν-VA-PNB skeleton), 963, 906 (δ-C=C-H). $M_w = 5.6 \times 10^4$ Da. Đ (M_w/M_n) = 2.4.



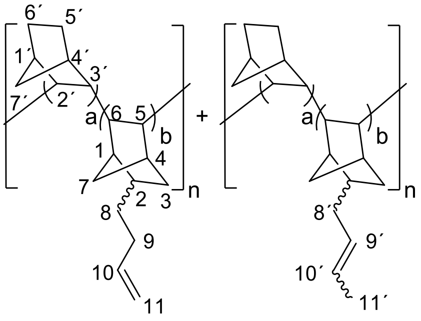
VA-PNB-*co*-VNB

A similar procedure was employed for the copolymerizations of NB and VNB collected in Tables 2-4 (main text), using the appropriate catalyst (**4**-BF_4, **4**-BAr^F_4 or **5**-BAr^F_4), NB:VNB:Pd initial molar ratios and reaction conditions (T, time).

High scale copolymerization of VNB and NB with catalyst 4-BF_4 (VA-PNB-*co*-VNB, mol ratio NB:VNB:Pd = 1000:12.5:1; a/b = 21.5/1). In a Schlenk tube were added a solution of NB in CH_2Cl_2 (19.5 mL, 100 mmol; 5.11 M) and the VNB (1.8 mL, 12.5 mmol). After, 61.8 mL of dry CH_2Cl_2 ($[VNB]_o$ = 0.15 M, $[NB]_o$ = 1.2 M) were added followed by the catalyst **4**-BF_4 (0.107 g, 0.1 mmol). After 20 min, a white precipitate appeared in the solution and the suspension was stirred 24 h at 25 ºC. MeOH (40 mL) were added to the suspension, the mixture was stirred for 1 h at room temperature and filtered off. The white solid was washed with MeOH (2 x 60 mL) and air dried (7.8 g, 71.5% yield).

Copolymerization of VNB and NB with catalyst 5-BAr^F_4 (VA-PNB-*co*-VNB, mol ratio NB:VNB:Pd = 50000:50000:1; a/b = 1.9/1, entry 2, Table 4, main text). In a Schlenk tube under N_2 was placed the catalyst **5**-BAr^F_4 (0.5 mg, $3.2x10^{-4}$ mmol). It was dissolved in 1 mL of dry CH_2Cl_2 and immediately a solution of norbornene in CH_2Cl_2 (4.1 mL, 16 mmol; 3.85 M) and 5-vinyl-2-norbornene (2.3 mL, 16 mmol) were added, $[VNB]_o$ = 2.1 M, $[NB]_o$ = 2.1 M. The intense yellow solution was stirred at 45 ºC for 3 hours. After 1 hour, the solution acquires a viscous aspect. Then, 30 mL of $CHCl_3$ were added to the viscous mixture and it was stirred for 30 min at room temperature. The polymer was precipitated adding 20 mL of MeOH. The solid was filtered off and washed with MeOH (2 x 20 mL) and Et_2O (2 x 10 mL). Finally, the white solid was air dried (3.0 g, 90% yield). $M_w = 1.62 \times 10^6$ Da. Đ (M_w/M_n) = 3.4.

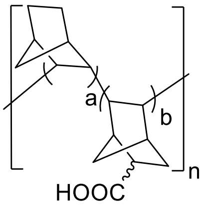
Copolymerization of BNB and NB with catalyst 4-BF_4 (VA-PNB-*co*-BNB, a/b = 2.1/1). A solution of norbornene in CH_2Cl_2 (0.63 mL, 5 mmol; 7.84 M), 5-(but-1-en-4-yl)-2-norbornene (0.74 g, 5 mmol) and 2.8 mL of dry CH_2Cl_2 were added in a Schlenk tube under N_2 ($[BNB]_o$ = 1.2 M, $[NB]_o$ = 1.2 M). Finally, the catalyst **4**-BF_4 (10.76 mg, 0.01 mmol) was added. After 1 h, a white precipitate appeared in the solution and the suspension was stirred for 24 h at 25 ºC. MeOH (15 mL) were added to the suspension, the mixture was stirred for 30 min at room temperature and it was filtered off. The white solid was washed with MeOH (2 x 20 mL) and Et_2O (2 x 5 mL) and then air dried (0.69 g, 57% yield). ^1H NMR (500.13 MHz, δ, $CDCl_3$): 5.9-5.7 (b, H^{10}), 5.6-5.3 (b, $H^{10'}$, $H^{9'}$) 5.1-4.9 (b, H^{11}), 3-0.5 (b, $H^{11'}$, H^9, H^8, $H^{8'}$, H^7, $H^{7'}$, H^6, $H^{6'}$, H^5, $H^{5'}$, H^4, $H^{4'}$, H^3, $H^{3'}$, H^2, $H^{2'}$, H^1, $H^{1'}$). $^{13}C\{^1H\}$ NMR (125.66 MHz, δ, $CDCl_3$): 140-138.5 (C^{10}), 133-124 ($C^{10'}$, $C^{9'}$), 115-113 (C^{11}), 60-30 (C^9, C^8, $C^{8'}$, C^7, $C^{7'}$, C^6, $C^{6'}$, C^5, $C^{5'}$, C^4, $C^{4'}$, C^3, $C^{3'}$, C^2, $C^{2'}$, C^1, $C^{1'}$), 17.0 (*trans* $C^{11'}$), 13.1 (*cis* $C^{11'}$). ^{19}F NMR (470.592 MHz, δ, $CDCl_3$): -142-143 (b, F_{ortho}), -157.9 (b, F_{para}), -163.5 (b, F_{meta}). IR (neat, cm^{-1}): 2925 (ν-CH asym.), 2871 (ν-CH sym.), 1639 (ν-C=C-), 1449 (ν-VAPNBskeleton), 963, 907 (δ-C=C-H). M_w = 2.99 x 10^4 Da. Đ (M_w/M_n) = 1.85.



VA-PNB-*co*-BNB

The copolymerization of NB and BNB with catalyst **5**-$BAr^F{}_4$ was carried out in the same way.

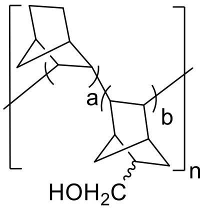
Copolymerization of NBCOOH and NB with catalyst 4-BF_4 (VA-NB-*co*-NBCOOH). A solution of norbornene in CH_2Cl_2 (0.63 mL, 5 mmol; 7.84 M), 5-norbornene-2-carboxylic acid (0.71 mL, 5 mmol) and 2.8 mL of dry CH_2Cl_2 were placed in a Schlenk tube under N_2 ($[NBCOOH]_0$ = 1.2 M, $[NB]_0$ = 1.2 M). Finally, the catalyst **4**-BF_4 (10.76 mg, 0.01 mmol) was added. After 1 h, a white precipitate appeared in the solution and the suspension was stirred for 24 h at 25 ºC. MeOH (15 mL) was added to the suspension and the mixture was stirred for 30 min at room temperature and filtered off. The white solid was washed with MeOH (2 x 20 mL) and air dried (0.61 g, 34.2% yield). IR (neat, cm^{-1}): 3500 (ν-OH), 2942 (ν-CH asym.), 2866 (ν-CH sym.), 1452 (ν-VAPNBskeleton), 1750 (ν-C=O), 1701 (ν-C=O), 1028 (ν-C-O).



VA-PNB-*co*-NBCOOH

Copolymerization of $NBCH_2OH$ and NB with catalyst 4-BF_4 (VA-PNB-*co*-$NBCH_2CH_2OH$). A solution of norbornene in CH_2Cl_2 (0.63 mL, 5 mmol; 7.84 M), 5-norbornene-2-methanol (0.6 mL, 5 mmol) and 2.9 mL of dry CH_2Cl_2 were placed in a Schlenk tube under N_2 ($[NBCH_2OH]_0 = 1.2$ M, $[NB]_0 = 1.2$ M). Finally, the catalyst **4-**BF_4 (10.76 mg, 0.01 mmol) was added. After 1 h, a white precipitate appeared in the solution and the suspension was stirred for 24 h at 25 ºC. MeOH (15 mL) was added to the suspension, the mixture was stirred for 30 min at room temperature and filtered off. The white solid was washed with MeOH (2 x 20 mL) and air dried first and then in a vacuum stove (60 mbar) at 40 ºC for 12 h (0.16 g, 14.4% yield). IR (neat, cm^{-1}): 3359 (ν-OH), 2940 (ν-CH asym.), 2864 (ν-CH sym.), 1449 (ν-VAPNBskeleton), 1028 (ν-C-O).

The copolymerization of $NBCH_2OH$ and NB with catalyst **5-BAr$^F_4$** was carried out in the same way (yield 37 %).



VA-PNB-*co*-$NBCH_2OH$

1.6- Determination of the composition of the soluble copolymers by ^1H NMR spectroscopy and of the insoluble copolymers by IR spectroscopy

1.6.1. Soluble copolymers by ^1H NMR spectroscopy

The determination of the composition of copolymers VA-PNB-*co*-VNB was made by ^1H NMR following this general equation: $a/b = \{(IntA-3IntB)/10\}/(IntB/3)$ where IntA = total integral value of the aliphatic region, IntB = total integral value of the alkene region and the numeric coefficients consider the number of aliphatic protons in norbornene and 5-vinyl-2-norbornene. As an example, for polymer VA-PNB-*co*-VNB shown in Figure S1 the result is: a/b = {(30.59 - 3 x 3.08)/10}/{3.08/3} = 2.1.

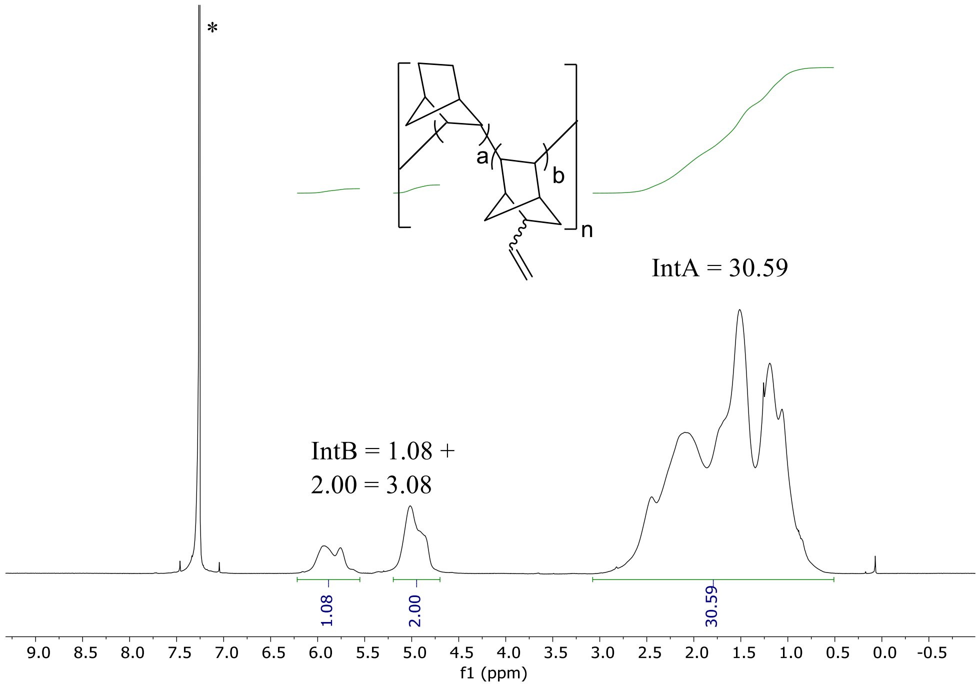


Figure S1. ^{1}H NMR (500.13 MHz, dry $CDCl_3$) for VA-PNB-*co*-VNB with a mol ratio a/b = 2.1 (entry 6, Table 3 main text). * Residual solvent ($CHCl_3$).

The equation for the calculation of the composition of VA-PNB-*co*-BNB takes into account the presence of two different double bonds due to the isomerization during the polymerization. The final equation is the following: a/b = {(IntA-(13IntB/3)-(14IntC/2))/10}/{(IntB/3)+IntC/2} where IntA = total integral value of the aliphatic region, IntB = total integral value of the alkene region for the terminal double bond and IntC = total integral value of the alkene region for the internal pendant double bond and the numeric coefficients take into account the number of aliphatic protons in norbornene, 5-(but-1-en-4-yl)-2-norbornene (BNB) and 5-(but-2-en-4-yl)-2-norbornene. For the copolymer shown in Figure S2 the result is: a/b = {(37.95-(13x2.91/3)-(14x0.3/2)/10}/{(2.91/3)+0.3/2} = 2.1

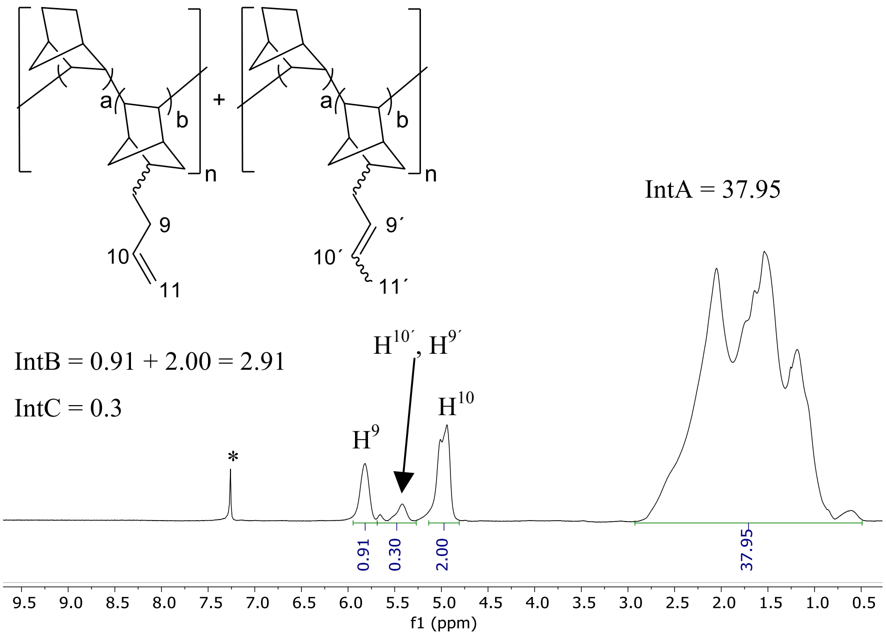


Figure S2. ^{1}H NMR (500.13 MHz, dry $CDCl_3$) for VA-PNB-*co*-BNB with a mol ratio a/b = 2.1 (entry 5, Table 2 main text). * Residual solvent ($CHCl_3$).

The composition of the copolymers in mmol functionalized monomer (FNB)/g polymer can be calculated from the ratio a/b: mmol FNB/g = $[1/[((a/b) \times M_{wNB}) + M_{wFNB}] \times 1000$ where M_{wNB} is the molecular weight of norbornene (94.16) and M_{wFNB} is the molecular weight of the VNB (120.19) or BNB (148.25).

1.6.2. Insoluble copolymers by FT-IR spectroscopy

The composition of the insoluble copolymers can be determined using IR spectroscopy. A calibration curve was made using some soluble VA-PNB-*co*-VNB, whose composition is known by ^{1}H NMR spectroscopy, and correlating that composition with the area of a selected IR band of the copolymers. We chose the absorption at 1634 cm^{-1} (stretching of the terminal ν-C=CH_2 double bond) because is it in a very clean part of the spectrum. The standard samples are collected in Table S1 and include the homopolymer VA-PVNB (maximum composition, entry 1, Table S1), some soluble copolymers VA-PNB-*co*-VNB where the composition is known by ^{1}H NMR spectroscopy (entries 2 and 3, Table S1) and some standards with low composition generated by mixing known amounts of VA-PNB and VA-PNB-*co*-VNB (entries 4, 5 and 6, Table S1). The plot of the absorption area versus the composition gives us the calibration line that is represented in Figure S3 and this was used to determine the composition of any insoluble copolymer by interpolation.

Table S1. Area of the IR absorption at 1634 cm^{-1} for different standard samples.

Entry	Area[a]	mmol VNB/g polymer
1	137.4	8.32[b]
2	75.2	4.04[b]
3	40.94	1.97[b]
4	31.97	1.42[c]
5	23.19	0.75[c]
6	16.57	0.52[c]

a) Determined by FTIR spectroscopy. b) Composition of the VA-PVNB and VA-PNB-*co*-VNB determined by ^{1}H NMR spectroscopy. c) Composition of mixtures of a known amount of VA-PNB and VA-PNB-*co*-VNB.

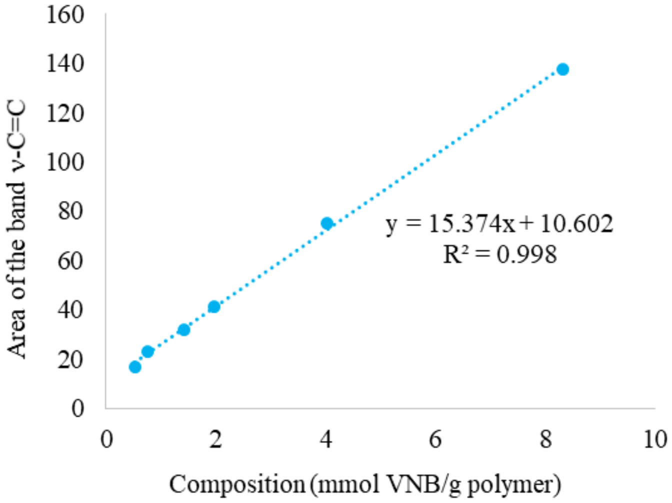


Figure S3. Plot of the area of the ν-C=C- absorption vs the composition of the copolymer (mmol VNB/g polymer).

1.7- Determination of the reactivity ratios of NB and VNB with catalysts **4**-BF_4 and **5**-BAr^F_4

The reactivity ratios of NB and VNB with catalysts **4**-BF_4 and **5**-BAr^F_4 were determined following the Fineman-Ross and Kelen-Tudos methods based in the copolymerization equation developed by Mayo-Lewis.[7,8] All the polymerization experiments shown in Tables S2 and S3 were performed at low conversion (<11 %) with different initial monomer ratios in the feed (f). The composition of the formed copolymer (mol ratio NB/VNB, F) was calculated by ^{1}H NMR spectroscopy in dry $CDCl_3$. The parameters for the Fineman-Ross and Kelen-Tudos equations for the reactivity ratios of NB and VNB are the next:

Based in the Fineman-Ross method:

$$G = r_{NB}H - r_{VNB}$$

$$\text{where } G = f(F-1)/F \text{ and } H = f^2/F$$

A plot of G versus H gives a straight line where the slope is r_{NB} and the intercept $-r_{VNB}$.

Based in the Kelen-Tudos method:

$$\eta = (r_{NB} + r_{VNB}/\alpha)\varepsilon - r_{VNB}/\alpha$$

$$\text{where } \eta = G/(\alpha+H),\ \varepsilon = H/(\alpha+H) \text{ and } \alpha = (H_{max} \text{ x } H_{min})^{1/2}$$

A plot of η versus ε gives a straight line where the intercepts when $\varepsilon = 0$ and $\varepsilon = 1$ gives $-r_{VNB}/\alpha$ and r_{NB}, respectively.

Table S2. Data for the copolymerization of NB and VNB at different initial mol ratios of monomers in the feed and the values for the determination of the reactivity ratios r_{NB} and r_{VNB} with catalyst **5**-BAr^F_4.[a]

Entry	NB/VNB (f)[b]	NB/VNB (F)[c]	G	H	η	ε
1	2	5.233	1.617	0.764	1.829	0.864
2	1.5	4.374	1.157	0.514	1.824	0.811
3	1.18	3.572	0.849	0.389	1.667	0.764
4	0.25	1.166	0.0355	0.0536	0.205	0.309
5	0.125	0.832	-0.0252	0.0187	-0.182	0.135

a) All the reactions were carried out in a Schlenk tube under N_2, CH_2Cl_2, 25 ºC, $[VNB]_0$ = 1.2 M. b) Initial molar ratio in the feed. c) Molar composition ratio in the formed copolymer determined by ^{1}H NMR in $CDCl_3$.

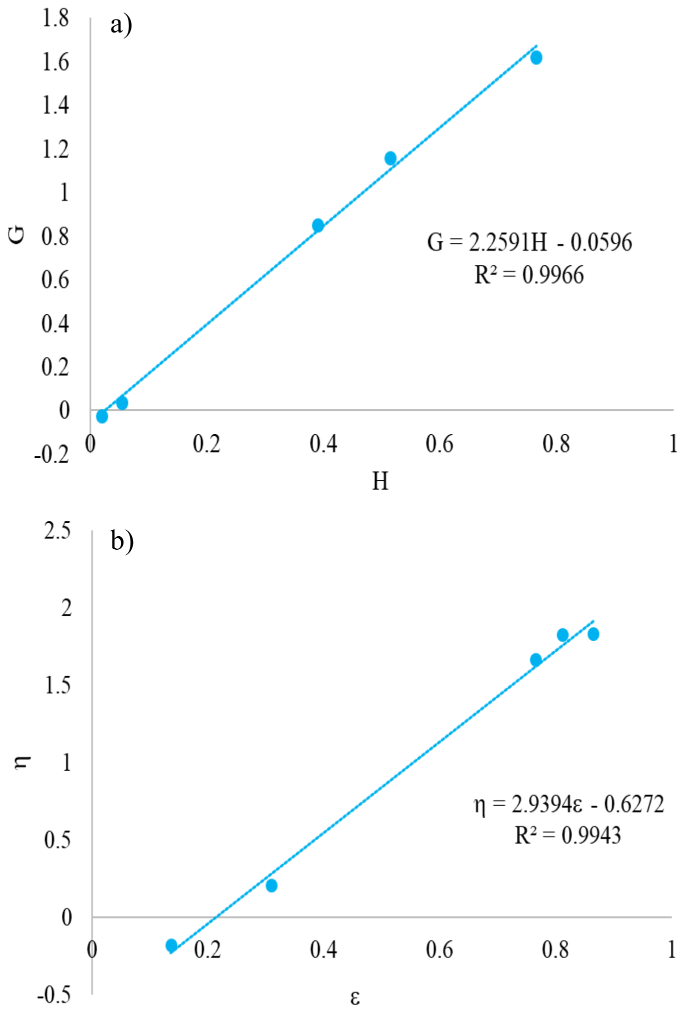


Figure S4. Plots to determine r_{NB} and r_{VNB} for the copolymerization of NB and VNB with catalyst **5-**$BAr^F{}_4$: a) Plot of G vs H, Fineman-Ross method. b) Plot of η vs ε, Kelen-Tudos method.

Table S3. Data for the copolymerization of NB and VNB at different initial mol ratio of monomers in the feed and the values for the determination of the reactivity ratios r_{NB} and r_{VNB} with catalyst **4**-BF_4.[a]

Entry	NB:VNB (f)[b]	NB:VNB (F)[c]	G	H	η	ε
1	0.5	1.8	0.222	0.138	0.418	0.261
2	1	2.7	0.629	0.370	0.826	0.486
3	2	4.9	1.591	0.816	1.317	0.675
4	2.5	6.8	2.132	0.919	1.626	0.701
5	3	8.155	2.632	1.103	1.760	0.738

a) All the reactions were carried out in a Schlenk tube under N_2, CH_2Cl_2, 25 °C, $[VNB]_0$ = 1.2 M. b) Initial molar ratio in the feed. c) Molar composition ratio in the formed copolymer determined by ^1H NMR in $CDCl_3$.

