Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

A Different Polynorbornene Backbone by Combination of Two Polymer Growth Pathways: Vinylic Addition and Ring Opening via β-C Elimination

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1. Experimental details

1.1- General Considerations.

^1H, $^{13}C\{^1H\}$, 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 293 K unless otherwise noted. Homonuclear (^1H-COSY) and heteronuclear (^1H-^{13}C HSQC and HMBC) 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. Glass transition temperatures (Tg) of polymer samples were measured using differential scanning calorimetry (DSC) on a TA Instruments Q20 DSC on 2-5 mg samples sealed in aluminum pans at a scanning rate of 20 ˚C/min in a N_2 atmosphere. All T_g values were obtained from a second heating scan. Thermogravimetric analysis (TGA) data were recorded using 4–5 mg of sample under a nitrogen atmosphere at 10 ˚C min^{-1} using a TA Instruments Q50 TGA analyser at the PCT-UBU.

CH_2Cl_2 was dried using a solvent purification system SPS PS-MD-5; CH_3CN was dried with CaH_2 and distilled; acetone was dried using $CaSO_4$ and distilled. $CDCl_3$ was dried using neutral activated aluminum oxide.

All catalytic reactions were conducted under N_2 atmosphere employing Schlenk techniques. A solution of norbornene was prepared dissolving the appropriate amount in dry CH_2Cl_2 (3.8 M). The solution was kept it under N_2 at -35 ºC and titrated with $C_6H_3Br_3$ as internal standard.

Norbornene (NB), acetophenone and DMA are commercially available and were purchased from Aldrich and Acros Organics. All commercial reagents and solvents were used as received unless otherwise indicated. *trans*-$[Ni(C_6F_5)_2(SbPh_3)_2]$ (**1**), *trans*-$[Ni(C_6F_5)_2(AsPh_3)_2]$ (**2**) and *trans*-$[Ni(C_6F_5)_2(PPh_3)_2]$ (**3**) were prepared according to the literature methods.[1]

1.2- Experimental procedure for the polymerization of norbornene with complexes [Ni(C_6F_5)$_2$L$_2$].

A representative example for the polymerization experiment in entry 4, Table 1 (main text) is given. The other polymerizations were carried out following the same procedure changing the catalyst or the appropriate reaction condition.

[Ni(C_6F_5)$_2$(AsPh$_3$)$_2$] (**2**) (10 mg, 0.00994 mmol) was placed in a Schlenk tube under N_2. The yellow solid was dissolved in 12.1 mL of dry CH_2Cl_2 and a solution of norbornene in CH_2Cl_2 (0.196 mL, 0.745 mmol; 3.8 M, $[NB]_0$ = 0.061 M) was added to the mixture. After 20 min, a white solid appeared in the yellow solution. The suspension was stirred for 24 h at 25 ºC. MeOH (10 mL) was added to induce the complete precipitation of the polymer and the suspension was stirred for 30 min at room temperature. The white solid was filtered off and washed with MeOH (2 x 10 mL) and Et_2O (5 mL). The white powder was air dried for 6 h (45 mg, 64% yield). NB_{VA}/NB_{RO} = 14.3, M_w = 14071 Da; Đ = 2.3. T_g = 225 ˚C. For characterization of the VA/RO-PNB, see below.

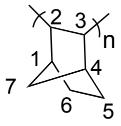
1.3- Experimental procedure for the polymerization of norbornene with complex **2** in the presence of a controlled amount of a coordinating solvent.

A representative procedure for the polymerization experiment in entry 5, Table 2 is given. The other polymerizations were carried out with the same procedure changing the appropriate reaction condition.

[Ni(C_6F_5)$_2$(AsPh$_3$)$_2$] (**2**) (10 mg, 0.00994 mmol) was placed in a Schlenk tube under N_2. The yellow solid was dissolved in 12 mL of dry CH_2Cl_2 followed by the addition of acetophenone (0.185 mL, 1.6 mmol). The solution was stirred for 5 min at room temperature. A solution of norbornene in CH_2Cl_2 (0.196 mL, 0.745 mmol; 3.8 M, $[NB]_0$ = 0.061 M) was added to the mixture. The suspension was stirred 24 h at 25 ºC. After that time, MeOH (10 mL) was added to the suspension to induce the complete precipitation of the polymer and it was stirred for 30 min at room temperature. The white solid was filtered off, washed with MeOH (2 x 10 mL) and Et_2O (5 mL). The white powder was air dried for 6 h (47 mg, 67% yield). NB_{VA}/NB_{RO} = 7.6/1. M_w = 17391 Da; Đ = 1.5. For characterization of the VA/RO-PNB, see below.

1.4- Characterization data for VA-PNB and VA/RO-PNB.