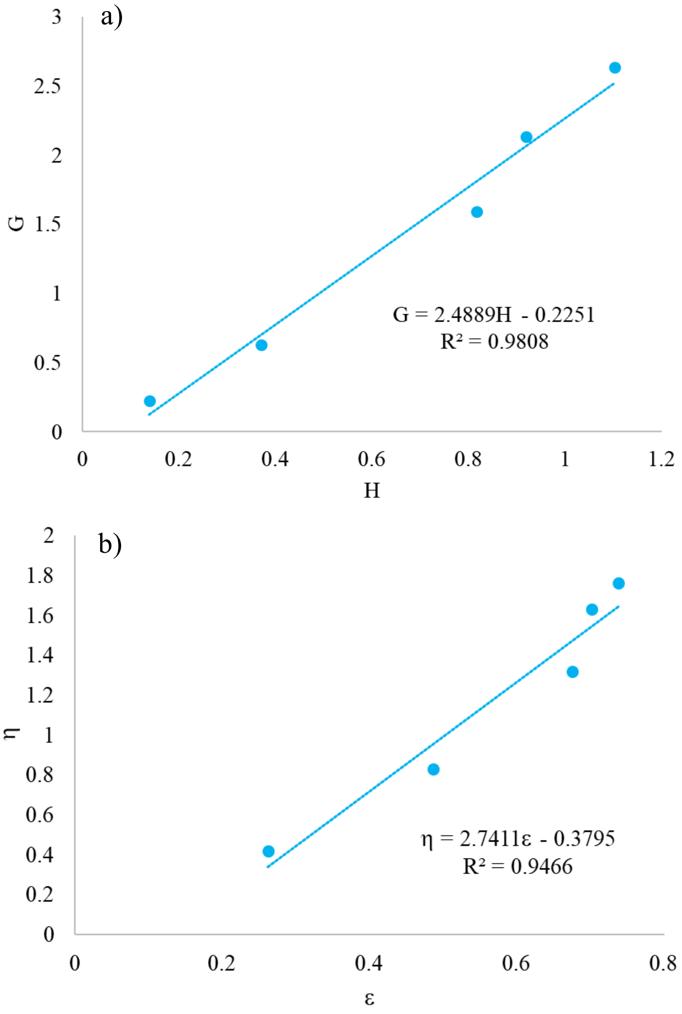


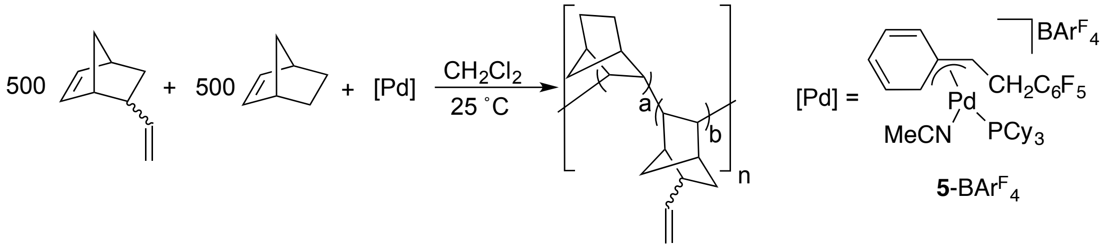
Figure S5. Plots to determine r_{NB} and r_{VNB} for the copolymerization of NB and VNB with catalyst **4**-BF$_4$: a) Plot of G vs H, Fineman-Ross method. b) Plot of η vs ε, Kelen-Tudos method.

Table S4. Summary of the reactivity ratios of NB and VNB with catalysts **4**-BF$_4$ and **5**-BAr$^F{}_4$.

	Fineman-Ross		Kelen-Tudos	
	5-BAr$^F{}_4$	**4**-BF$_4$	**5**-BAr$^F{}_4$	**4**-BF$_4$
r_{NB}	2.26 ± 0.07	2.5 ± 0.2	2.31± 0.13	2.4 ± 0.6
r_{VNB}	0.06 ± 0.03	0.2 ± 0.1	0.07 ±0.01	0.15 ±0.09
$r_{NB}{\cdot}r_{VNB}$	0.14	0.5	0.17	0.36

1.8- Variation of the composition and molecular weight of VA-PNB-*co*-VNB with time in the copolymerization with catalysts **4**-BF_4 and **5**-BAr^F_4

1.8.1. Analysis of the composition and molecular weight in the copolymerization of NB and VNB with catalysts 5-BAr^F_4



In a Schlenk tube under N_2 was placed the catalyst **5**-BAr^F_4 (5 mg, 0.0032 mmol). It was dissolved in 0.7 mL of dry CH_2Cl_2 and immediately a solution of norbornene in CH_2Cl_2 (0.41 mL, 1.6 mmol; 3.85 M) and 5-vinyl-2-norbornene (0.23 mL, 1.6 mmol) were added ($[VNB]_0$ = 1.2 M, $[NB]_0$ = 1.2 M). The polymerization was quenched adding 10 mL of MeOH to the reaction mixture at the times collected in Table S5. The solid was filtered off and washed with MeOH (2 x 10 mL) and Et_2O (5 mL). The white powder was air dried.

Table S5. Copolymerization of NB and VNB with catalyst **5**-BAr^F_4 (mol ratio NB:VNB:**5**-BAr^F_4 = 500:500:1) at different times.[a]

Entry	Time (min)	Yield[b]	χ_{NB}[c]	χ_{VNB}[c]	M_n[d]	M_w[d]
1	1.25	0.01	0.86	0.17	9076	17722
2	2.5	0.03	0.77	0.23	10046	21182
3	5	0.09	0.73	0.27	36312	55083
4	7.5	0.25	0.68	0.32	59150	81231
5	10	0.49	0.61	0.39	81658	143854
6	20	0.99	0.5	0.5	147021	386671

a) Reaction conditions: $[NB]_0$ = $[VNB]_0$ = 1.2 M, CH_2Cl_2, 25 °C, under N_2. b) Yields are referred to the total monomer mass (max yield = 1). c) Mole fractions χ_{NB} and χ_{VNB} in the copolymers were determined by integration of ^1H NMR signals (see Section 1.6.1). d) Determined by GPC in $CHCl_3$ using polystyrene standards; M_w and M_n in Dalton.

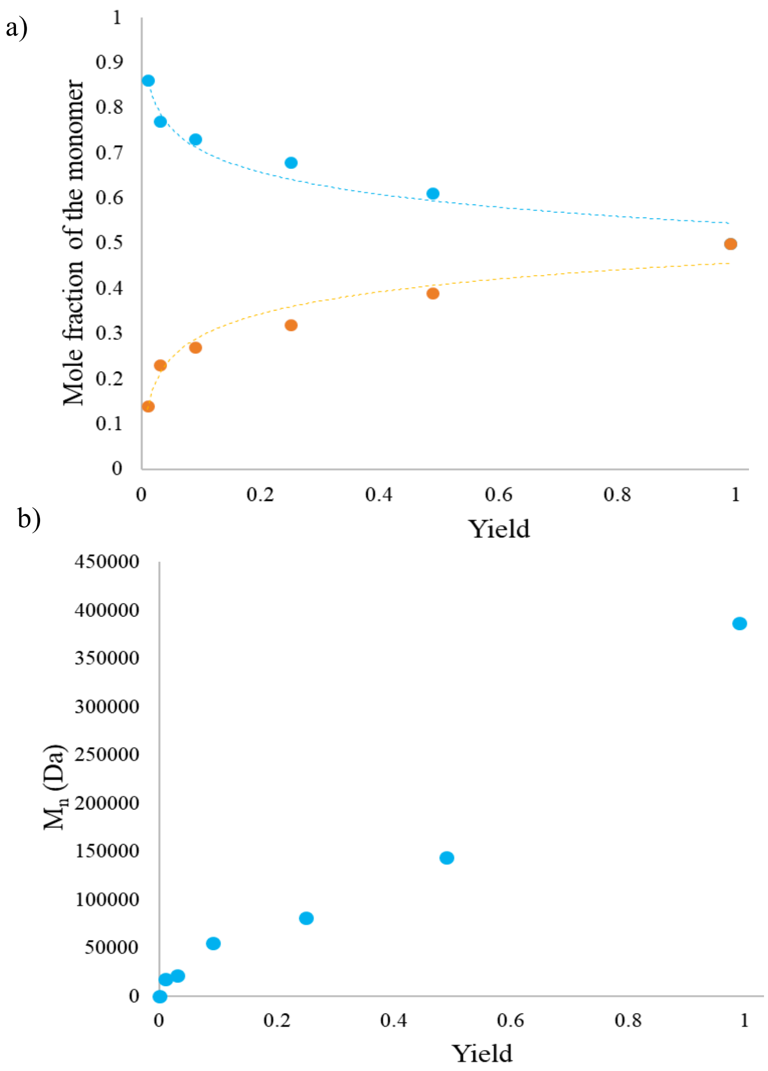
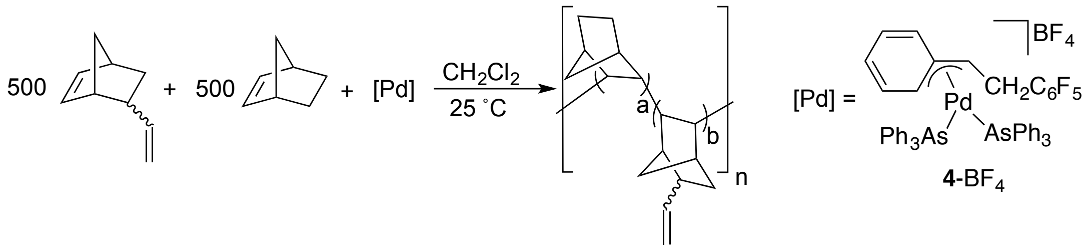


Figure S6. a) Plot of the cumulative mole fraction of the monomers in the formed copolymer VA-PNB-*co*-VNB synthesized with **5**-BAr$^F{}_4$ versus the yield. The blue dots represent the mole fraction of NB and the orange dots the mole fraction of VNB. b) Plot of the M_n vs the yield of the VA-copolymerization of NB and VNB with **5**-BAr$^F{}_4$. Reaction conditions and data shown in Table S5.

1.8.2. Analysis of the composition and molecular weight in the copolymerization of NB and VNB with catalysts 4-BF$_4$



In a Schlenk tube a solution of norbornene in CH_2Cl_2 (0.524 mL, 1.85 mmol; 3.54 M) and 5-vinyl-2-norbornene (0.265 mL, 1.85 mmol) were placed under N_2. The two monomers were diluted in 0.75 mL of dry CH_2Cl_2, $[VNB]_0$ = 1.2 M, $[NB]_0$ = 1.2 M. Finally, the catalyst **4**-BF$_4$ (4 mg, 3.71×10^{-3} mmol) was added. The polymerization was quenched adding 10 mL of MeOH to the reaction mixture at the times collected in Table S6. The solid was filtered off and washed with MeOH (2 x 10 mL) and Et_2O (5 mL). The white powder was air dried.

Table S6. Copolymerization of NB and VNB with catalyst **4**-BF_4 (mol ratio NB:VNB:**4**-BF_4 = 500:500:1) at different times.[a]

Entry	Time (min)	Yield[b]	χ_{NB}[c]	χ_{VNB}[c]	M_n[d]	M_w[d]
1	1.25	0.017	0.8	0.2	9566	21415
2	2.5	0.03	0.74	0.26	11803	27694
3	5	0.068	0.71	0.29	17090	37628
5	20	0.22	0.69	0.31	25773	46686
6	40	0.31	0.678	0.322	30308	55296
7	80	0.45	0.65	0.35	32332	60569
8	180	0.56	0.64	0.36	33000	61317

a) Reaction conditions: $[NB]_0 = [VNB]_0 = 1.2$ M, CH_2Cl_2, 25 ºC, under N_2. b) Yields are referred to the total monomer mass (max yield = 1). c) Mole fractions χ_{NB} and χ_{VNB} in the copolymers were determined by integration of ^1H NMR signals (see Section 1.6.1). d) Determined by GPC in $CHCl_3$ using polystyrene standards; M_w and M_n in Dalton.

Plots of the cumulative mole fraction of the monomer in the formed copolymer VA-PNB-*co*-VNB synthesized with **4**-BF_4 versus the yield and of the M_n versus the yield are shown in Figure 2 (main text).

1.9- Experiments on the initiation of the polymerization.

1.9.1. Determination of the concentration of *trans*-PhCH=$CH_2C_6F_5$ (6) versus the initial concentration of NB.

In an NMR tube, complex **4**-BF_4 (20 mg, 0.01858 mmol) and C_6F_5-C_6F_5 as internal standard (5.43 mg, 0.01622) were placed under N_2. The solids were dissolved in 0.6 mL of dry $CDCl_3$ and a solution of norbornene in $CDCl_3$ (5.2 μL, 0.0371 mmol; 6.99 M) was added to the yellow solution ($[NB]_0$ = 0.0618 M). The mixture was checked by ^{19}F NMR spectroscopy after 1 hour at 25 ºC. Table S7 collects the resulting concentrations of *trans*-PhCH=$CH_2C_6F_5$ (**6**) at different initial concentrations of NB.

Table S7. Concentration of **6** at different initial concentrations of NB.

Entry	$[NB]_0$[a]	[**6**][b]
1	0.0618	0.00568
2	0.247	0.00374
3	0.868	0.00223
4	1.355	0.00191

a) Initial molar concentration. $[\mathbf{4}\text{-}BF_4]_0$ = 0.0309 M. b) Molar concentration of **6** calculated by ^{19}F NMR spectroscopy.

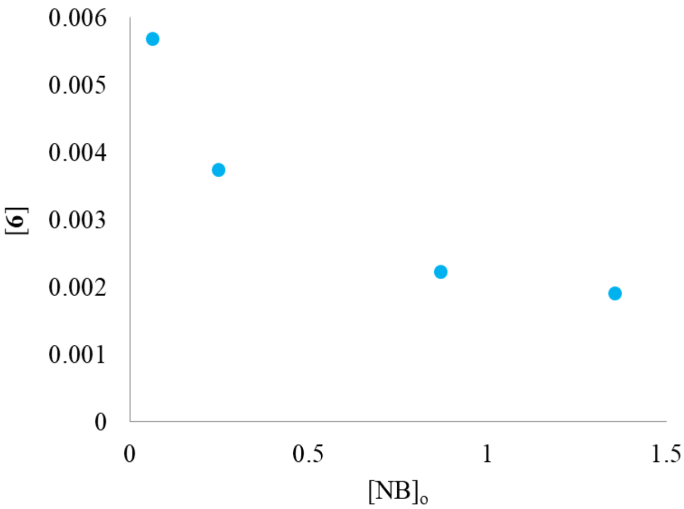


Figure S7. Plot of the concentration of *trans*-$PhCH=CH_2C_6F_5$ (**6**) versus the initial concentration of NB after 1 hour of reaction.

1.9.2. Analysis by ^{19}F NMR spectroscopy of the reaction mixture in a VA-polymerization experiment of VNB with 4-BF_4.

In a Schlenk tube, 5-vinyl-2-norbornene (0.21 mL, 1.46 mmol) was dissolved in 1 mL of dry CH_2Cl_2 under N_2 ($[VNB]_0$ = 1.2 M). Subsequently, the catalyst **4**-BF_4 was added (60 mg, 0.0586 mmol) and the yellow solution was stirred for 24 h at 25 ºC. After this time, the yellow solution was analyzed by ^{19}F NMR at 298 K.

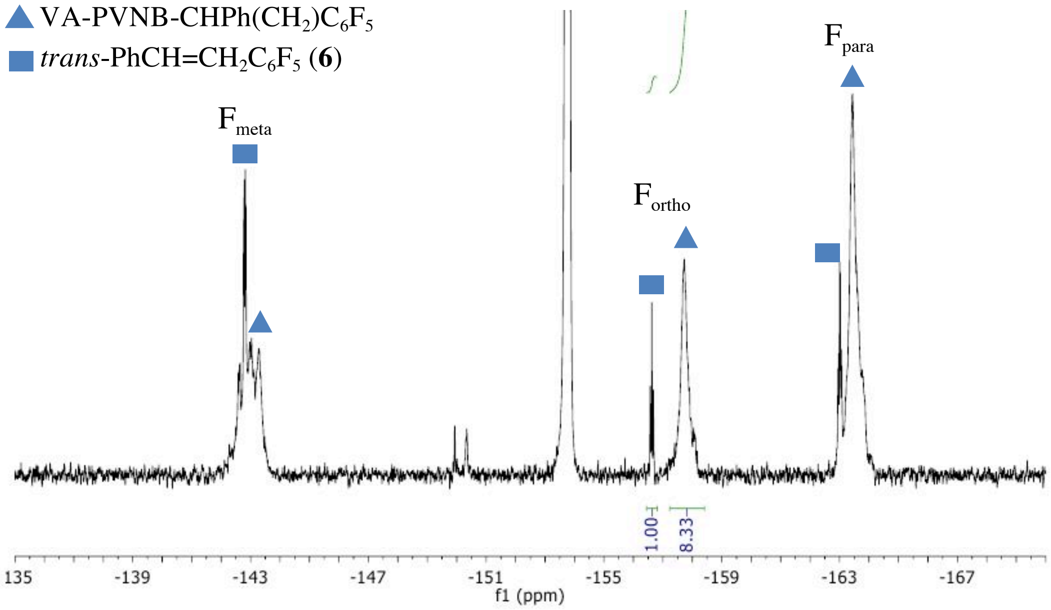
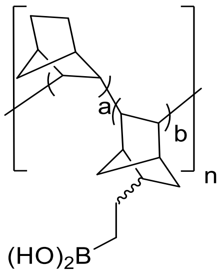


Figure S8. ^{19}F NMR spectrum for the polymerization of VNB with catalyst **4**-BF_4 after 24 h (mol ratio VNB:**4**-BF_4 = 25:1).

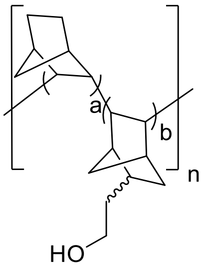
1.10- Post-polymerization functionalization by hydroboration

Synthesis of VA-PNB-*co*-NB($(CH_2)_2B(OH)_2$) (a/b = 2.1). In a 100 mL Schlenk tube the polymer VA-PNB-*co*-VNB (0.10 g, 0.31 mmol; 3.1 mmol-CH=CH_2/g pol. M_w = 63915 Da, Đ (M_w/M_n) = 2.1) was dissolved in 10 mL of dry CH_2Cl_2 under N_2. The polymer was stirred for 10 min until complete dissolution. $BHBr_2{\cdot}SMe_2$ (0.31 mL, 0.31 mmol; 1 M in CH_2Cl_2) was added and the mixture was stirred for 5 h at reflux. The suspension was allowed to reach room temperature and then, a mixture of MeOH/H_2O (20 mL, 1:1 v/v) was added. The suspension was stirred at room temperature for 30 min. The white solid was filtered off and washed with MeOH (2 x 10 mL). The solid was air dried (0.1 g, 88% yield). IR (neat, cm^{-1}): 3354 (ν-OH), 2940 (ν-CH asym.), 2864 (ν-CH sym.), 1450 (ν-VAPNBskeleton), 1348 (ν-B-O).



VA-PNB-*co*-NB($(CH_2)_2B(OH)_2$)

Synthesis of VA-PNB-*co*-NB(CH_2)$_2$OH (a/b = 2.1). In a 100 mL Schlenk tube the polymer VA-PNB-Co-VNB (0.10 g, 0.31 mmol; 3.1 mmol-CH=CH_2/g pol. M_w = 63915 Da, Đ (M_w/M_n) = 2.1) was dissolved in 10 mL of dry CH_2Cl_2 under N_2. The polymer was stirred for 10 minutes until complete dissolution. $BHBr_2 \cdot SMe_2$ (0.31 mL, 0.31 mmol; 1 M in CH_2Cl_2) was added and the mixture was stirred for 5 h at reflux. The suspension was allowed to reach room temperature and then MeOH (10 mL) was added followed by an aqueous solution of NaOH (0.67 mL, 4 mmol; 6 M) and $H_2O_{2(aq)}$ (0.72 mL, 7 mmol; 33 %). The suspension was stirred at room temperature for 2 h. The white solid was filtered off and washed with MeOH (2 x 10 mL), a mixture of MeOH/H_2O (2 x 20 mL, 1:1 v/v) and finally with MeOH (10 mL). The solid was air dried first and then in a vacuum stove (60 mb) at 70 ºC (0.1 g, 95 % yield). ^{13}C CP-MAS NMR (100.61 MHz, δ): 74-25 (br). IR (neat, cm^{-1}): 3354 (ν-OH), 2940 (ν-CH asym.), 2864 (ν-CH sym.), 1450 (ν-VAPNBskeleton), 1047 (ν-C-O).

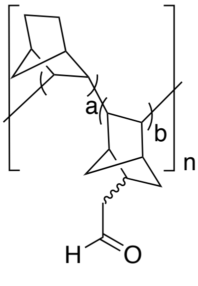


VA-PNB-*co*-NB(CH_2)$_2$OH

A similar procedure was employed for the hydroboration/oxidation of a VA-PNB-*co*-VNB polymer (a/b = 1.9; M_w = 1623063 Da, Đ (M_w/M_n) = 3.4) synthesized with catalyst **5**-BAr$^F_4$ (94.3% yield).

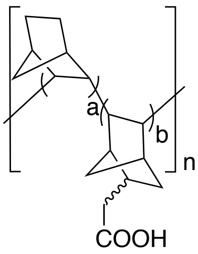
Large scale synthesis of a VA-PNB-*co*-NB(CH_2)$_2$OH with low functionalization (a/b = 21.5). In a 500 mL Schlenk tube was added VA-PNB-*co*-VNB (7.8 g, 3.59 mmol; 0.46 mmol-CH=CH_2/g pol.) under N_2. Then 200 mL of dry CH_2Cl_2 were added and the suspension was stirred for 20 min at room temperature. Subsequently, $BHBr_2 \cdot SMe_2$ was added (3.59 mmol, 3.59 mL; 1 M in CH_2Cl_2) and it was stirred for 5 h at reflux. The suspension was allowed to reach room temperature and then, 100 mL of MeOH were added followed by an aqueous solution of NaOH (1.8 mL, 10.9 mmol, 6 M) and $H_2O_{2(aq)}$ (0.6 mL, 5.81 mmol; 33 %). The suspension was stirred at room temperature for 2 h. The white solid was filtered off and washed with MeOH (2 x 70 mL), a mixture of MeOH/H_2O (2 x 500 mL, 1:1 v/v) and finally with MeOH (60 mL). The solid was air dried first and then in a vacuum stove (60 mb) at 70 ºC (7.5 g, 96.5% yield).

Synthesis of VA-PNB-*co*-NB(CH_2)$_2$CHO (a/b = 1.9). The oxidation of the alcohol to the aldehyde was performed following the general procedure for the Swern oxidation.[9] In a 100 mL Schlenk tube oxalyl chloride (1.26 mL, 9.45 mmol) was dissolved in 50 mL of dry CH_2Cl_2. The solution was cooled to -78 ºC. Subsequently, a solution of dry DMSO (1.34 mL, 18.9 mmol) in 5 mL of CH_2Cl_2 was added to the former cooled solution. The mixture was stirred at -78 ºC for 10 min. After this time, the VA-NB-*co*-NB(CH_2)$_2$OH (0.3 g, 0.93 mmol; 3.1 mmol OH/g pol.) was added and the suspension was stirred for 3 hours at -78 ºC. The suspension was allowed to warm to room temperature and dry NEt_3 (4 mL, 28.35 mmol) was added. The suspension was stirred for 12 hours at room temperature. Then, it was filtered off and the white solid was washed with CH_2Cl_2 (3 x 20 mL), MeOH (2 x 20 mL) and Et_2O (1 x 10 mL). The solid was air dried (0.28 g, 93% yield). IR (neat, cm^{-1}): 2941 (ν-CH asym.), 2864 (ν-CH sym.), 2706 (C-H combination of CHO), 1722 (ν-C=O), 1450 (ν-VAPNBskeleton).



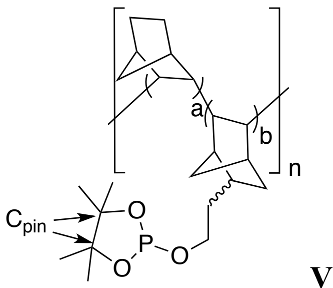
VA-PNB-*co*-NB(CH_2)$_2$CHO

Synthesis of VA-PNB-*co*-NB(CH_2)$_2$COOH (a/b = 1.9). In a Schlenk tube VA-NB-*co*-NB(CH_2)$_2$OH (0.08 g, 0.248 mmol; 3.1 mmol OH/g pol.) was suspended in 10 mL of dry DMF. Pyridinium dichromate (PDC) (0.91 g, 2.48 mmol) was added to the suspension and the mixture was stirred for 24 hours at room temperature. After this time, the suspension was filtered off. The orange solid was washed with a mixture of THF/MeOH (1:1, 2 x 15 mL), THF/HCl_{aq} (10 %) (1:1, 4 x 20 mL), MeOH (1 x 10 mL) and Et_2O (1 x 10 mL). The resulting white solid was air dried (0.075 g, 90% yield). IR (neat, cm^{-1}): 2941 (ν-CH asym.), 2864 (ν-CH sym.), 1711 (ν-C=O), 1454 (ν-VAPNBskeleton).



VA-PNB-*co*-NB$(CH_2)_2$COOH

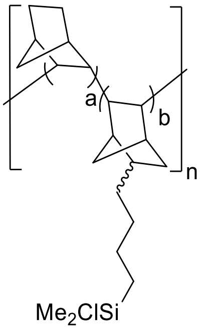
Synthesis of VA-PNB-*co*-NB$(CH_2)_2$OPpin (a/b = 21.5). VA-PNB-*co*-NB$(CH_2)_2$OH (3.8 g, 1.748 mmol; 0.46 mmol OH/gr pol.) was placed in a 250 mL Schlenk tube under N_2. The polymer was suspended in 80 mL of dry CH_2Cl_2 and the suspension was stirred for 20 min at 263 K. Then, NEt_3 (0.54 mL, 3.85 mmol) was added and the suspension was stirred for 1 h at 263 K. After this time, a solution of PClpin (0.69 mL, 4.37 mmol) in 20 mL of dry CH_2Cl_2 was added slowly at 263 K. The suspension was stirred for 12 h at room temperature. The white solid was filtered under N_2 and washed with dry CH_2Cl_2 (3 x 50 mL), dry MeOH (3 x 50 mL), dry THF (3 x 50 mL) and dry Et_2O (3 x 50 mL). It was vacuum dried for 12 h (3.74 g, 90% yield). ^{31}P MAS NMR (161.976 MHz, δ): 147.7. ^{13}C MAS NMR (100.61 MHz, δ): 95-90 (C$_{pin}$), 76-20 (VA-PNB carbons and methyl's of the phosphite). IR (neat, cm^{-1}): 2942 (ν-CH asym), 2865 (ν-CH sym), 1451 (ν-VAPNBskeleton), 963 (ν-P-O).



VA-PNB-*co*-NB$(CH_2)_2$O$(C_6H_{12}PO_2)$

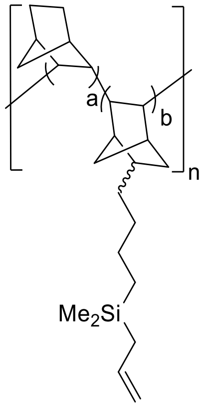
1.11- Post-Funcionalization by hydrosilylation of VA-PNB-*co*-BNB

Synthesis of VA-NB-*co*-NB(CH_2)$_4$SiClMe$_2$ (a/b = 2.1). In a 250 mL Schlenk flask, VA-PNB-*co*-BNB (1.37 g, 4 mmol; 2.9 mmol-CH=CH_2/g pol. M_w = 29875 Da, Đ (M_w/M_n) = 1.; 13 mol% internal double bond) was dissolved in 30 mL of dry CH_2Cl_2 under N_2. After complete dissolution, SiHClMe$_2$ (2.15 g, 22.32 mmol) and Karstedt′s Catalyst (0.128 g, 2% in Pt, 6.6x10^{-4} mmol) were added. The colorless solution was stirred at reflux for 16 h. Then, 40 mL of dry MeCN were added inducing the precipitation of a white solid. The supernatant grey solution was transferred via cannula, and the solid was washed with MeCN (2 x 40 mL). The white solid was vacuum dried for 3 h and stored in the freezer under N_2 (1.5 g, 88.7 % yield). IR (neat, cm^{-1}): 1450 cm^{-1} (ν-VAPNBskeleton), 846 cm^{-1} (ν-Si-C), 809 cm^{-1} (ν-Si-C), 789 cm^{-1} (ν-Si-C), 475 cm^{-1} (ν-Si-Cl). Note: The polymer needs to be kept in rigorous anhydrous conditions, since the Si-Cl bond hydrolizes easily.



VA-PNB-*co*-NB(CH_2)$_4$SiClMe$_2$

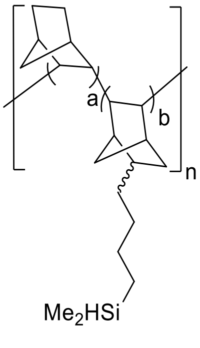
Synthesis of VA-PNB-*co*-NB(CH_2)$_4$Si(C_3H_5)Me$_2$ (a/b = 2.1). In a 50 mL Schlenk flask VA-PNB-*co*-NB(CH_2)$_4$SiClMe$_2$ (0.7 g, 1.7 mmol; 2.4 mmol Si-Cl/g pol.) was suspended in 20 mL of dry THF under N_2. A freshly prepared solution of allylmagnesium bromide in Et_2O (3.8 mL, 2.41 mmol; 0.62 M) was added. The suspension was stirred at reflux for 5 h. Then, 30 mL of MeOH were added and the mixture was stirred for 30 min at room temperature. The white solid was filtered off and washed with a solution of $HCl_{(aq)}$ (3 x 20 mL, 10%), a solution of $KOH_{(aq)}$ (2 x 20 mL, 6 M), MeOH (20 mL) and Et_2O (20 mL). The white solid was vacuum dried and stored in the freezer (0.60 g, 85.7%). IR (neat, cm^{-1}): 1634 cm^{-1} (ν-C=C-), 1450 cm^{-1} (ν-VAPNBskeleton), 837 cm^{-1} (ν-Si-C), 783 cm^{-1} (ν-Si-C).



VA-PNB-*co*-NB(CH$_2$)$_4$Si(C$_3$H$_5$)Me$_2$

<u>*Preparation of the allylmagnesiumbromide solution:*</u> In a 50 mL Schlenk tube Mg turnings (85 mg, 3.5 mmol) were placed together with an iodine crystal under N_2. The mixture was heated until the complete consumption of the I_2. The Mg was suspended in 2 mL of dry Et_2O and a solution of allylbromide (0.3 ml, 3.5 mmol) in 2 mL of dry Et_2O was added. The suspension was stirred for 3 h at 25 ºC. The resultant grey solution was titrated by ^{1}H NMR using biphenyl as an internal standard.

Synthesis of VA-PNB-*co*-NB(CH$_2$)$_4$SiHMe$_2$ (a/b = 2.1). In a 50 mL Schlenk tube VA-NB-*co*-NB(CH$_2$)$_4$SiClMe$_2$ (0.45 g, 1.08 mmol; 2.4 mmol Si-Cl/g pol.) was suspended in 15 mL of dry Et_2O under N_2. The suspension was cooled at 273 K and $AlLiH_4$ (0.1 g, 2.6 mmol) was added. The suspension was stirred for 12 h at room temperature. Then, 20 mL of MeOH were added and the grey solid was filtered off. The solid was washed with a solution of $HCl_{(aq)}$ (3 x 20 mL, 10%), a solution of $KOH_{(aq)}$ (2 x 20 mL, 6 M), MeOH (20 mL) and Et_2O (20 mL). The white solid was vacuum dried and stored in the freezer (0.37 g, 90% yield). IR (neat, cm^{-1}): 2108 cm^{-1} (ν-Si-H), 1450 cm^{-1} (ν-VAPNBskeleton), 884 cm^{-1} (ν-Si-C), 834 cm^{-1} (ν-Si-C), 787 cm^{-1} (ν-Si-C).



VA-PNB-*co*-NB(CH$_2$)$_4$SiHMe$_2$

2. Selected GPC chromatograms.

Some of the chromatograms shown below, especially those for very dilute samples, show a signal at about 30 min retention time. That peak is also found when a blank sample was run in our GPC chromatographer (see Figure S9 for a sample containing two polystyrene standards). It is an artifact of our equipment that we could not eliminate.

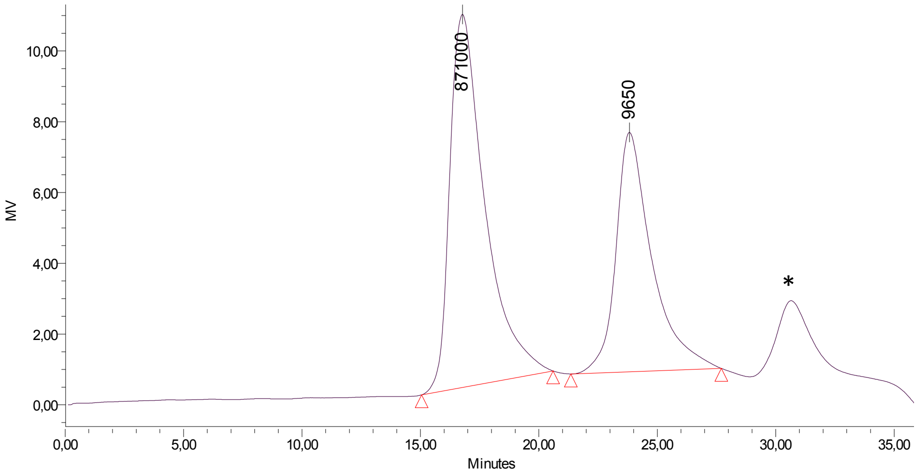
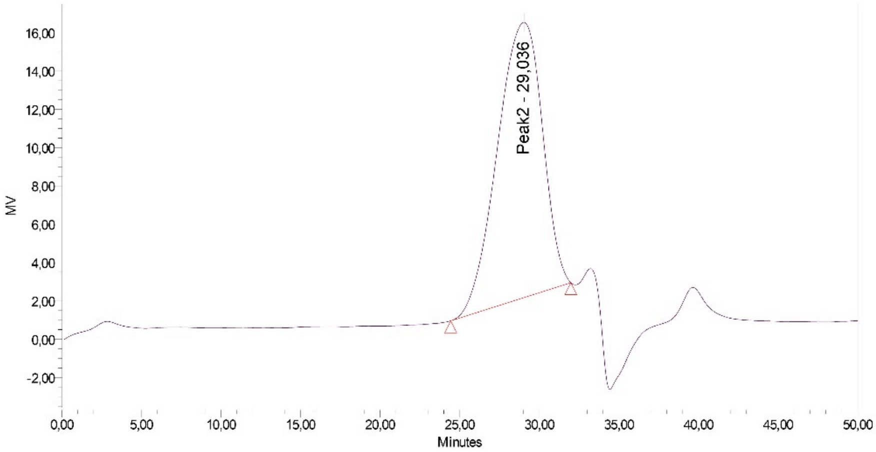


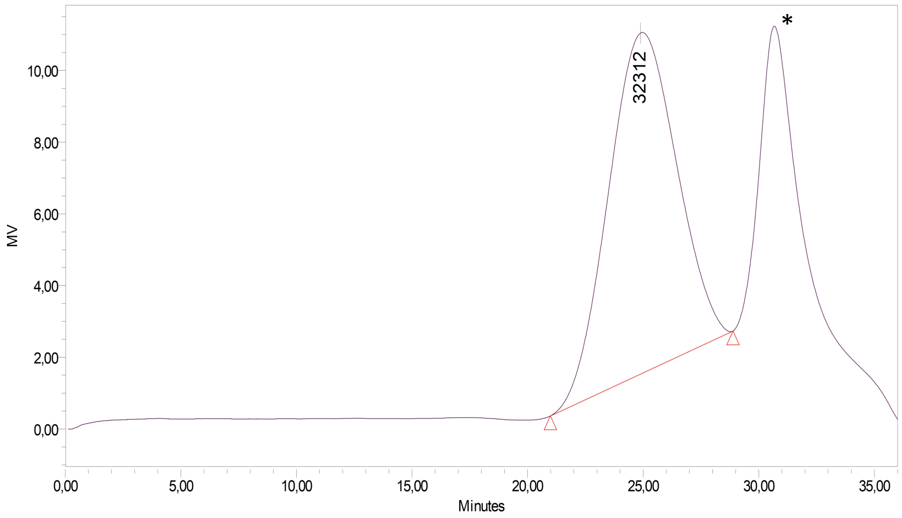
Figure S9. GPC chromatogram for two polystyrene standards. * Spurious signal.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		29,036	29,036	29,036	5994	7161		8952	11347	1,250076	1,584616

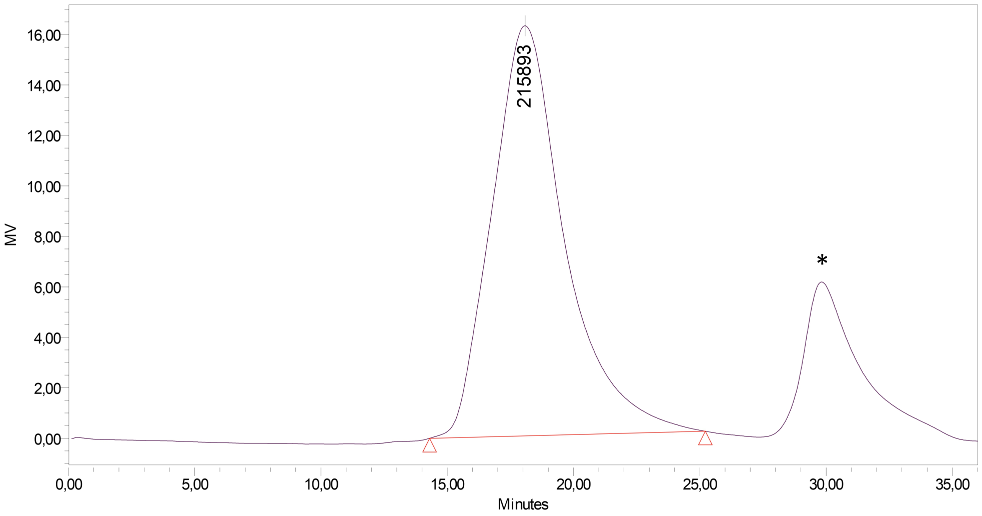
Figure S10. GPC chromatogram for VA-PVNB synthesized with catalyst **4**-BF_4 (mol ratio VNB:**4**-BF_4 = 500:1, entry 1, Table 1).



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		24,883	24,883	24,883	25268	34698	32312	45321	57010	1,306169

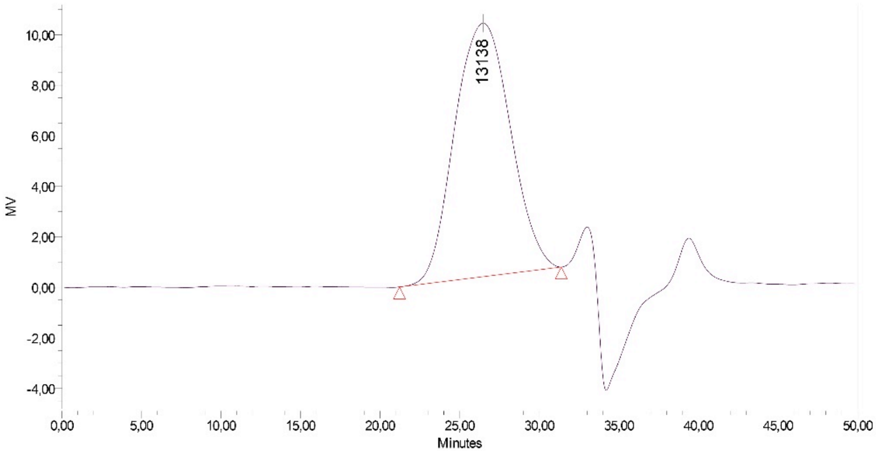
Figure S11. GPC chromatogram for VA-PVNB synthesized with catalyst **4**-BAr$^F{}_4$ (mol ratio VNB:**4**-BAr$^F{}_4$ = 500:1, entry 2, Table 1). * Spurious signal.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		18,083	18,083	18,083	114261	486642	215893	2166509	4004903	4,451956

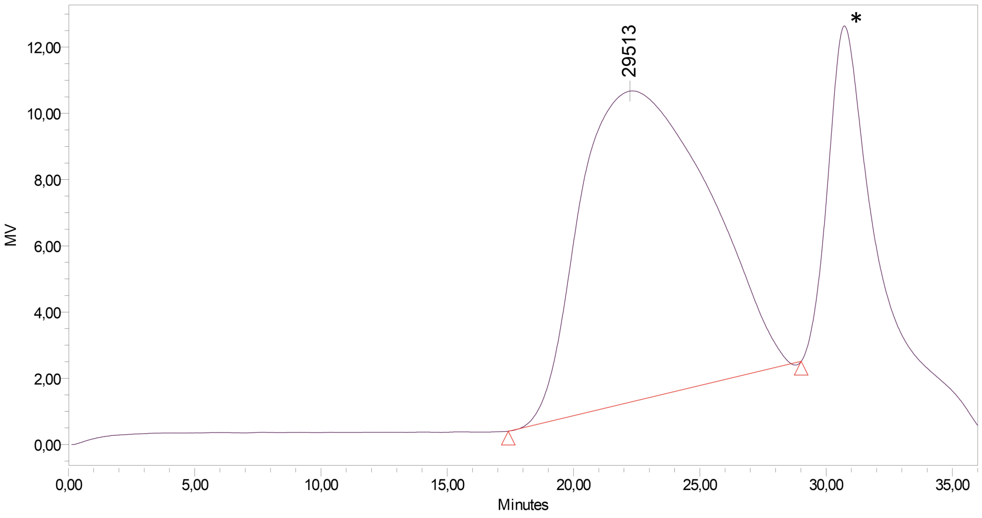
Figure S12. GPC chromatogram for VA-PVNB synthesized with catalyst **5**-BAr$^F{}_4$ (mol ratio VNB:**5**-BAr$^F{}_4$ = 500:1, entry 3, Table 1). * Spurious signal.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		26,469	26,469	26,469	11296	17287	13138	25523	34622	1,476444

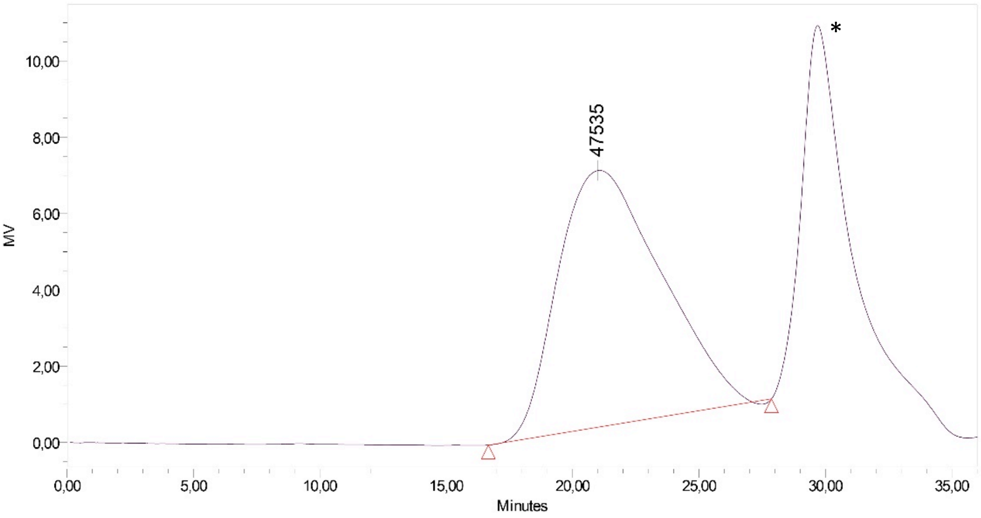
Figure S13. GPC chromatogram for VA-PBNB synthesized with catalyst **4**-BF_4 (mol ratio BNB:**4**-BF_4 = 500:1, entry 4, Table 1).



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		22,236	22,236	22,236	4332	30517	29513	58414	81530	1,914129	2,671603

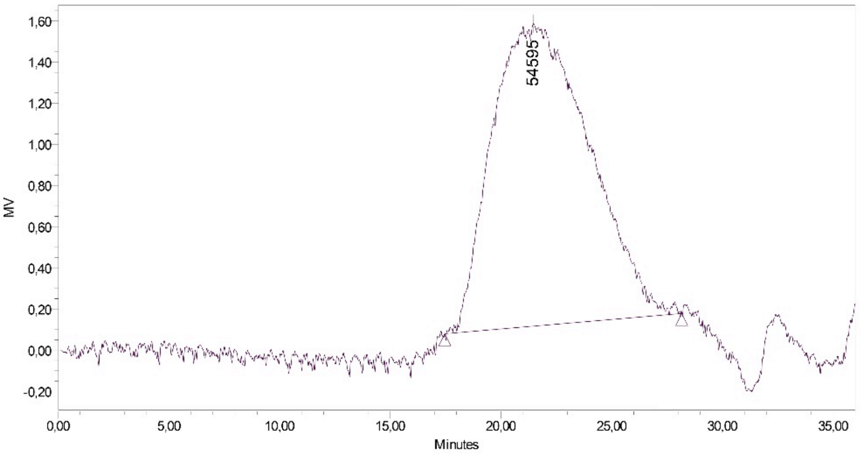
Figure S14. GPC chromatogram for VA-PBNB synthesized with catalyst **4**-BAr^F_4 (mol ratio BNB: **4**-BAr^F_4 = 500:1, entry 5, Table 1). * Spurious signal.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		21,000	21,000	21,000	17769	45090	47535	75615	115897	1,676967
2			29,433							

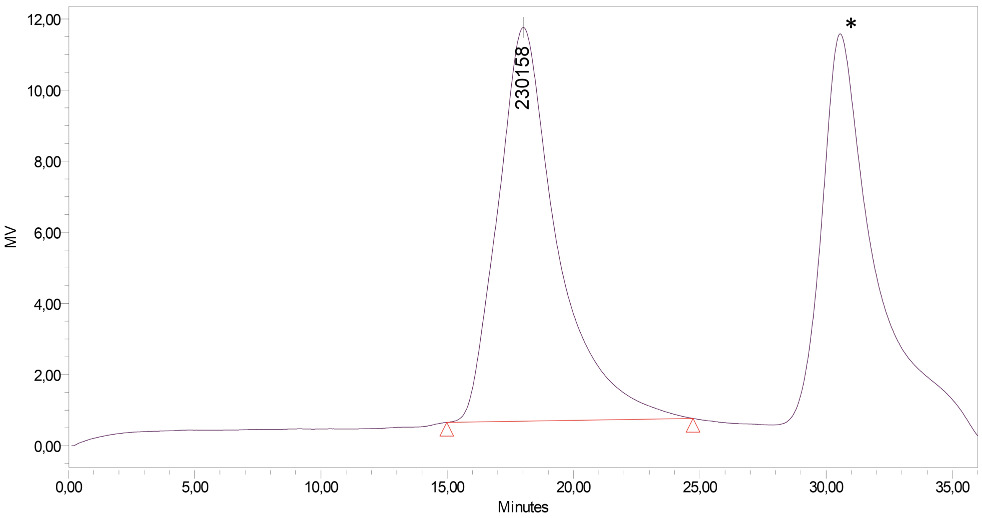
Figure S15. GPC chromatogram for VA-PBNB synthesized with catalyst **5**-BAr$^F{}_4$ (mol ratio BNB:**5**-BAr$^F{}_4$ = 500:1, entry 6, Table 1). * Spurious signal.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		23008	56464	54595	133441	2,454145	1,665523	2,363296

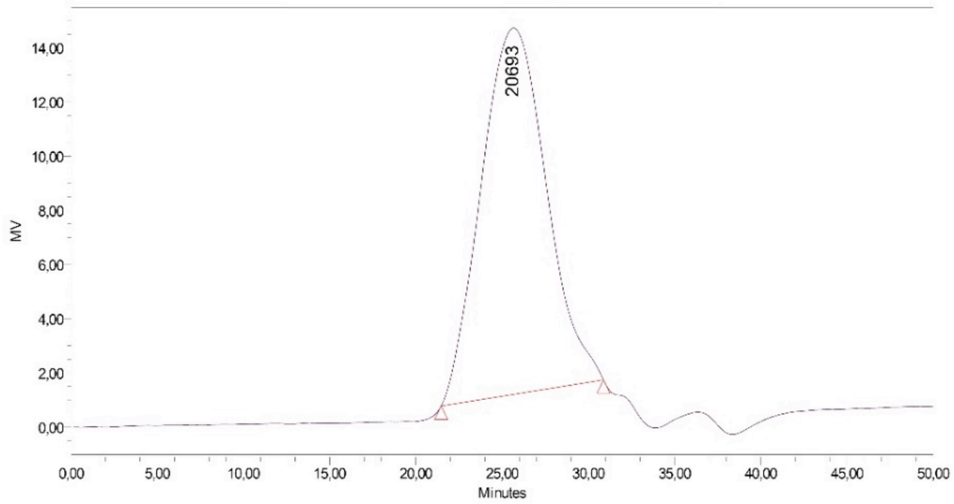
Figure S16. GPC chromatogram for VA-PNB-Co-VNB synthesized with catalyst **4**-BF$_4$ (mol ratio NB:VNB:**4**-BF$_4$ = 500:500:1, entry 1, Table 2)



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		18,014	18,014	18,014	123710	410817	230158	1648232	3469510	4,012084

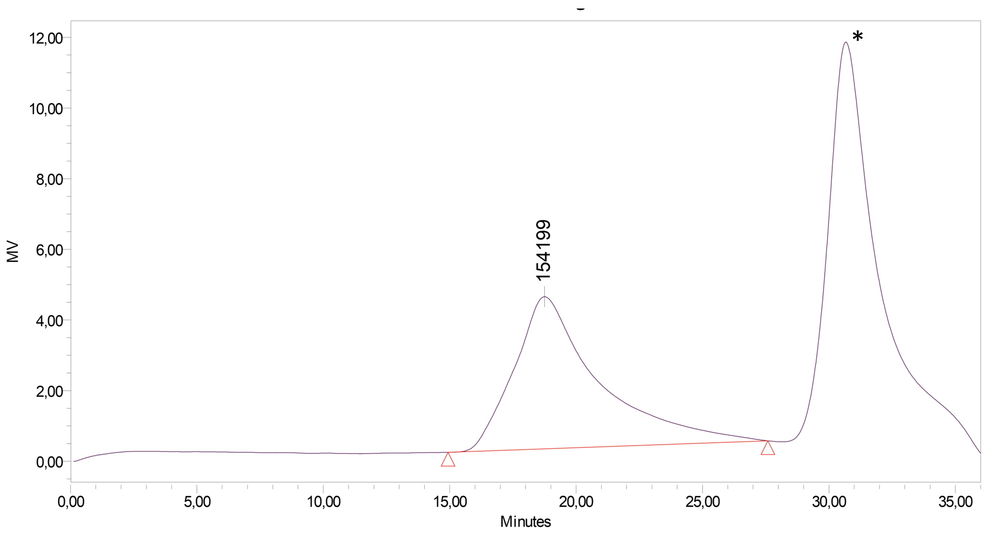
Figure S17. GPC chromatogram for VA-PNB-Co-VNB synthesized with catalyst **5**-BAr$^F{}_4$ (mol ratio NB:VNB:**5**-BAr$^F{}_4$ = 500:500:1, entry 4, Table 2). * Spurious signal.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		25,650	25,650	25,650	14962	29875	20693	54327	80860	1,818495

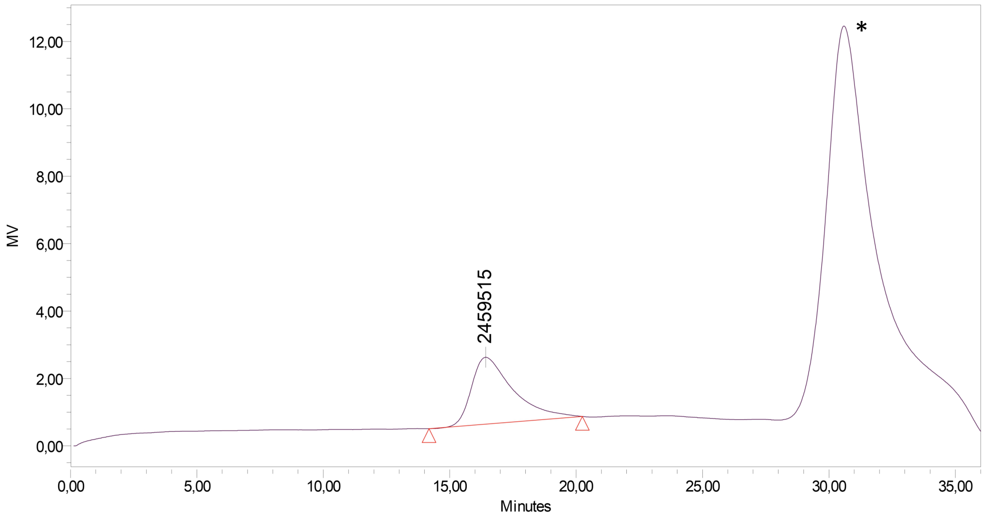
Figure S18. GPC chromatogram for VA-PNB-Co-BNB synthesized with catalyst **4**-BF$_4$ (mol ratio NB:BNB:**4**-BF$_4$ = 500:500:1, entry 5, Table 2).



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		18,750	18,750	18,750	38147	197511	154199	766552	1935979	3,881053

Figure S19. GPC chromatogram for VA-PNB-Co-BNB synthesized with catalyst **5**-BAr$^{F}_{4}$ (mol ratio NB:BNB:**5**-BAr$^{F}_{4}$ = 500:500:1, entry 6, Table 2). * Spurious signal.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		16,424	16,424	16,424	473579	1623063	2459515	3306930	4435168	2,037463

Figure S20. GPC chromatogram for VA-PNB-Co-VNB synthesized with catalyst **5**-BAr$^{F}_{4}$ (mol ratio NB:VNB:**5**-BAr$^{F}_{4}$ = 50000:50000:1, entry 2, Table 4). * Spurious signal.

3. Selected NMR spectra for complex 4-BAr$^F{}_4$

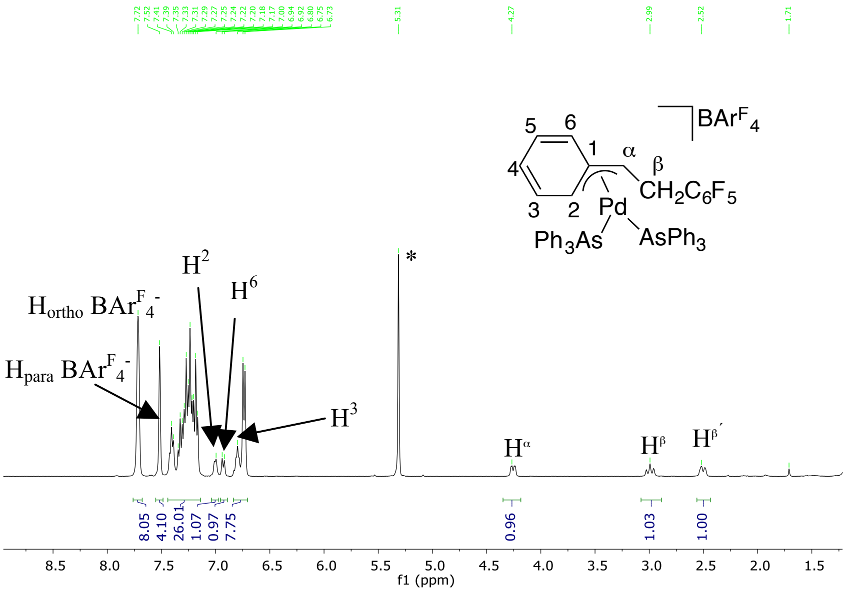


Figure S21. ^{1}H NMR (400.13 MHz, CD_2Cl_2) of complex **4**-BAr$^F{}_4$ at 233 K. *Signal corresponding to the solvent.

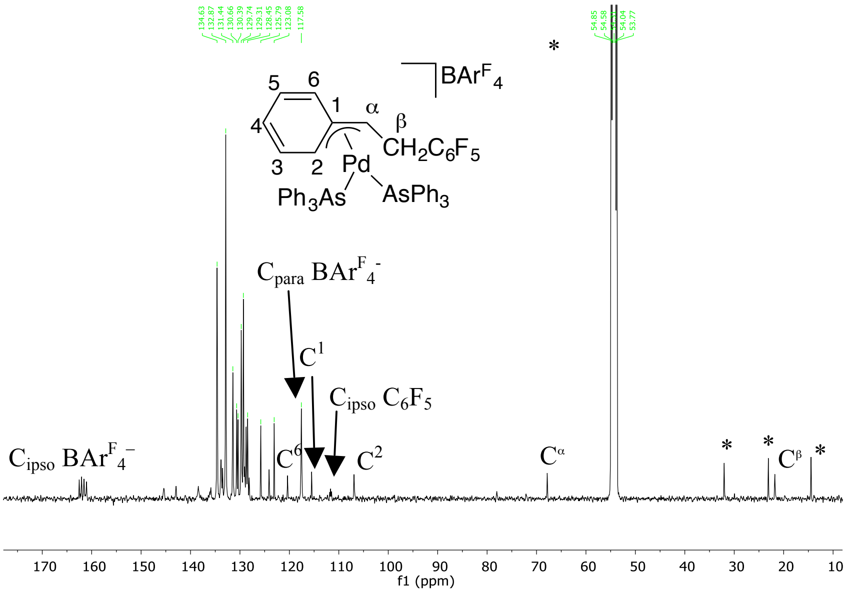


Figure S22. $^{13}C\{^1H\}$ NMR (100.613 MHz, CD_2Cl_2) of complex **4**-BAr$^F{}_4$ at 233 K. *Signal corresponding to the solvent and hexane.

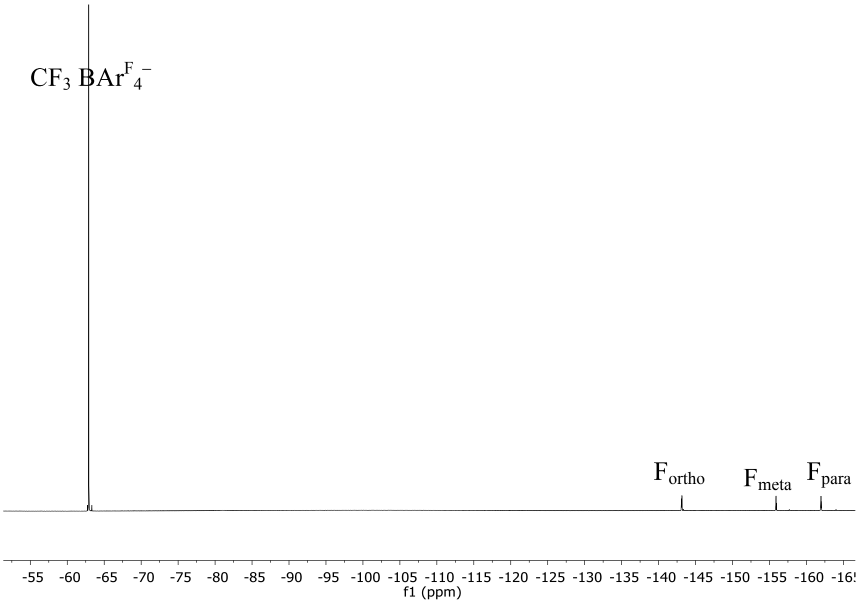


Figure S23. ^{19}F NMR (376.498 MHz, CD_2Cl_2) of complex **4**-BAr$^F_4$ at 233 K.

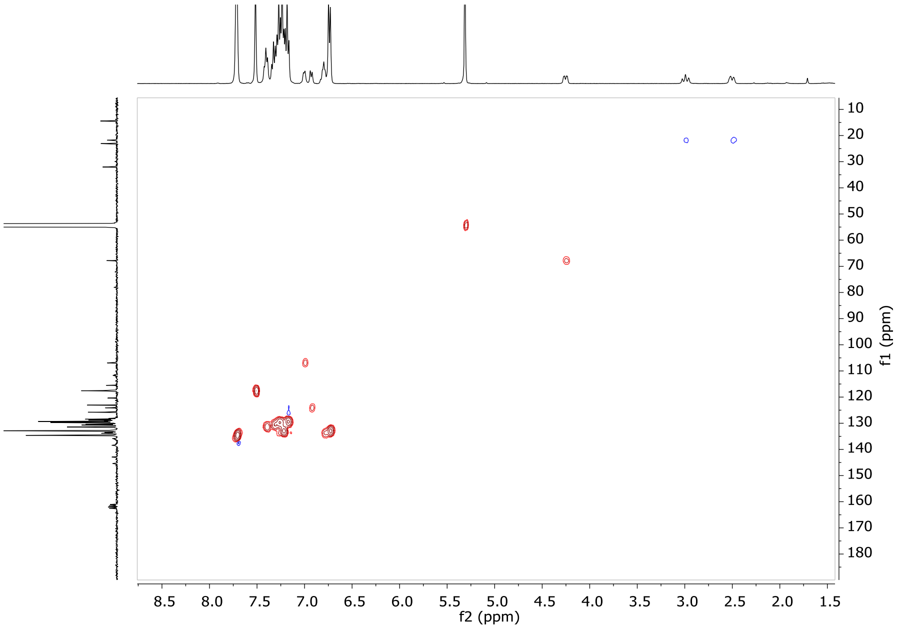


Figure S24. ^{1}H-^{13}C gHSQC NMR (400.13 MHz, CD_2Cl_2) of complex **4**-BAr$^F_4$ at 233 K.

4. Selected NMR and IR spectra for homopolymers VA-PNB, VA-PVNB, VA-PENB and VA-PBNB.

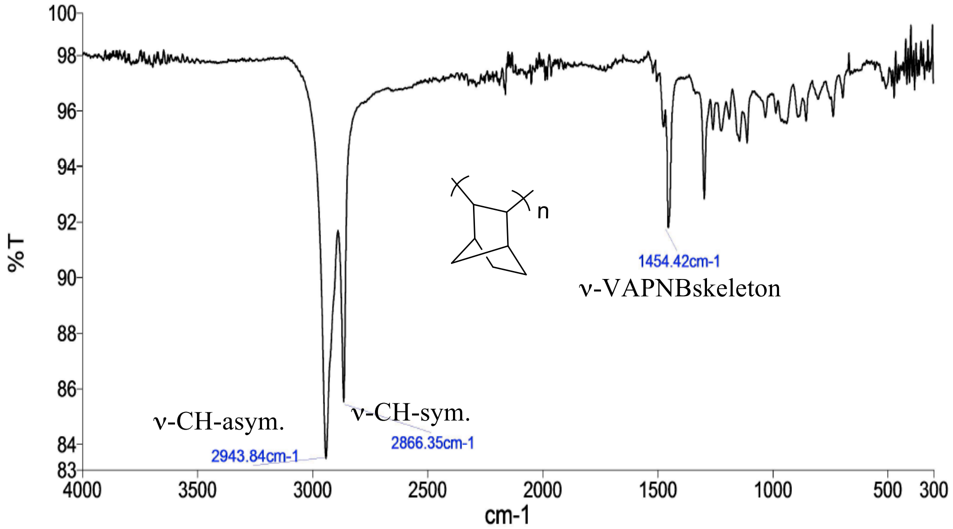


Figure S25. IR Spectrum (neat, cm^{-1}) of VA-PNB (mol ratio NB:Pd = 500:1) synthesized with catalyst **4**-BF_4.

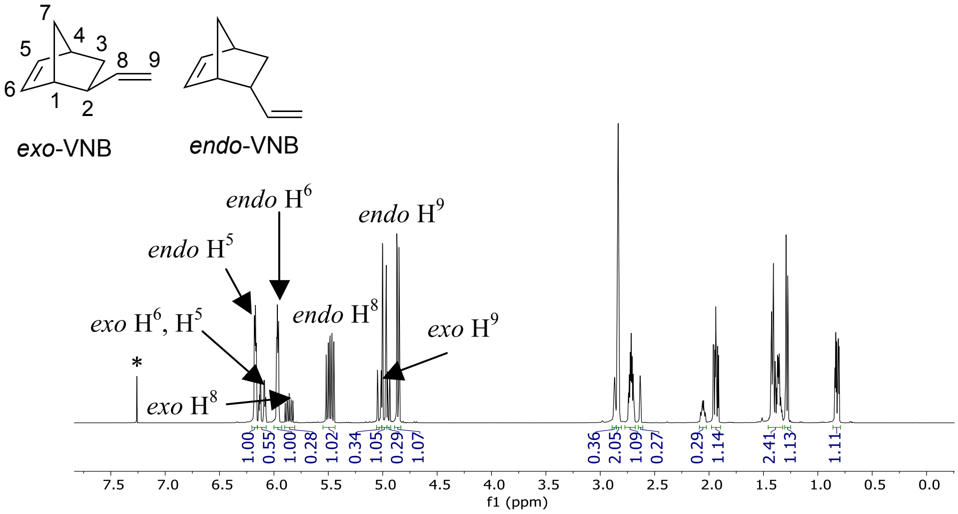


Figure S26. ^1H NMR (500.13 MHz, dry $CDCl_3$) of monomer VNB (exo, endo mixture) at 298 K. *Signal corresponding to the solvent.

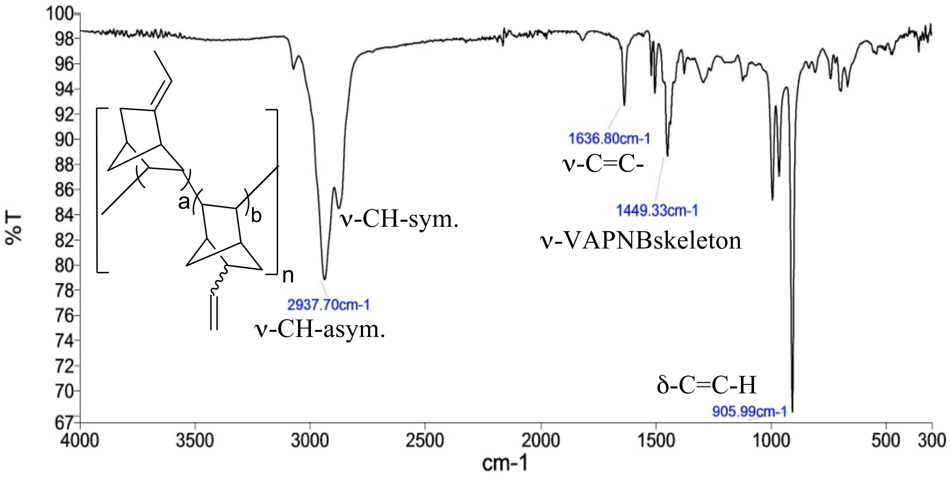


Figure S27. IR Spectrum (neat, cm^{-1}) of VA-PVNB (mol ratio VNB:Pd = 500:1, M_w = 7.2 x 10^3 Da; entry 1, Table 1) synthesized with catalyst **4**-BF_4.

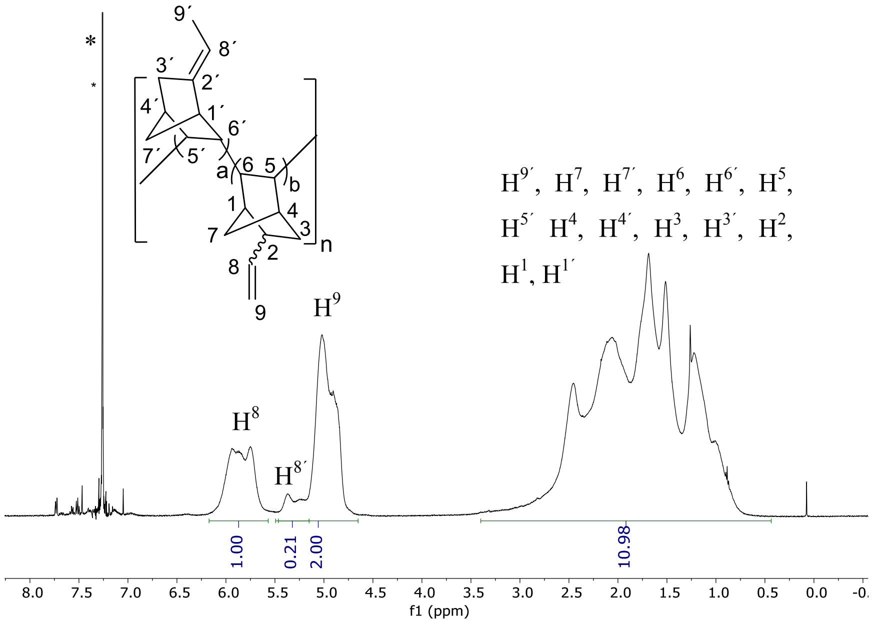


Figure S28.^{1}H NMR (500.13 MHz, dry $CDCl_3$) of polymer VA-PVNB (mol ratio VNB:Pd = 500:1, M_w = 7.2 x 10^3 Da; entry 1, Table 1) at 298 K synthesized with catalyst **4**-BF_4. *Signal corresponding to the solvent.

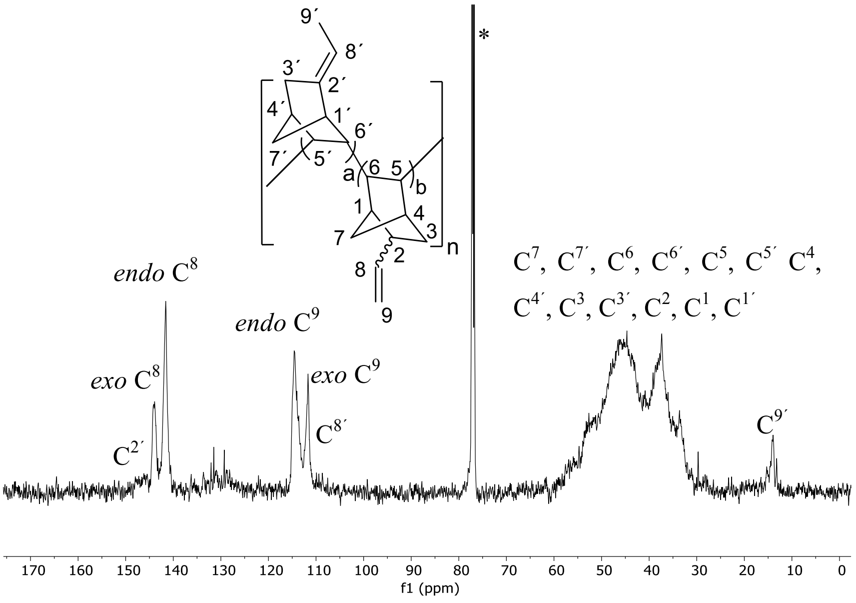


Figure S29. $^{13}C\{^1H\}$ NMR (125.758 MHz, dry $CDCl_3$) of polymer VA-PVNB (mol ratio VNB:Pd = 500:1, M_w = 7.2 x 10^3 Da; entry 1, Table 1) at 298 K synthesized with catalyst **4**-BF_4. *Signal corresponding to the solvent.

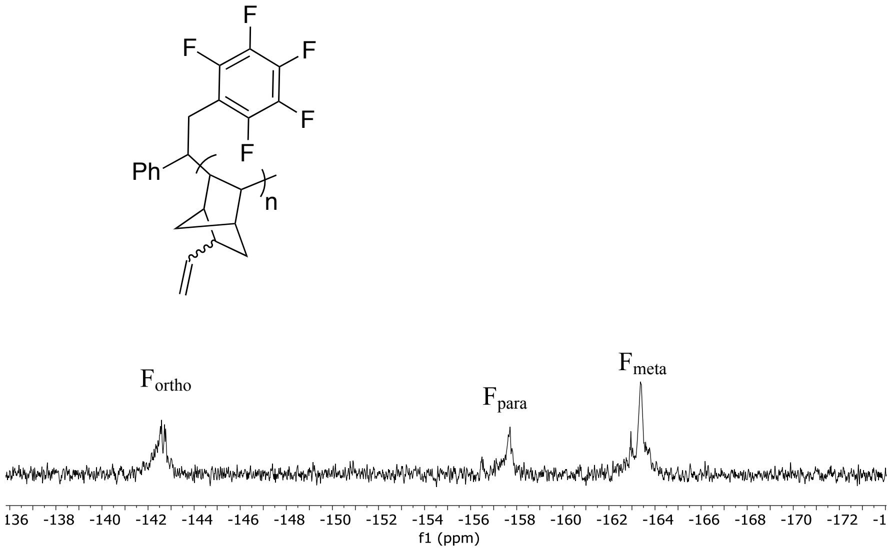


Figure S30. ^{19}F NMR (470.592 MHz, dry $CDCl_3$) of polymer VA-PVNB (mol ratio VNB:Pd = 500:1, M_w = 7.2 x 10^3 Da; entry 1, Table 1) at 298 K synthesized with catalyst **4**-BF_4.

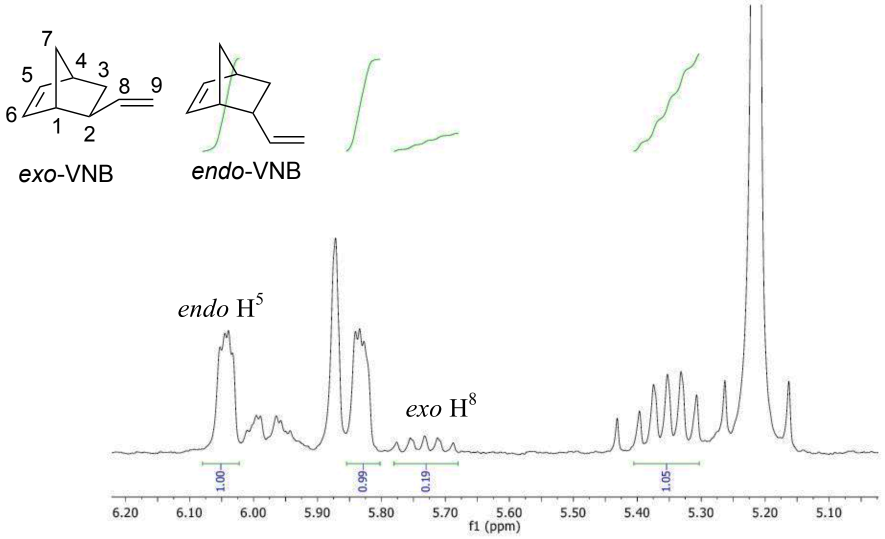


Figure S31. ^{1}H NMR (500.13 MHz, dry $CDCl_3$) of the unreacted monomer after the vinylic addition polymerization of VNB with catalyst **4**-BF_4 (molar ratio VNB:Pd = 500:1, entry 1, Table 1) at 298 K.

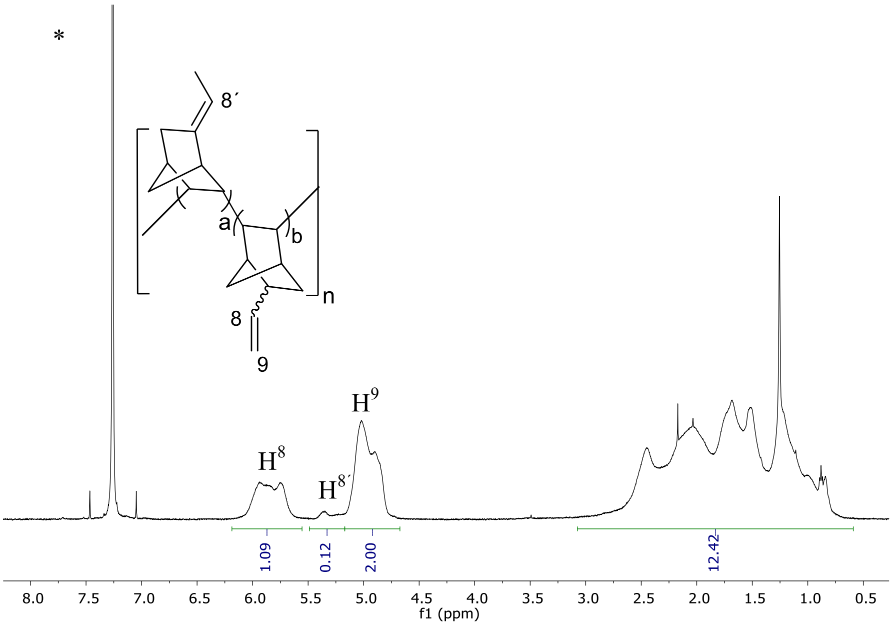


Figure S32. ^{1}H NMR (500.13 MHz, dry $CDCl_3$) of polymer VA-PVNB (mol ratio VNB:Pd = 500:1, $M_w = 3.46 \times 10^4$ Da; entry 2, Table 1) at 298 K synthesized with catalyst **4**-BAr^F_4. *Signal corresponding to the solvent.

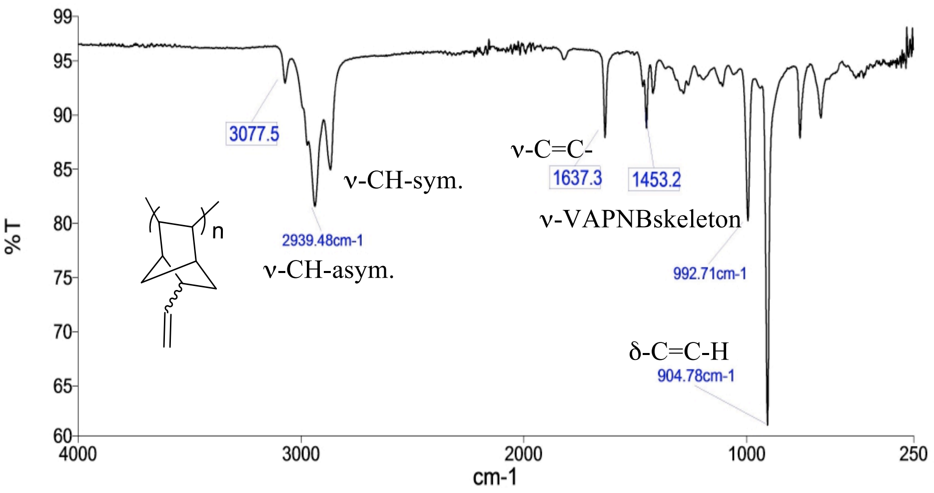


Figure S33. IR Spectrum (neat, cm^{-1}) of VA-PVNB (mol ratio VNB:Pd = 500:1, M_w = 4.9 x 10^5 Da; entry 3, Table 1) synthesized with catalyst **5**-BAr^F_4.

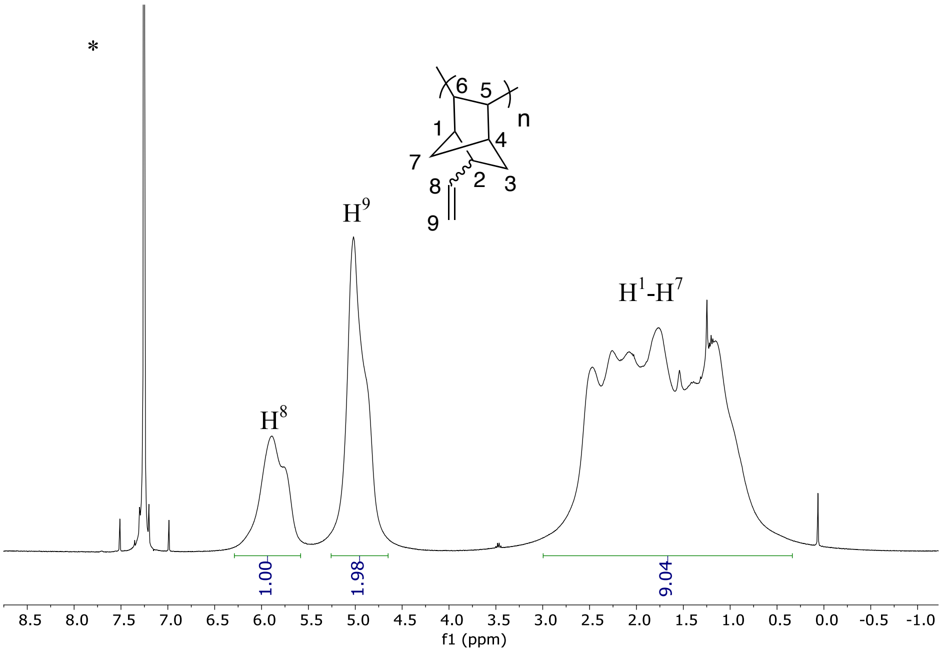


Figure S34. ^{1}H NMR (500.13 MHz, dry $CDCl_3$) of polymer VA-PVNB (mol ratio VNB:Pd = 500:1, M_w = 4.9 x 10^5 Da; entry 3, Table 1) at 298 K synthesized with catalyst **5**-BAr^F_4. *Signal corresponding to the solvent.

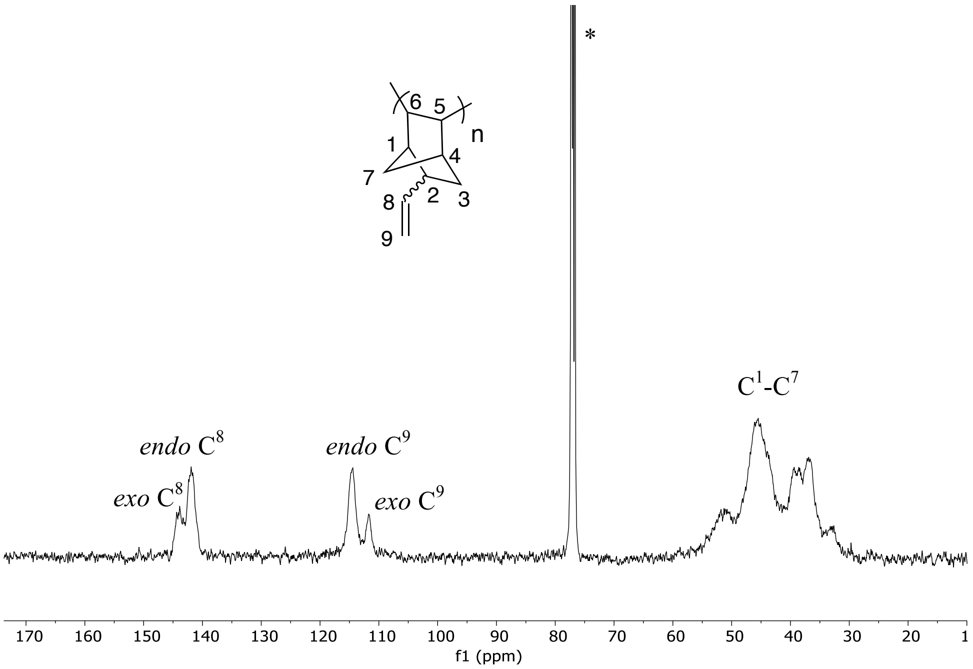


Figure S35. $^{13}C\{^{1}H\}$ NMR (125.758 MHz, dry $CDCl_3$) of polymer VA-PVNB (mol ratio VNB:Pd = 500:1, M_w = 4.9 x 10^5 Da; entry 3, Table 1) at 298 K synthesized with catalyst **5**-BAr^F_4. *Signal corresponding to the solvent.

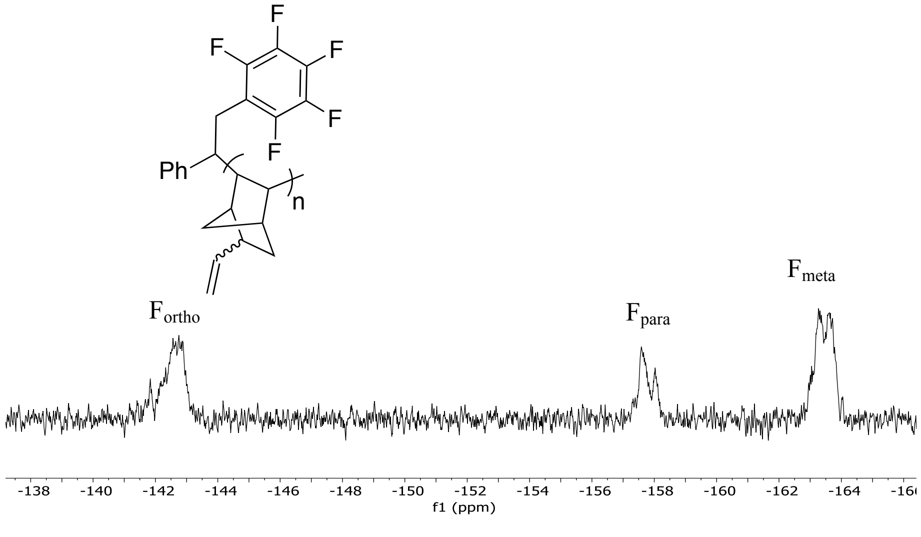


Figure S36. ^{19}F NMR (470.592 MHz, dry $CDCl_3$) of polymer VA-PVNB (mol ratio VNB:Pd = 500:1, M_w = 4.9 x 10^5 Da; entry 3, Table 1) at 298 K synthesized with catalyst **5**-BAr^F_4.

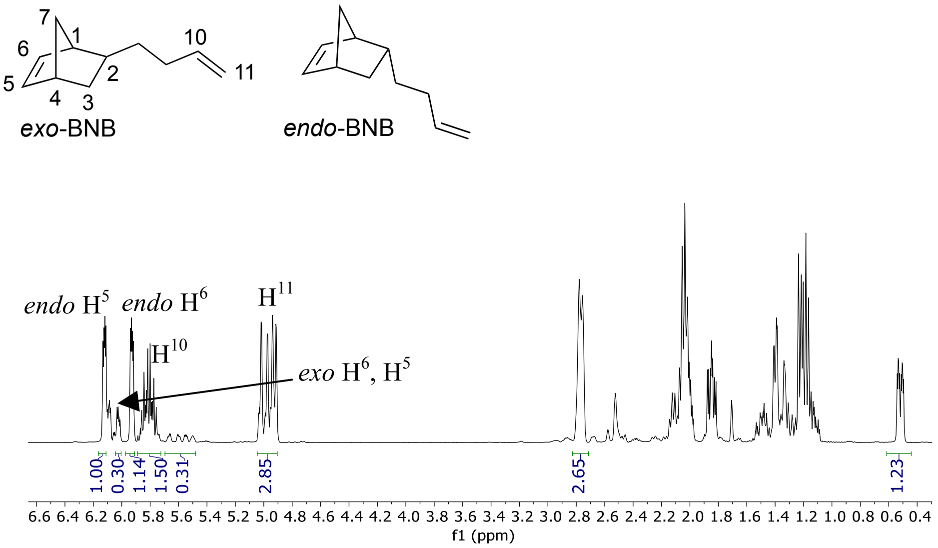


Figure S37. ^{1}H NMR (500.13 MHz, dry $CDCl_3$) of monomer BNB (exo, endo mixture) at 298 K. *Signal corresponding to the solvent.

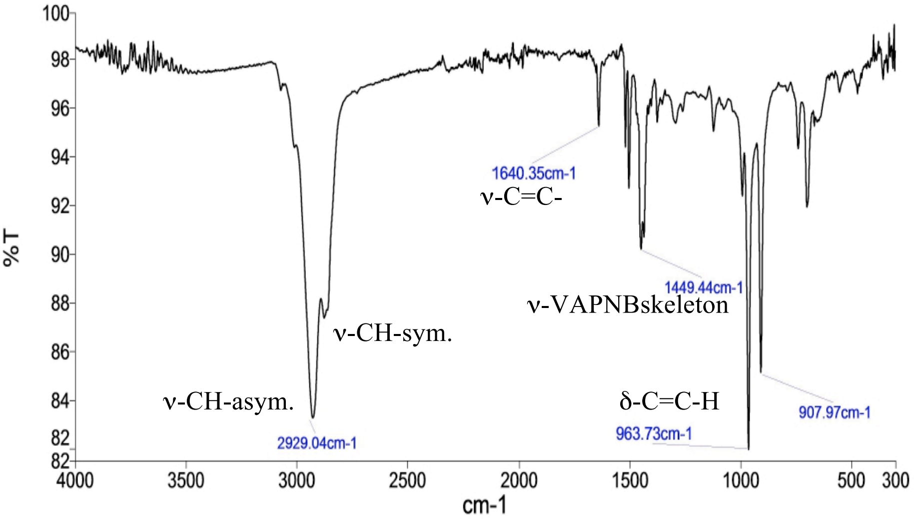


Figure S38. IR Spectrum (neat, cm^{-1}) of VA-PBNB (mol ratio BNB:Pd = 500:1, $M_w = 1.73 \times 10^4$, entry 4, Table 1) synthesized with catalyst **4**-BF_4.

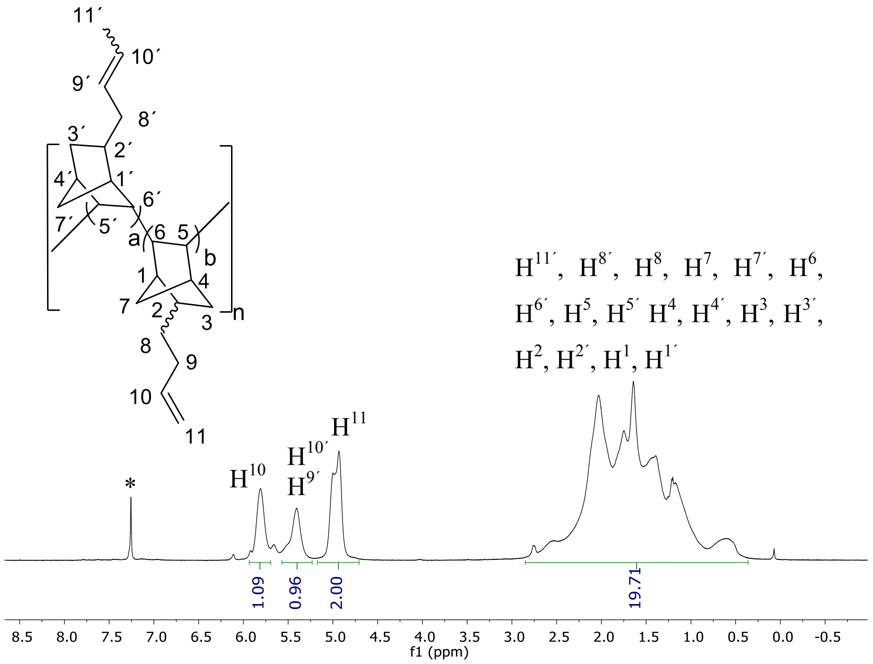


Figure S39. ^{1}H NMR (500.13 MHz, dry CDCl$_3$) of polymer VA-PBNB (mol ratio BNB:Pd = 500:1, M$_w$ = 1.73 x 10^4; entry 4, Table 1) at 298 K synthesized with catalyst **4**-BF$_4$. *Signal corresponding to the solvent.

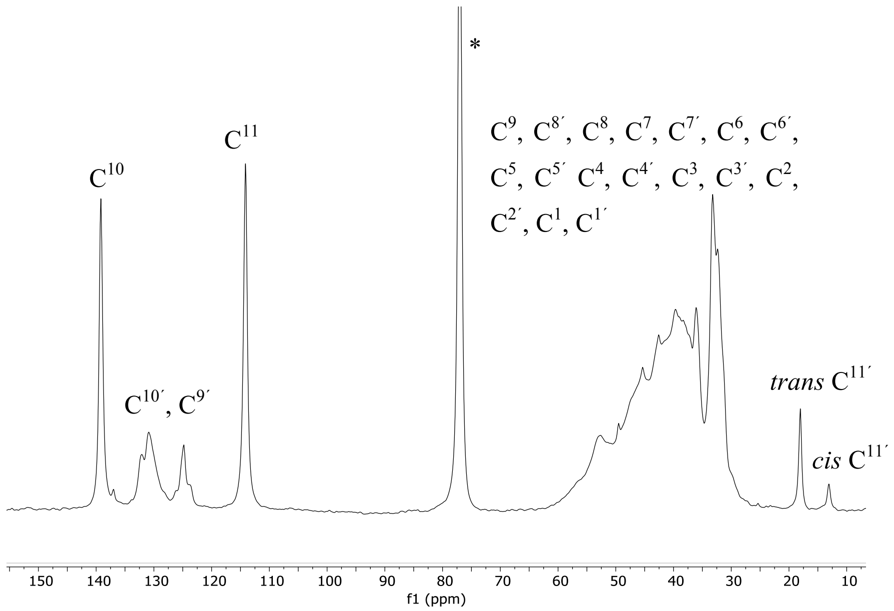


Figure S40. ^{13}C{^{1}H} NMR (125.758 MHz, dry CDCl$_3$) of polymer VA-PBNB (mol ratio BNB:Pd = 500:1, M$_w$ = 1.73 x 10^4; entry 4, Table 1) at 298 K synthesized with catalyst **4**-BF$_4$. *Signal corresponding to the solvent.

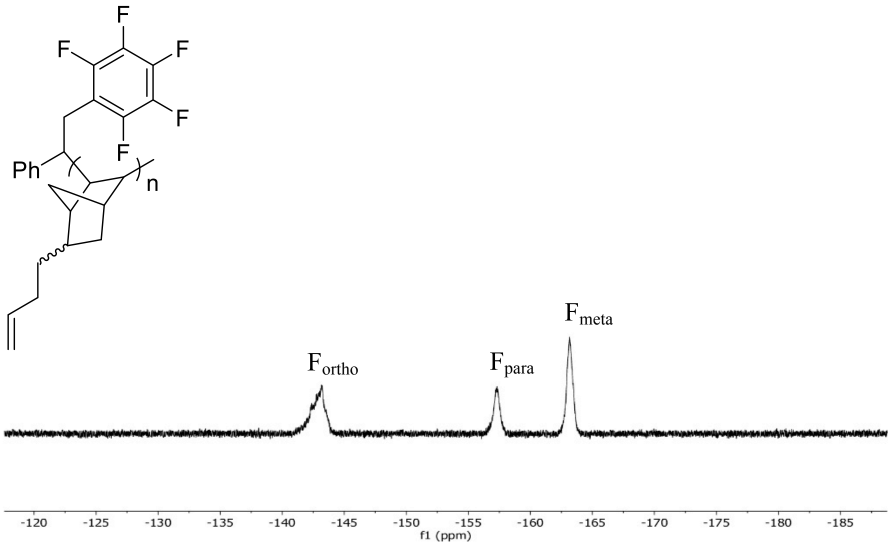


Figure S41. ^{19}F NMR (470.592 MHz, dry CDCl$_3$) of polymer VA-PBNB (mol ratio BNB:Pd = 500:1, M$_w$ = 1.73 x 10^4; entry 4, Table 1) at 298 K synthesized with catalyst **4**-BF$_4$.

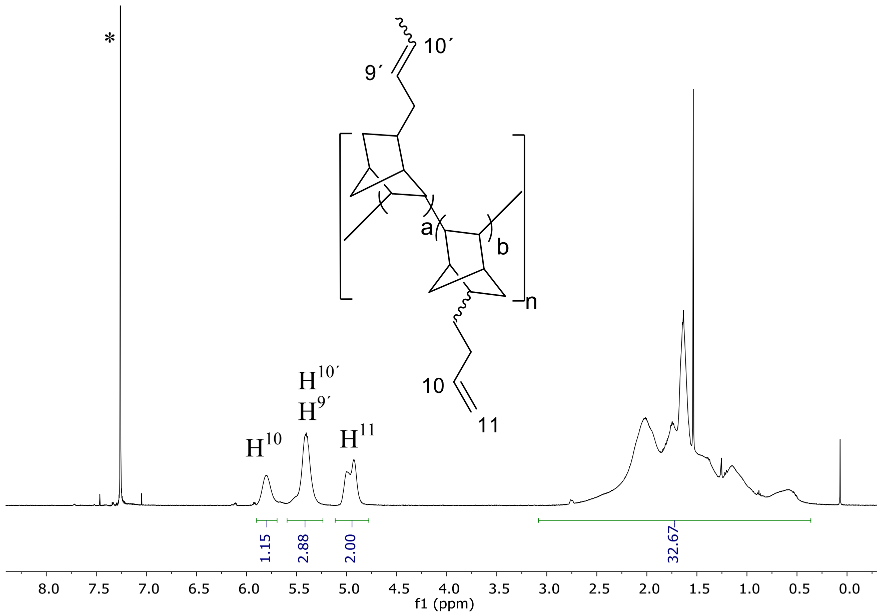


Figure S42. ^{1}H NMR (500.13 MHz, dry CDCl$_3$) of polymer VA-PBNB (mol ratio BNB:Pd = 500:1, M$_w$ = 3.05 x 10^4; entry 5, Table 1) at 298 K synthesized with catalyst **4**-BAr$^F{}_4$. *Signal corresponding to the solvent.

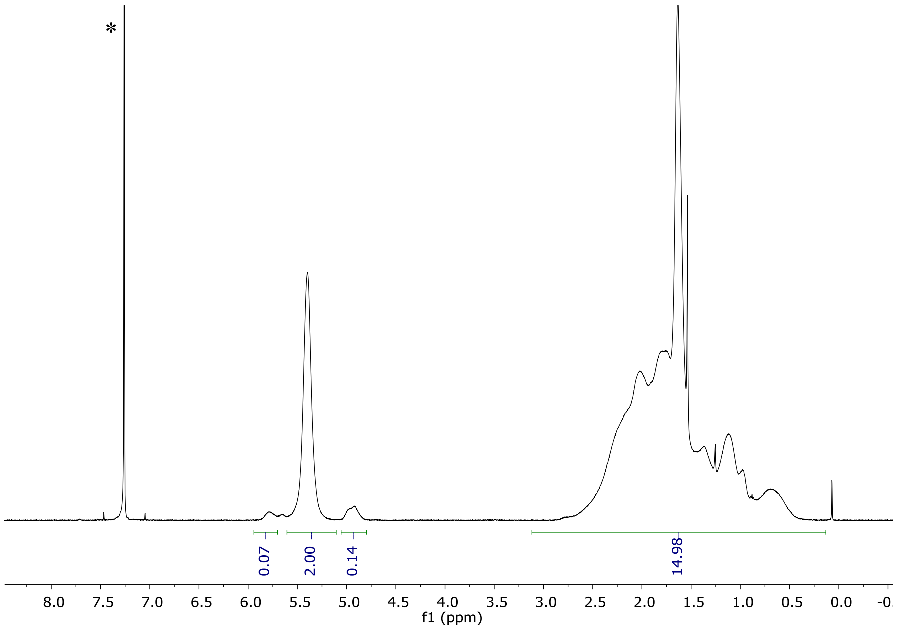


Figure S43. ^{1}H NMR (500.13 MHz, dry $CDCl_3$) of polymer VA-PBNB (mol ratio BNB:Pd = 500:1, $M_w = 4.5 \times 10^4$; entry 6, Table 1) at 298 K synthesized with catalyst **5**-$BAr^F{}_4$. *Signal corresponding to the solvent.

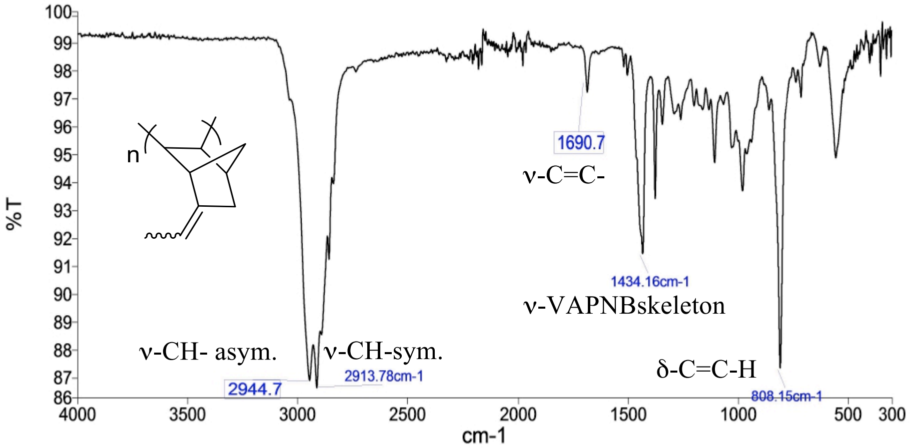


Figure S44. IR spectrum (neat, cm^{-1}) of polymer VA-PENB (mol ratio ENB:Pd = 500:1, $M_w = 1.64 \times 10^4$ Da).

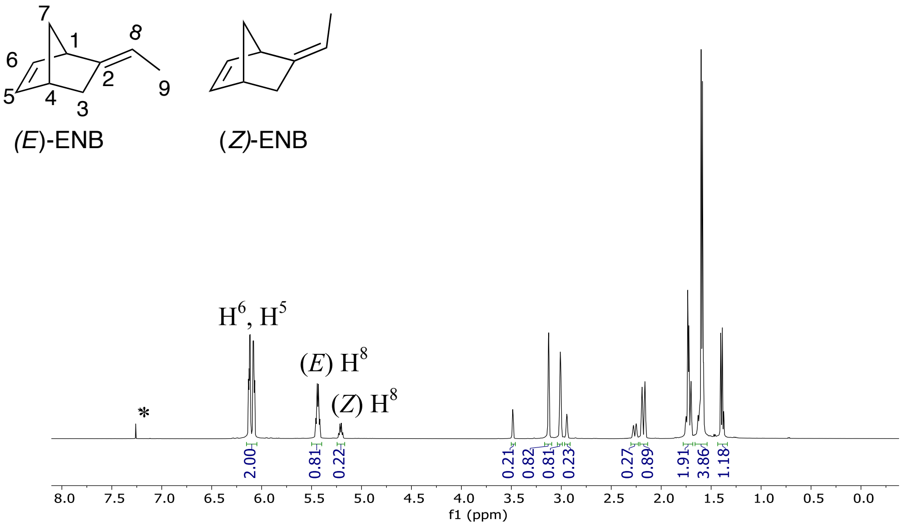


Figure S45. ^{1}H NMR (500.13 MHz, dry $CDCl_3$) of monomer ENB at 298 K. *Signal corresponding to the solvent.

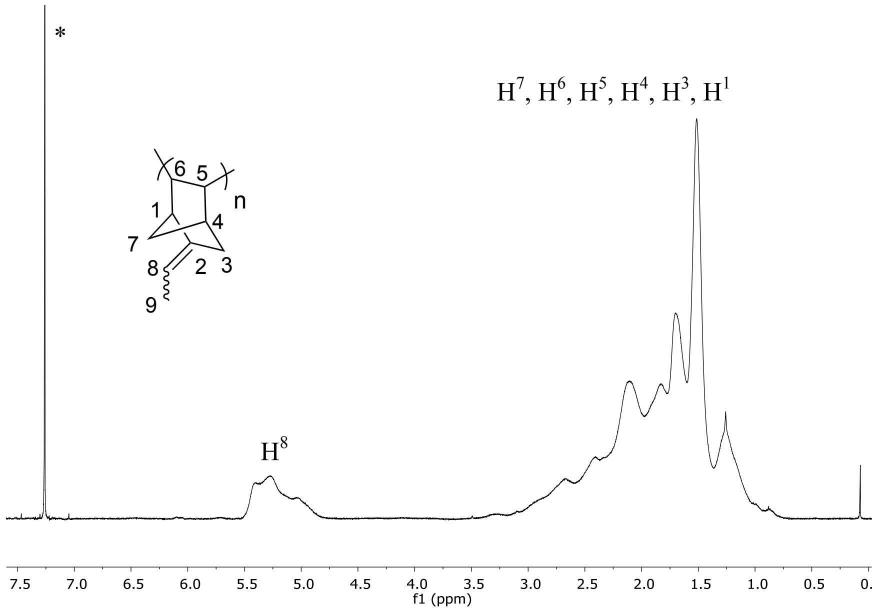


Figure S46. ^{1}H NMR (500.13 MHz, dry $CDCl_3$) of polymer VA-PENB (mol ratio ENB:Pd = 500:1, $M_w = 1.64 \times 10^4$ Da) synthesized with catalyst **4**-BF_4 at 298 K. *Signal corresponding to the solvent.

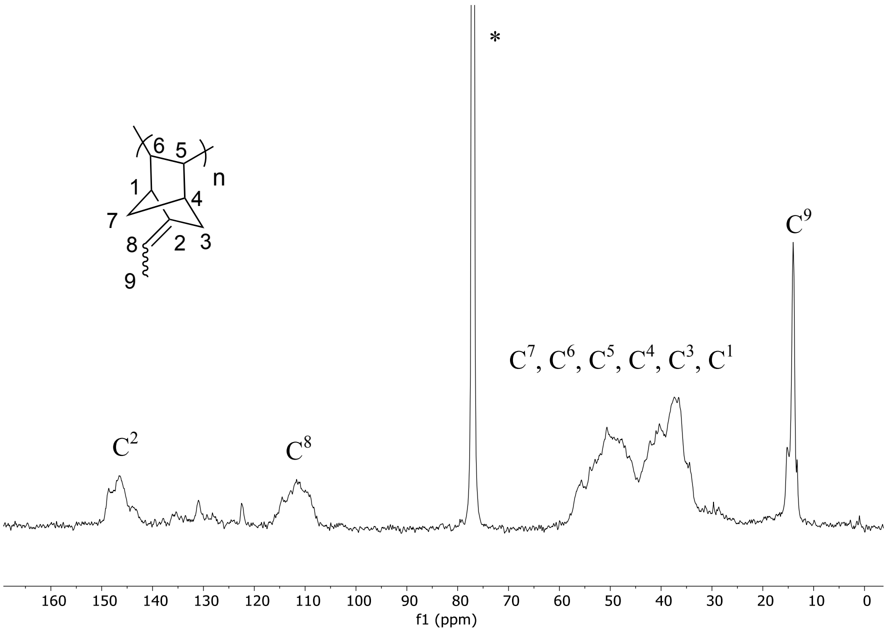


Figure S47. ^{13}C NMR (125.758 MHz, dry $CDCl_3$) of polymer VA-PENB (mol ratio ENB:Pd = 500:1, M_w = 1.64 x 10^4 Da) synthesized with catalyst **4**-BF_4 at 298 K. *Signal corresponding to the solvent.

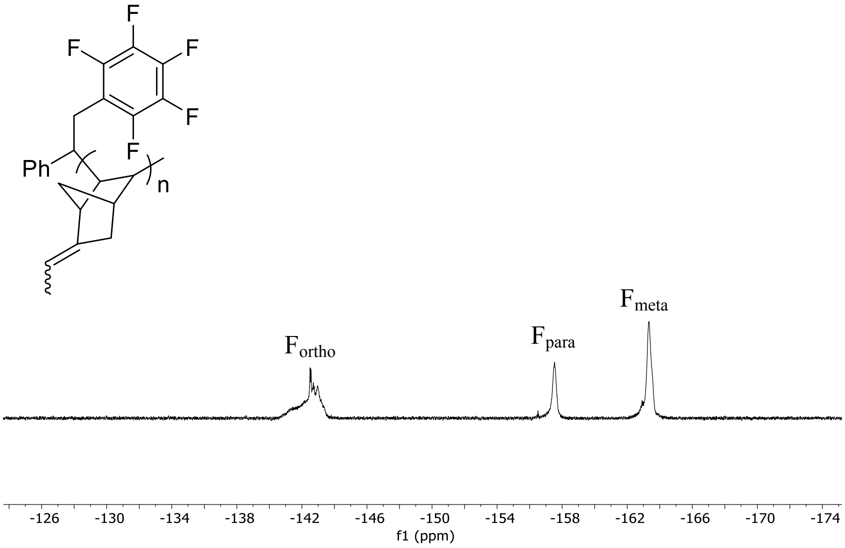


Figure S48. ^{19}F NMR (470.592 MHz, dry $CDCl_3$) of polymer VA-PENB (mol ratio ENB:Pd = 500:1, M_w = 1.64 x 10^4 Da) synthesized with catalyst **4**-BF_4 298 K.

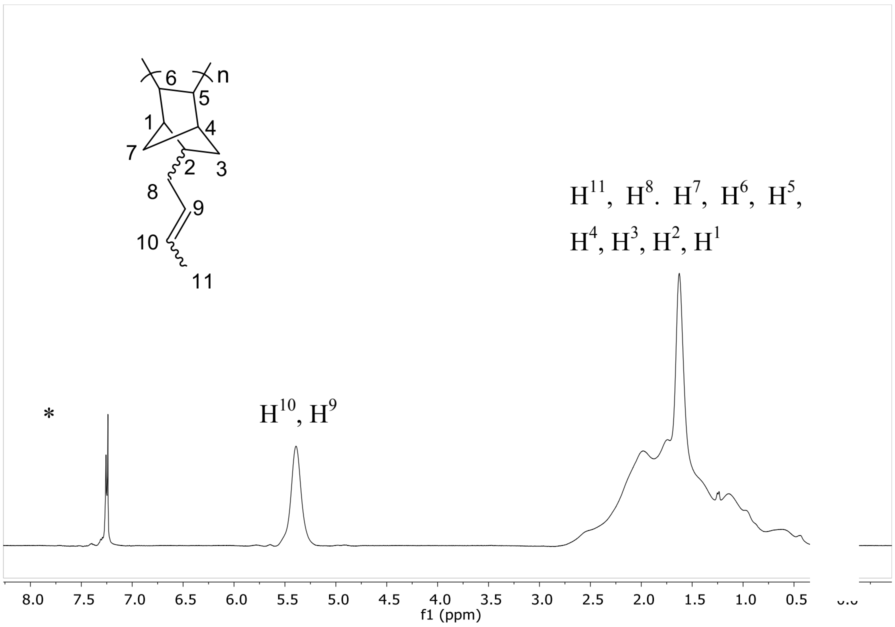


Figure S49. ^{1}H NMR (500.13 MHz, dry CDCl$_3$) of a VA-PBNB (37 mol% internal double bond from isomerization during polymerization) after complete isomerization with complex **4**-BF$_4$ at 298 K. *Signal corresponding to the solvent.

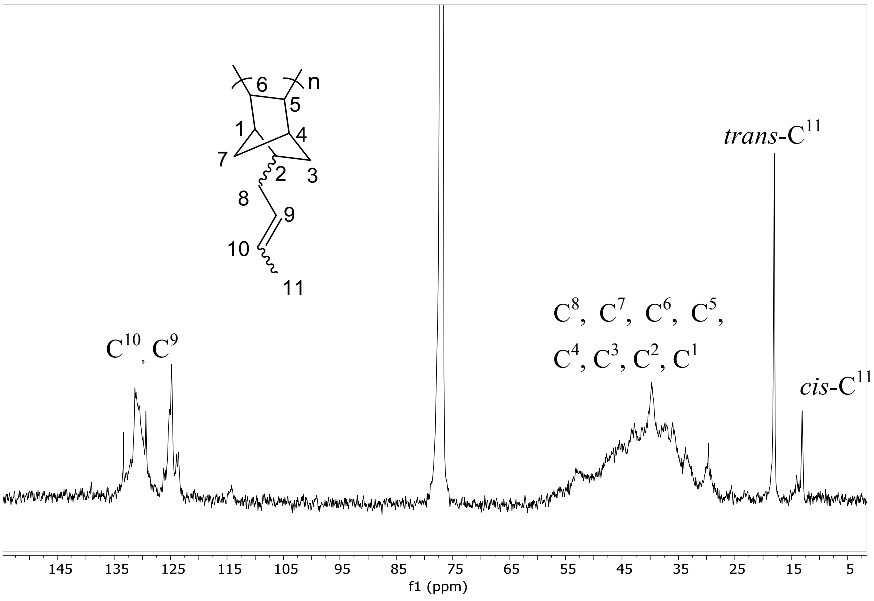


Figure S50. ^{13}C{^{1}H} NMR (125.758 MHz, dry CDCl$_3$) of a VA-PBNB (37 mol % internal double bond from isomerization during polymerization) after complete isomerization with complex **4**-BF$_4$ at 298 K *Signal corresponding to the solvent.

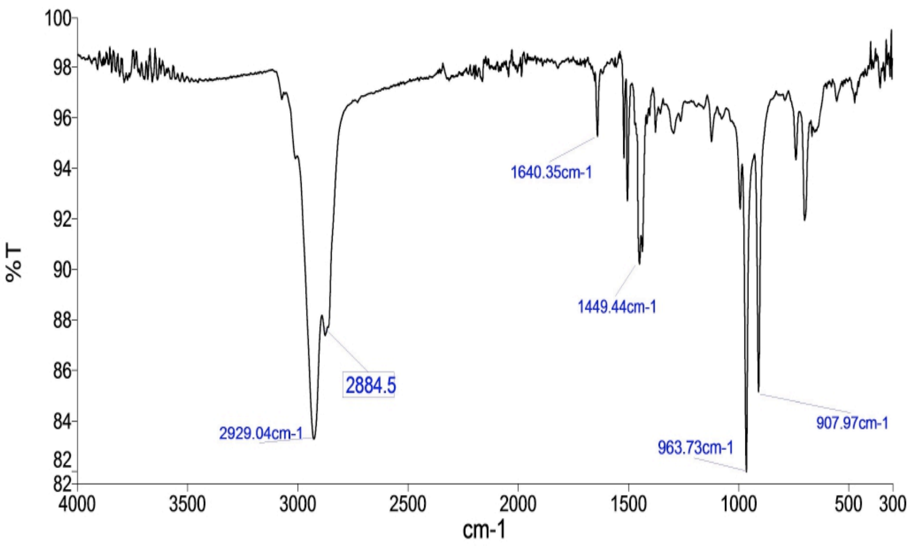


Figure S51. IR Spectrum (neat, cm^{-1}) of a VA-PBNB (37 mol% internal double bond from isomerization during polymerization) after complete isomerization with complex **4**-BF_4.

5. Selected NMR and IR spectra for copolymers VA-PNB-co-VNB and VA-PNB-co-BNB.

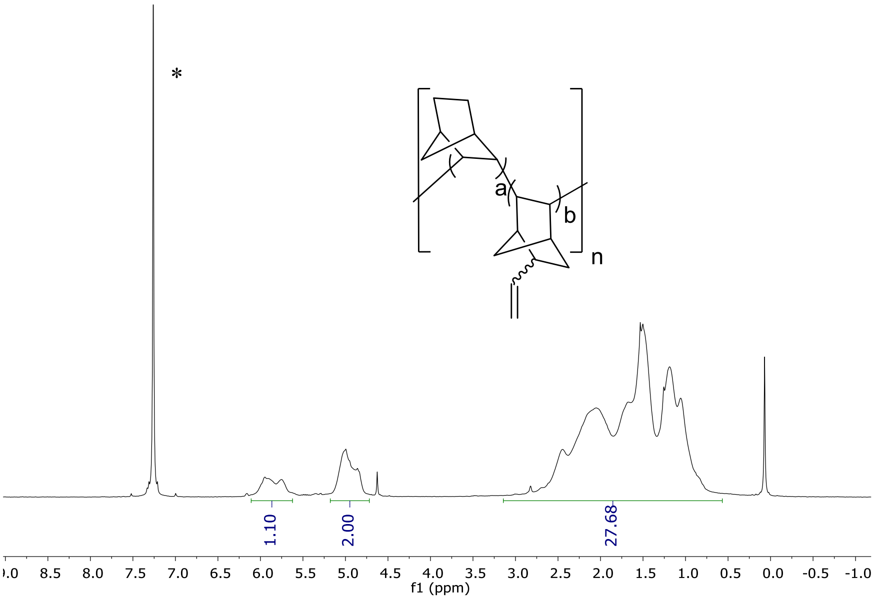


Figure S52. ^{1}H NMR (500.13 MHz, dry $CDCl_3$) of VA-PNB-*co*-VNB synthesized with catalyst **4**-BF_4 (mol ratio NB:VNB:Pd 500:500:1, $M_w = 5.6 \times 10^4$ Da; entry 1, Table 2) at 298 K. *Signal corresponding to the solvent.

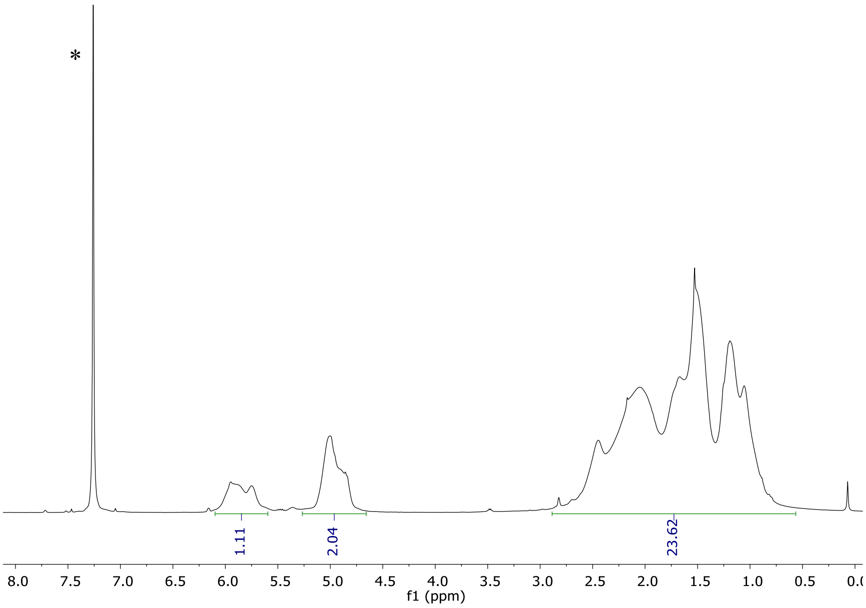


Figure S53. ^{1}H NMR (500.13 MHz, dry $CDCl_3$) of VA-PNB-*co*-VNB synthesized with catalyst **4**-BAr^F_4 (mol ratio NB:VNB:Pd 500:500:1, $M_w = 4.8 \times 10^4$ Da; entry 3, Table 2) at 298 K. *Signal corresponding to the solvent.

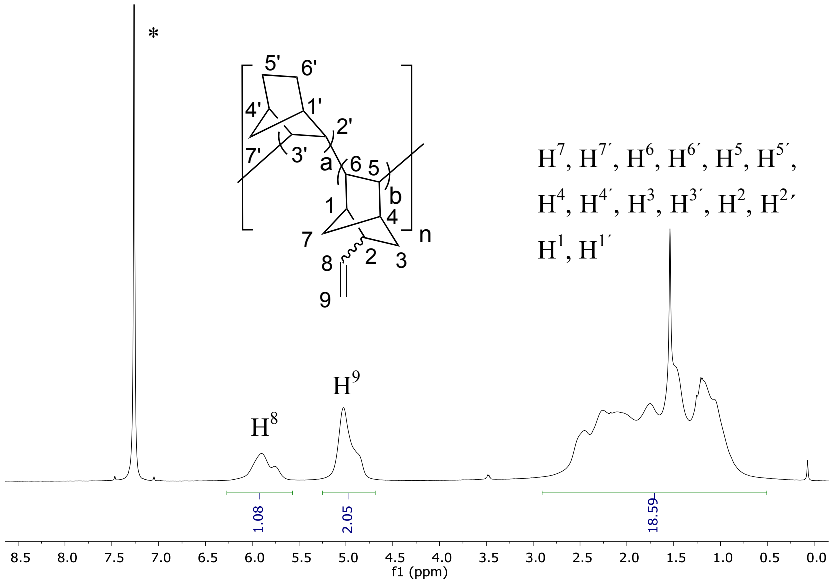


Figure S54. ^{1}H NMR (500.13 MHz, dry CDCl$_3$) of VA-PNB-*co*-VNB synthesized with catalyst **5**-BAr$^F{}_4$ (mol ratio NB:VNB:Pd 500:500:1, $M_w = 4.1 \times 10^5$ Da; entry 4, Table 2) at 298 K. *Signal corresponding to the solvent.

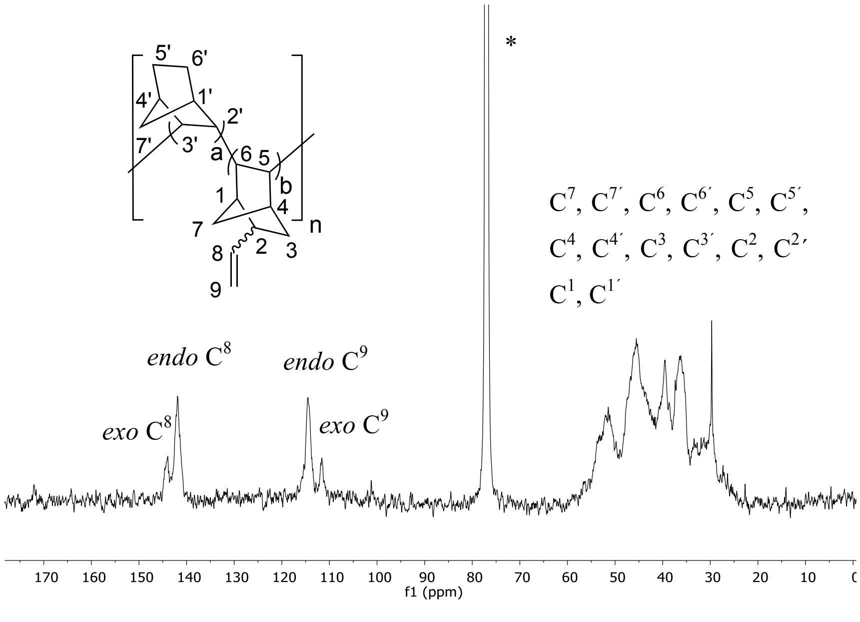


Figure S55. ^{13}C{^{1}H} NMR (125.758 MHz, dry CDCl$_3$) of VA-PNB-*co*-VNB synthesized with catalyst **5**-BAr$^F{}_4$ (mol ratio NB:VNB:Pd 500:500:1, 4.1×10^5 Da; entry 4, Table 2) at 298 K. *Signal corresponding to the solvent.

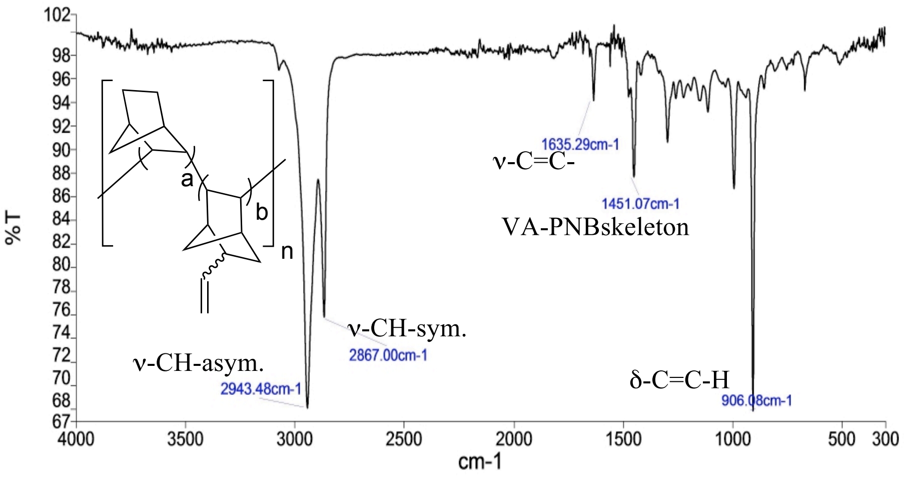


Figure S56. IR spectrum (neat, cm^{-1}) of VA-PNB-*co*-VNB synthesized with catalyst **4**-BF_4 (mol ratio NB:VNB:Pd 1000:1000:1, $M_w = 6.4 \times 10^4$ Da; entry 6, Table 3).

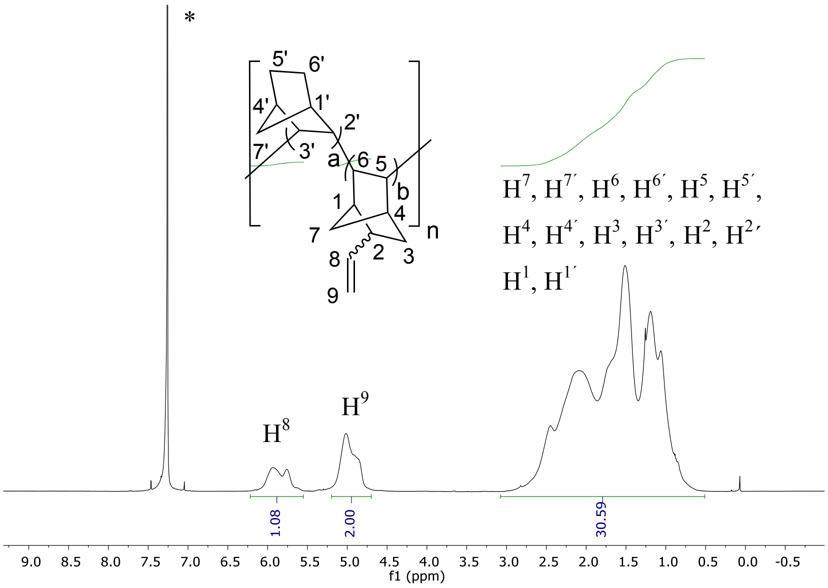


Figure S57. ^1H NMR (500.13 MHz, dry $CDCl_3$) of VA-PNB-*co*-VNB synthesized with catalyst **4**-BF_4 (mol ratio NB:VNB:Pd 1000:1000:1, $M_w = 6.4 \times 10^4$ Da; entry 6, Table 3) at 298 K. *Signal corresponding to the solvent.

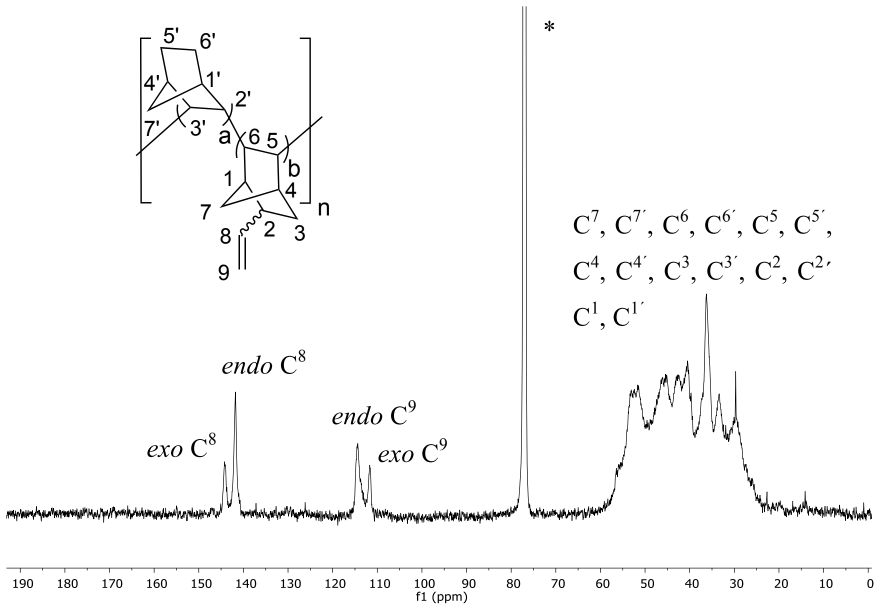


Figure S58. $^{13}C\{^1H\}$ NMR (125.758 MHz, dry $CDCl_3$) of VA-PNB-*co*-VNB synthesized with catalyst **4**-BF_4 (mol ratio NB:VNB:Pd 1000:1000:1, $M_w = 6.4 \times 10^4$ Da; entry 6, Table 3) at 298 K. *Signal corresponding to the solvent.

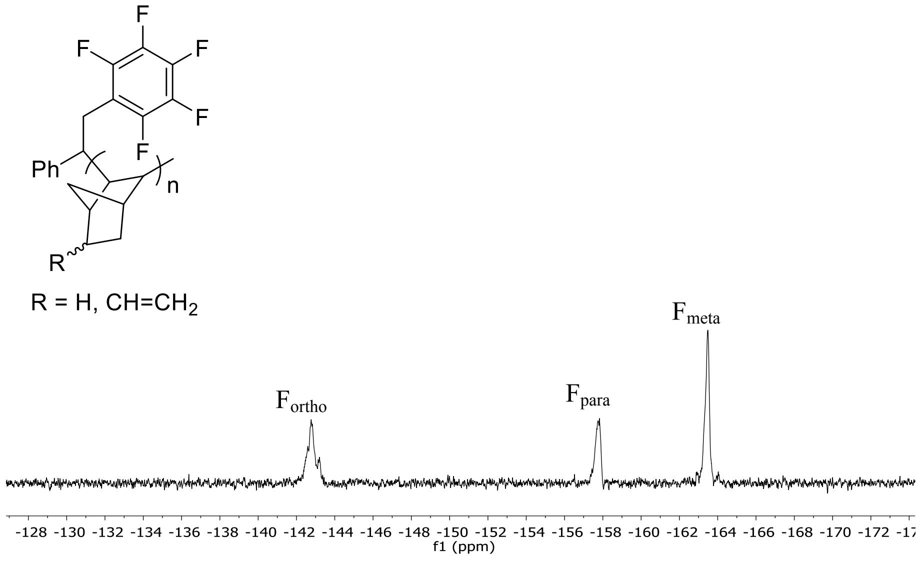


Figure S59. ^{19}F NMR (470.592 MHz, dry $CDCl_3$) of VA-PNB-*co*-VNB synthesized with catalyst **4**-BF_4 (mol ratio NB:VNB:Pd 1000:1000:1, $M_w = 6.4 \times 10^4$ Da; entry 6, Table 3) at 298 K.

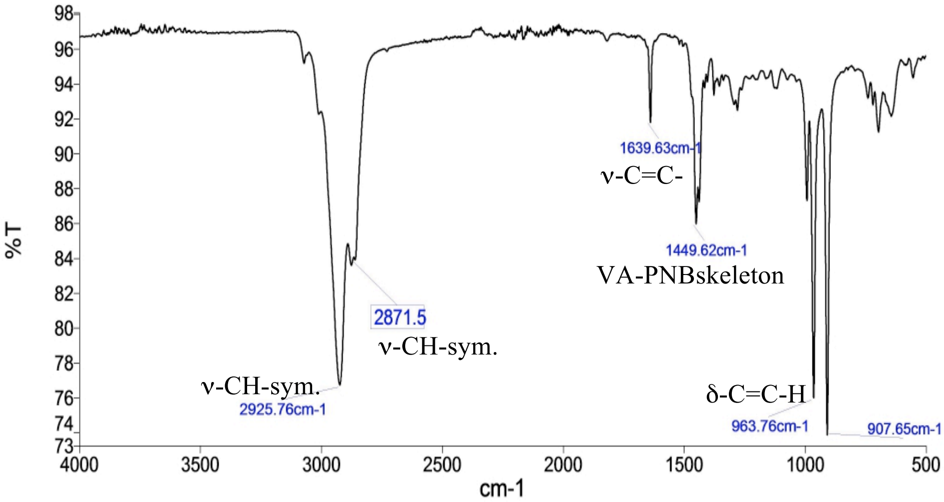


Figure S60. IR spectrum (neat, cm^{-1}) of VA-PNB-*co*-BNB synthesized with catalyst **4**-BF$_4$ (mol ratio NB:BNB:Pd 500:500:1, M$_w$ = 2.99 x 10^4 Da; entry 5, Table 2).

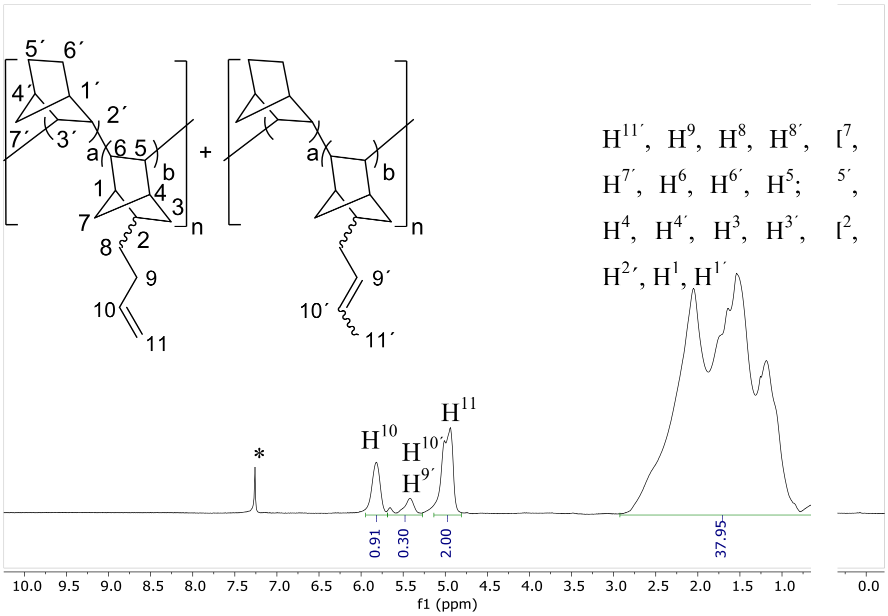


Figure S61. ^{1}H NMR (500.13 MHz, dry CDCl$_3$) of VA-PNB-*co*-BNB synthesized with catalyst **4**-BF$_4$ (mol ratio NB:BNB:Pd 500:500:1, M$_w$ = 2.99 x 10^4 Da; entry 5, Table 2) at 298 K. *Signal corresponding to the solvent.

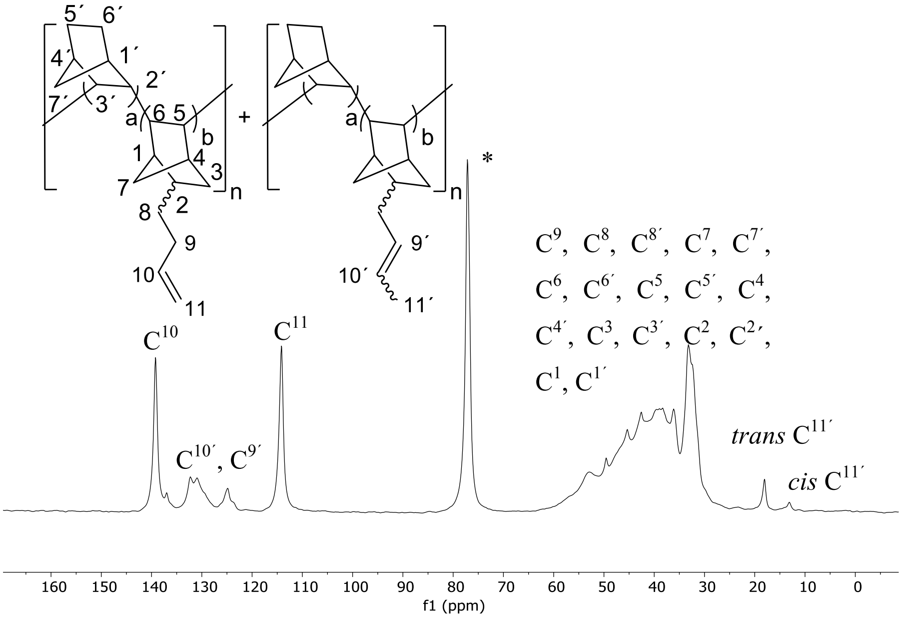


Figure S62. $^{13}C\{^1H\}$ NMR (125.758 MHz, dry $CDCl_3$) of VA-PNB-*co*-BNB synthesized with catalyst **4**-BF_4 (mol ratio NB:BNB:Pd 500:500:1, $M_w = 2.99 \times 10^4$ Da; entry 5, Table 2) at 298 K. *Signal corresponding to the solvent.

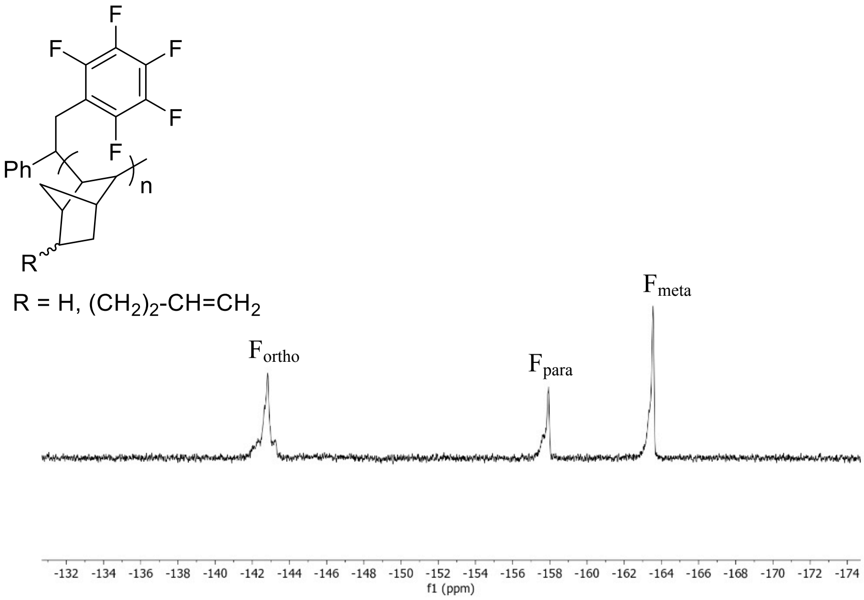


Figure S63. ^{19}F NMR (470.592 MHz, dry $CDCl_3$) of VA-PNB-*co*-BNB synthesized with catalyst **4**-BF_4 (mol ratio NB:BNB:Pd 500:500:1, $M_w = 2.99 \times 10^4$ Da; entry 5, Table 2) at 298 K.

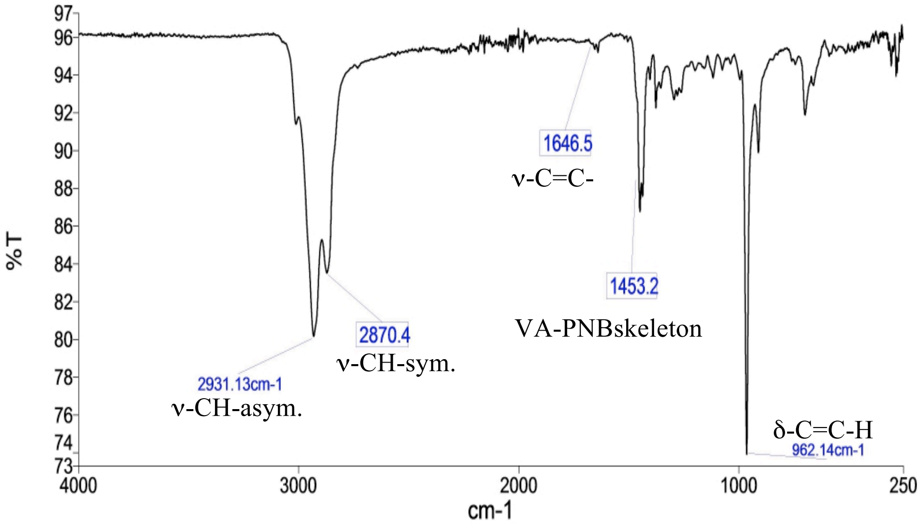


Figure S64. IR spectrum (neat, cm^{-1}) of VA-PNB-*co*-BNB synthesized with catalyst **5**-BAr^F_4 (mol ratio NB:BNB:Pd 500:500:1, $M_w = 1.98 \times 10^5$ Da; entry 6, Table 2).

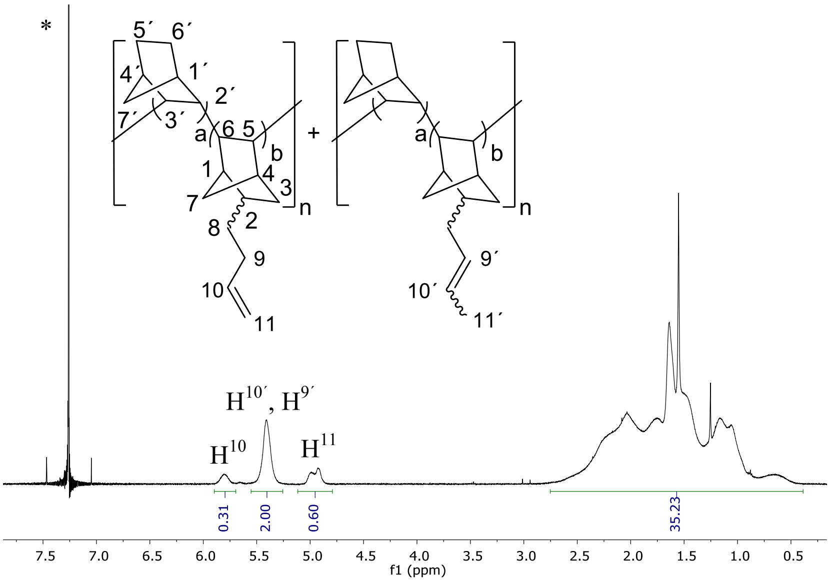


Figure S65. ^1H NMR (500.13 MHz, dry $CDCl_3$) of VA-PNB-*co*-BNB synthesized with catalyst **5**-BAr^F_4 (mol ratio NB:BNB:Pd 500:500:1, $M_w = 1.98 \times 10^5$ Da; entry 6, Table 2) at 298 K. *Signal corresponding to the solvent.

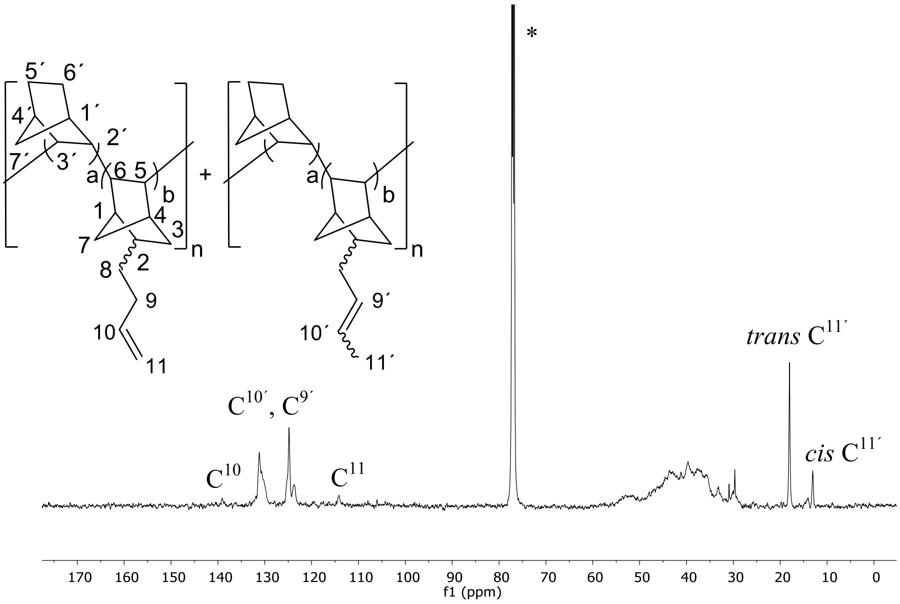


Figure S66. $^{13}C\{^1H\}$ NMR (125.758 MHz, dry $CDCl_3$) of VA-PNB-*co*-BNB synthesized with catalyst **5**-$BAr^F{}_4$ (mol ratio NB:BNB:Pd 500:500:1, $M_w = 1.98 \times 10^5$ Da; entry 6, Table 2) at 298 K. *Signal corresponding to the solvent.

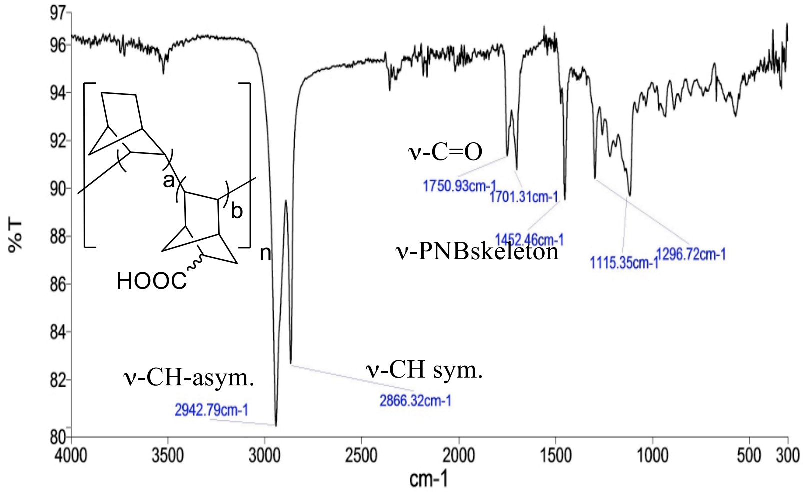


Figure S67. IR Spectrum (neat, cm^{-1}) of VA-PNB-*co*-NBCOOH synthesized with catalyst **4**-BF_4 (mol ratio NB:NBCOOH:Pd 500:500:1).

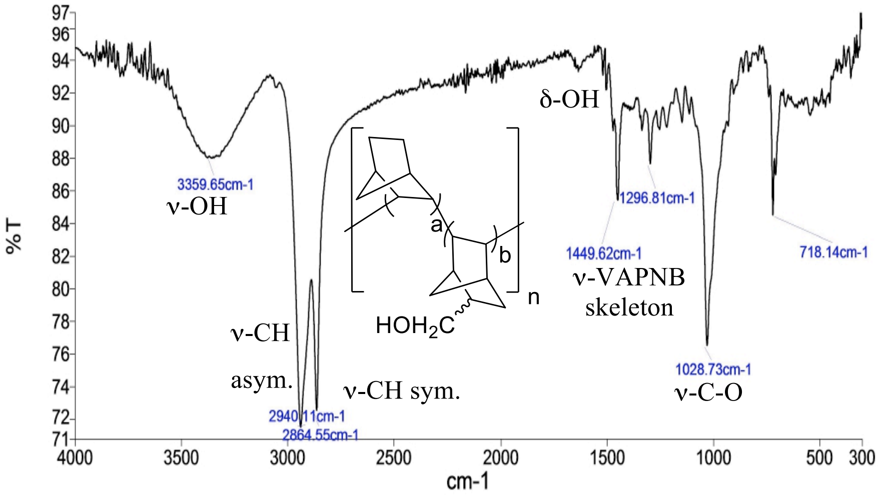


Figure S68. IR Spectrum (neat, cm^{-1}) of VA-PNB-*co*-NBCH$_2$OH synthesized with catalyst **4**-BF$_4$ (mol ratio NB:NBCH$_2$OH:Pd 500:500:1).

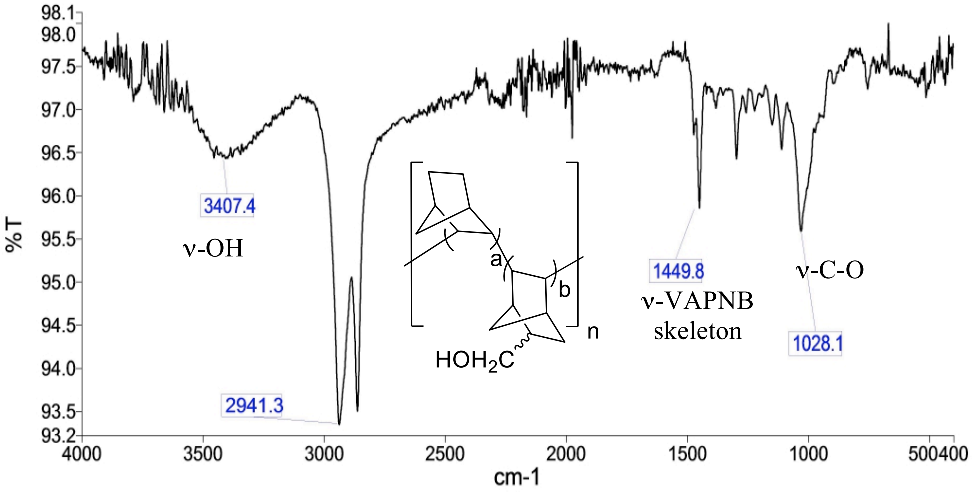


Figure S69. IR Spectrum (neat, cm^{-1}) of VA-PNB-*co*-NBCH$_2$OH synthesized with catalyst **5**-BAr$^F{}_4$ (mol ratio NB:NBCH$_2$OH:Pd 500:500:1).

6. Selected NMR and IR spectra for the functionalization post-polymerization of copolymers VA-PNB-co-VNB and VA-PNB-co-BNB.

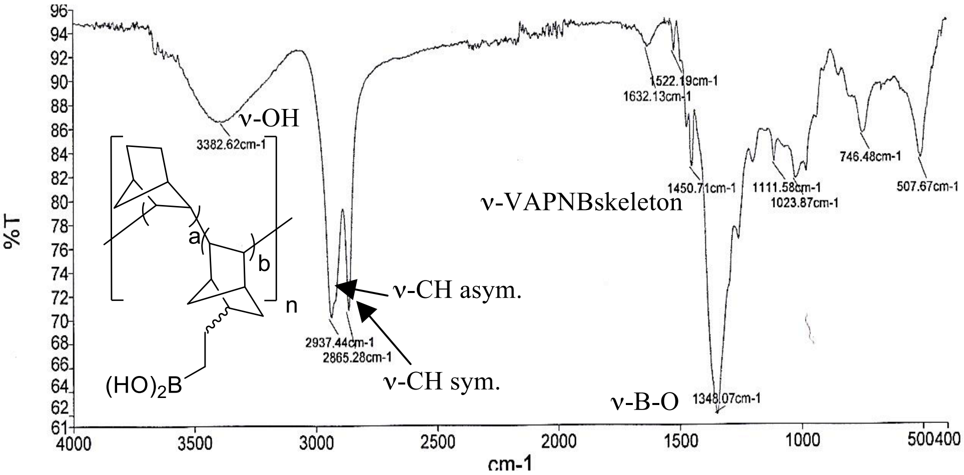


Figure S70. IR spectrum (neat, cm^{-1}) of VA-PNB-*co*-NB$(CH_2)_2B(OH)_2$ (a/b = 2.1) synthesized from VA-PNB-*co*-VNB (a/b = 2.1; $M_w = 6.4 \times 10^4$ Da, Đ (M_w/M_n) = 2.1).

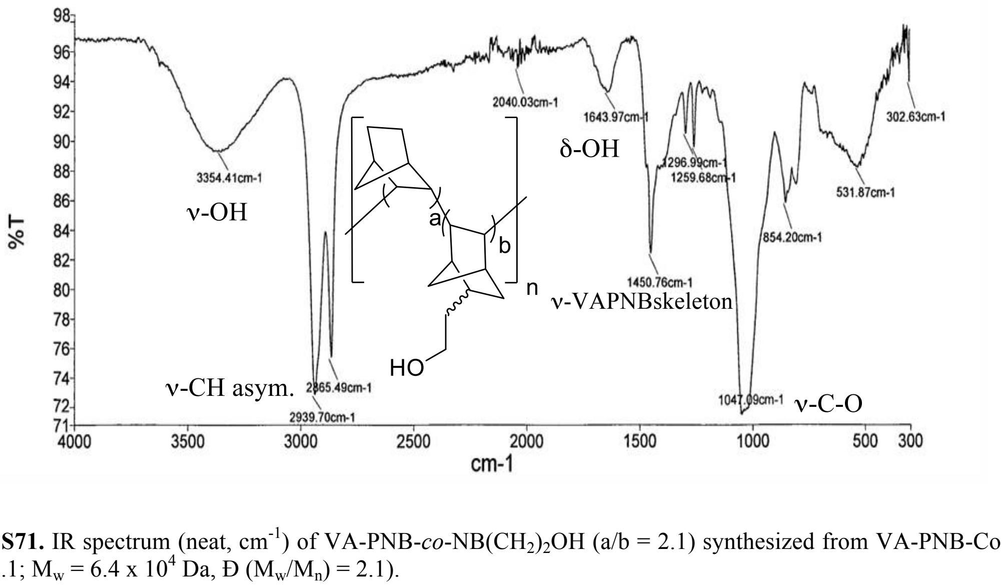


Figure S71. IR spectrum (neat, cm^{-1}) of VA-PNB-*co*-NB$(CH_2)_2OH$ (a/b = 2.1) synthesized from VA-PNB-Co-VNB (a/b = 2.1; $M_w = 6.4 \times 10^4$ Da, Đ (M_w/M_n) = 2.1).

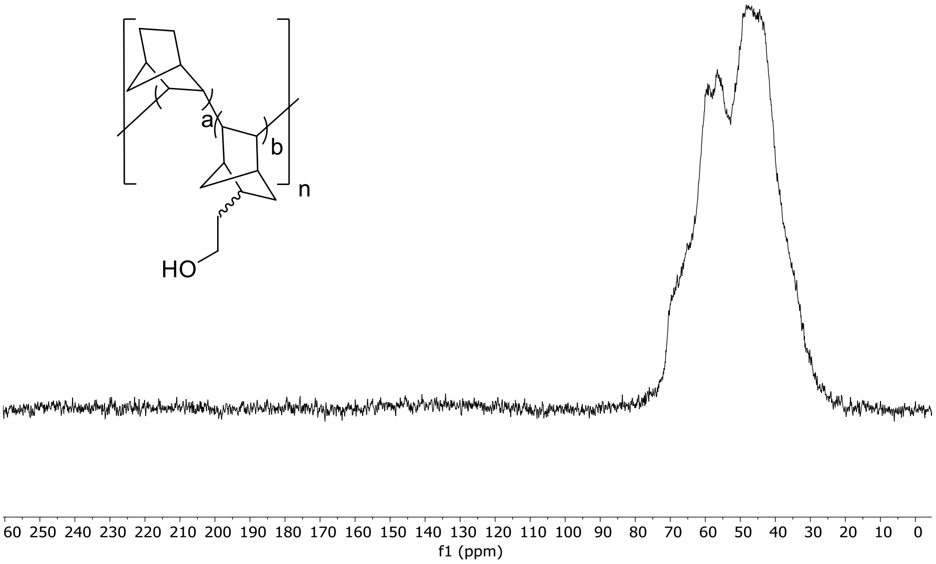


Figure S72. ^{13}C CP-MAS NMR (100.61 MHz) of VA-PNB-*co*-NB$(CH_2)_2$OH (a/b = 2.1) synthesized from VA-PNB-*co*-VNB (a/b = 2.1; $M_w = 6.4 \times 10^4$ Da, Đ $(M_w/M_n) = 2.1$).

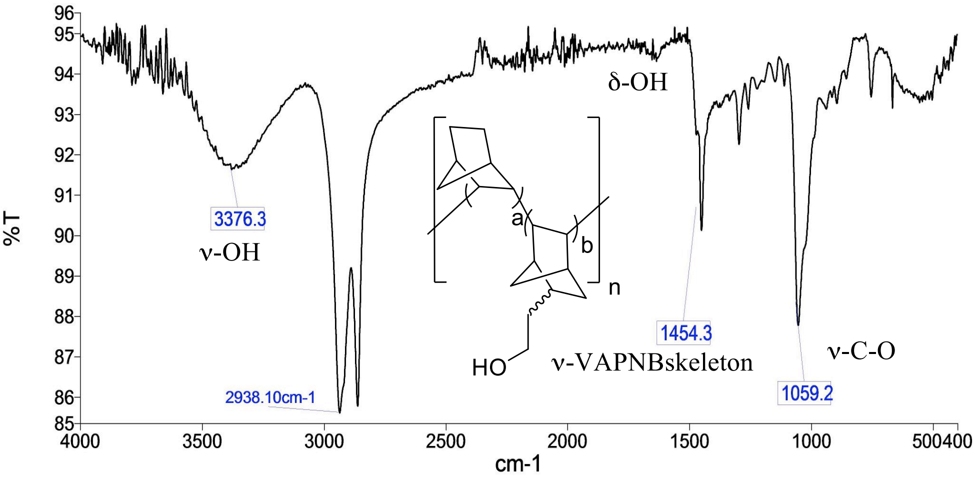


Figure S73. IR spectrum (neat, cm^{-1}) of VA-PNB-*co*-NB$(CH_2)_2$OH (a/b = 1.9) synthesized from VA-PNB-*co*-VNB (a/b = 1.9; $M_w = 1.62 \times 10^6$ Da, Đ $(M_w/M_n) = 3.4$).

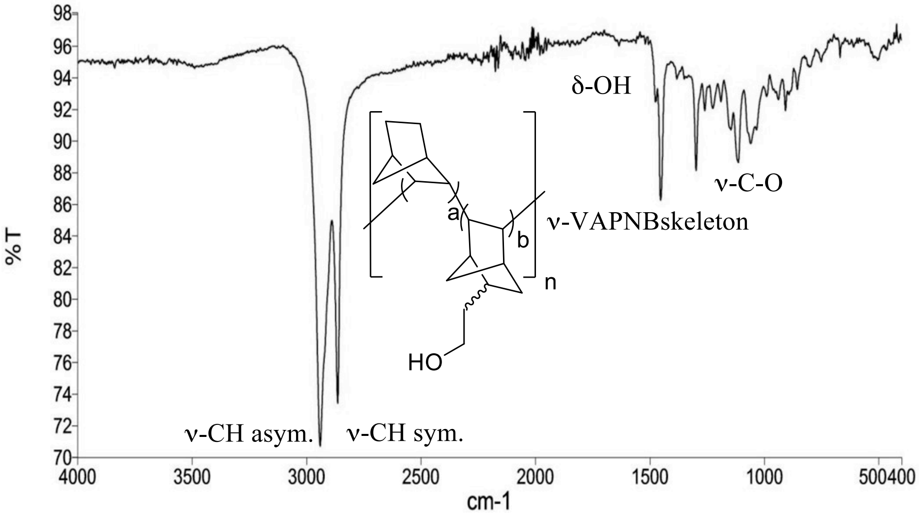


Figure S74. IR spectrum (neat, cm^{-1}) of VA-PNB-*co*-NB$(CH_2)_2$OH synthesized from VA-PNB-*co*-VNB (a/b = 21.5).

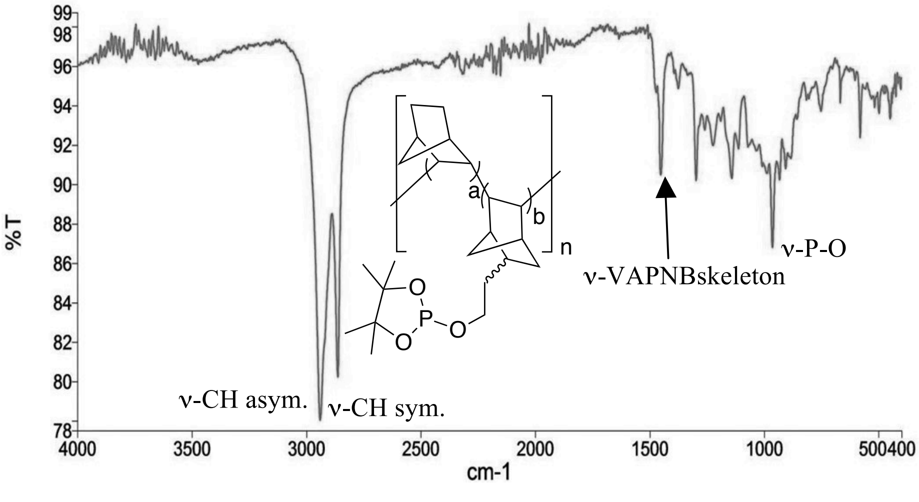


Figure S75. IR spectrum (neat, cm^{-1}) of VA-PNB-*co*-NB$(CH_2)_2$OPpin synthesized from VA-PNB-*co*-NB$(CH_2)_2$OH (a/b = 21.5).

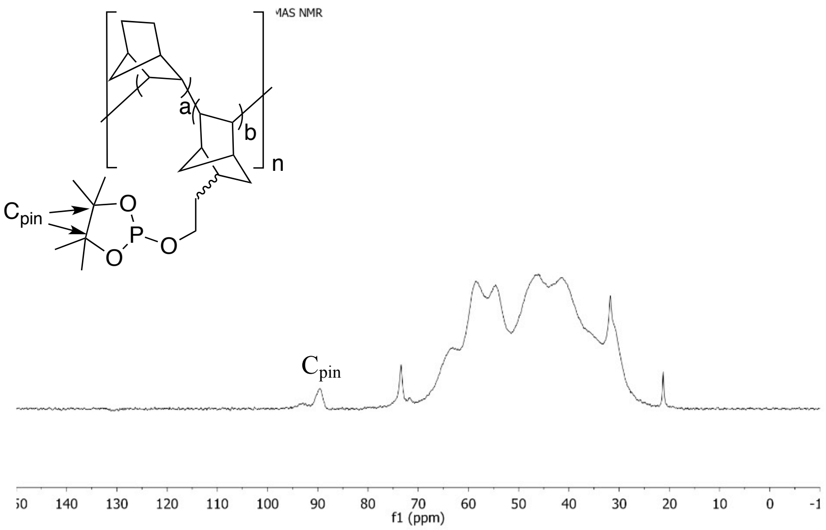


Figure S76. ^{13}C CP-MAS NMR (100.61 MHz) of VA-PNB-*co*-NB$(CH_2)_2$OPpin synthesized from VA-PNB-*co*-NB$(CH_2)_2$OH (a/b = 21.5).

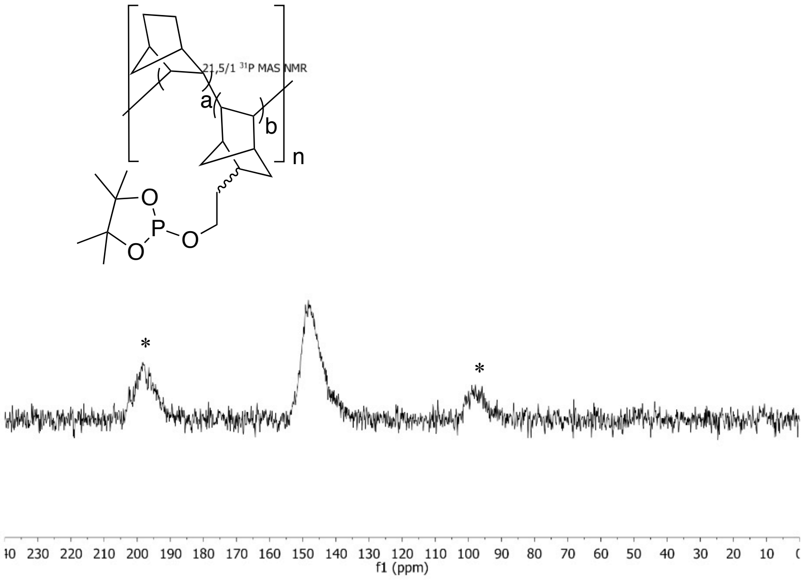


Figure S77. ^{31}P CP-MAS NMR (161.976 MHz) of VA-PNB-Co-NB$(CH_2)_2$OPpin synthesized from VA-PNB-*co*-NB$(CH_2)_2$OH (a/b = 21.5). * Spinning sidebands.

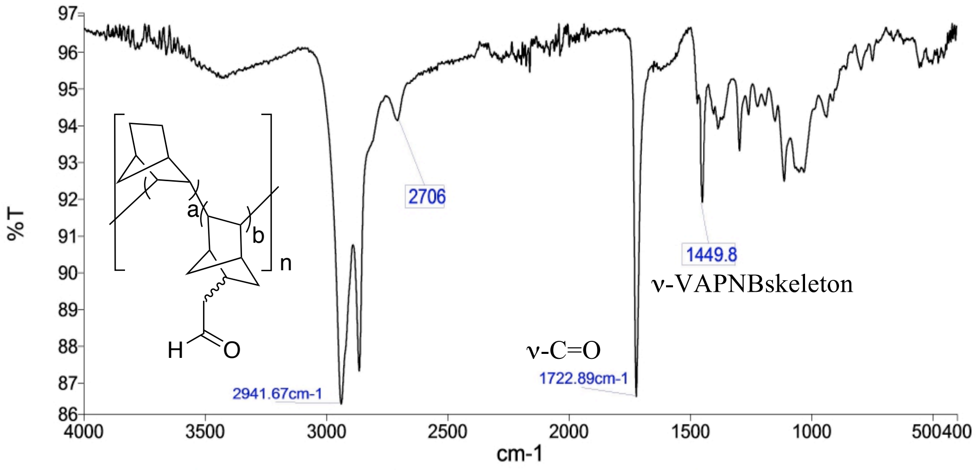


Figure S78. IR spectrum (neat, cm^{-1}) of VA-PNB-*co*-NB$(CH_2)_2$CHO synthesized from VA-PNB-*co*- NB$(CH_2)_2$OH (a/b = 1.9).

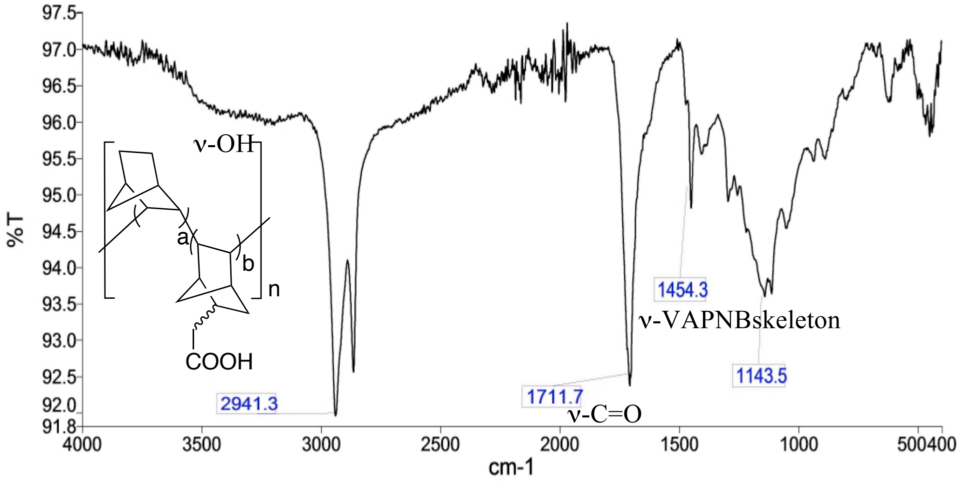


Figure S79. IR spectrum (neat, cm^{-1}) of VA-PNB-*co*-NB$(CH_2)_2$COOH synthesized from VA-PNB-*co*- NB$(CH_2)_2$OH (a/b = 1.9).

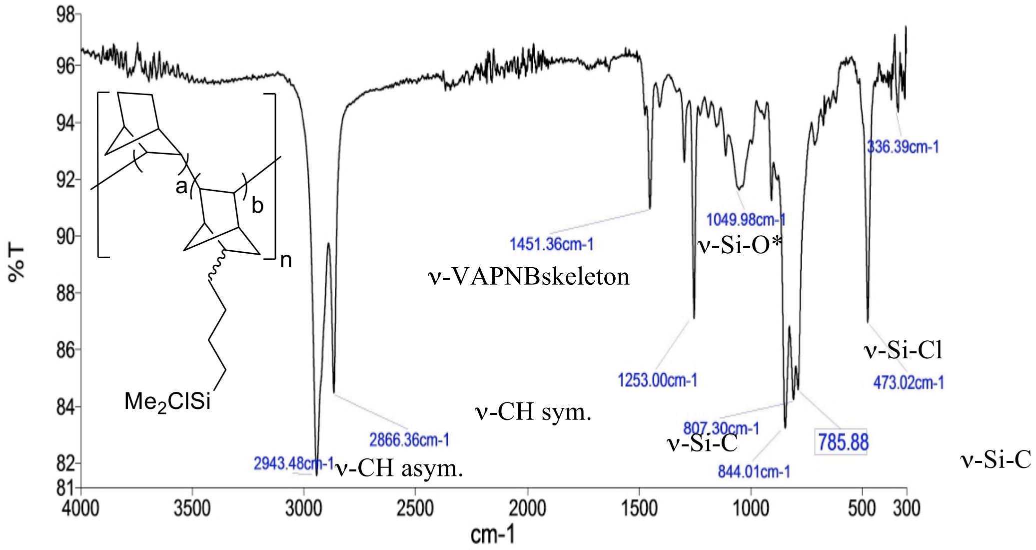


Figure S80. IR spectrum (neat, cm^{-1}) of VA-PNB-*co*-NB$(CH_2)_4$SiClMe$_2$ synthesized from VA-PNB-*co*-BNB (a/b = 2.1, M_w = 2.99 x 10^4 Da, Đ (M_w/M_n) = 1.9). *Absorption due to a small amount of Si-Cl hydrolysis.

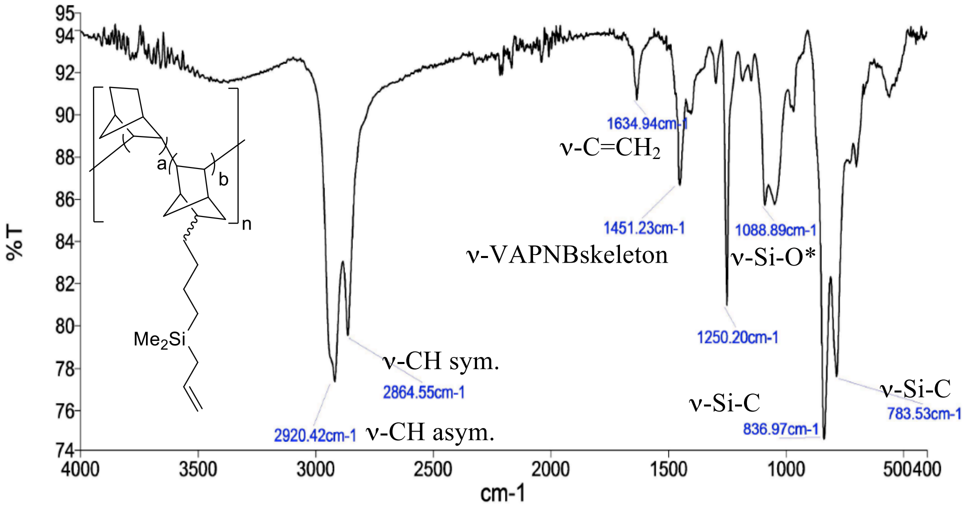


Figure S81. IR spectrum (neat, cm^{-1}) of VA-PNB-*co*-NB$(CH_2)_4$Si(C_3H_5)Me$_2$ synthesized from a VA-PNB-*co*-NB$(CH_2)_4$SiClMe$_2$ (a/b = 2.1). *Absorption due to a small amount hydrolysis in the starting material.

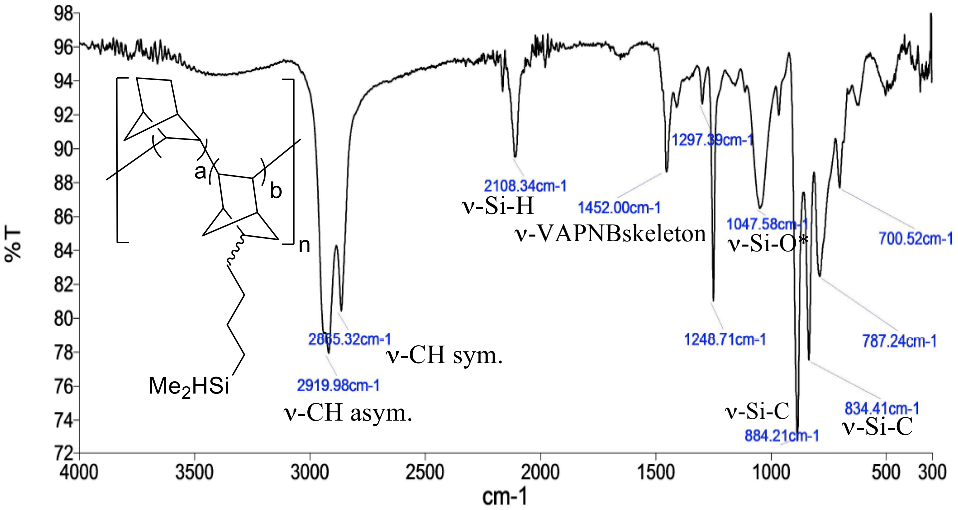


Figure S82. IR spectrum (neat, cm^{-1}) of VA-PNB-*co*-NB$(CH_2)_4$SiHMe$_2$ synthesized from a VA-PNB-*co*-NB$(CH_2)_4$SiClMe$_2$ (a/b = 2.1). *Absorption due to a small amount hydrolysis in the starting material.

7. References

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