VA-PNB (polymers obtained in entries 1, 3 and 5 in Table 1):[2] ^{1}H NMR (500.13 MHz, δ, $CDCl_3$): 2.5-2 (b, H^1, H^4), 2-0.61 (b, H^7, H^6, H^5, H^3, H^2). $^{13}C\{^1H\}$ NMR (125.66 MHz, δ, $CDCl_3$): 55-50 (C^3, C^2), 48-38 (C^4, C^1), 37-35 (C^7), 32.5-28 (C^6, C^5). ^{19}F NMR (470.592 MHz, δ, $CDCl_3$): -133.4, -137.7, -140 (multiple signals, F_{ortho}), -158.1, -158.3, -160.3 (multiple signals, F_{para}), -156.1 (b, F_{meta}).



VA-PNB

VA/RO-PNBs

The amount of NB_{ROs} or ring-opened units was quantified by ^{1}H NMR using the following equation for the mol ratio between NB_{VA} and NB_{RO} units: NB_{VA}/NB_{RO}= [IntA-((IntB/2) x 8)]/10(IntB/2) where IntA = integral value of the aliphatic region and IntB = integral value of the 5.8-5.4 region (cyclohexene double bond). An example is shown in Figure S1 and the equation is: NB_{VA}/NB_{RO}= [151.62-((2/2) x 8)]/10(2/2) = 14.3. From this mol ratio the percentage of NB_{RO} units can be deduced.

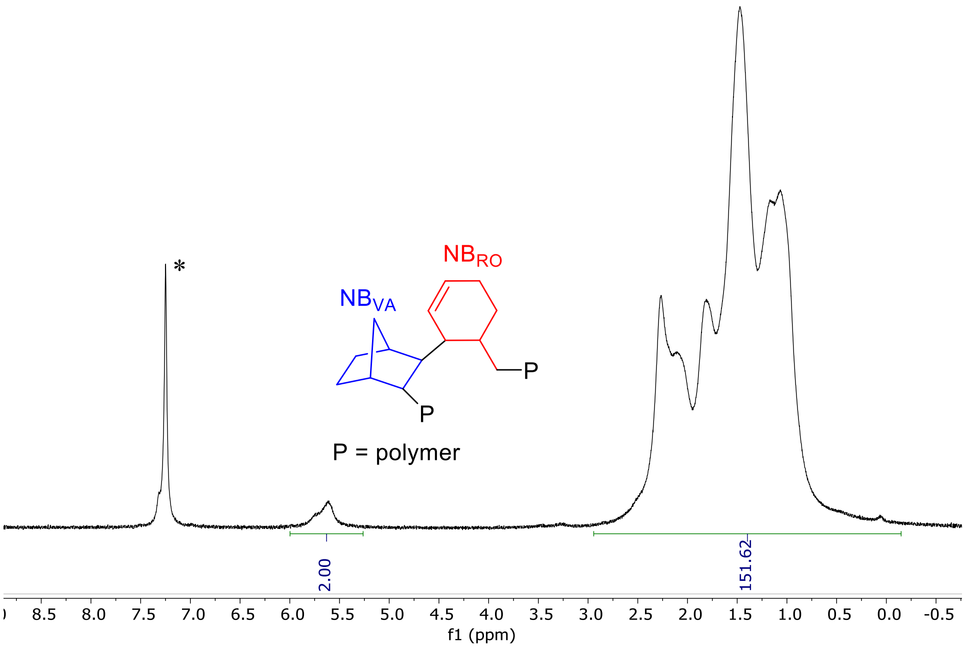
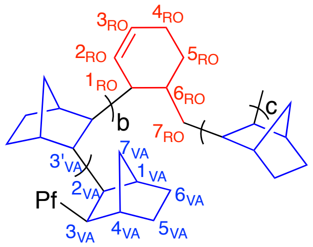


Figure S1. ^{1}H NMR in dry $CDCl_3$ of a VA/RO-PNB synthesized in the conditions of entry 4, Table 1. Mol ratio NB_{VA}/NB_{RO} = 14.3/1. *Signal corresponding to the solvent.

VA/RO-PNB (entry 5, Table 2): NB_{VA}/NB_{RO} = 7.6/1. M_w = 17.391; Đ = 1.5. ^1H NMR (500.13 MHz, δ, $CDCl_3$): 5.8-5.4 (b, H^{3RO}, H^{2RO}), 2.5-1.5 (b, H^{6RO}, H^{5RO}, H^{4RO}, H^{4VA}, H^{3VA}, $H^{3'VA}$, H^{2VA}, H^{1VA}, H^{1RO}), 1.5-0.55 (b, H^{7RO}, H^{7VA}, H^{6VA}, H^{5VA}). $^{13}C\{^1H\}$ NMR (125.66 MHz, δ, $CDCl_3$): 132-125 (C^{3RO}, C^{2RO}), 54.3-36.6 (C^{6RO}, C^{4VA}, C^{3VA}, $C^{3'VA}$, C^{2VA}, C^{1VA}, C^{1RO}), 36.3-28 (C^{7VA}, C^{7RO}, C^{6VA}, C^{5VA}), 25.4-22.6 (C^{5RO}, C^{4RO}). ^{19}F NMR (470.592 MHz, δ, $CDCl_3$): -133 to -143 (multiple signals, F_{ortho}), -157 to -158.5 (b, F_{para}), -162 to -163.5 (b, F_{meta}).

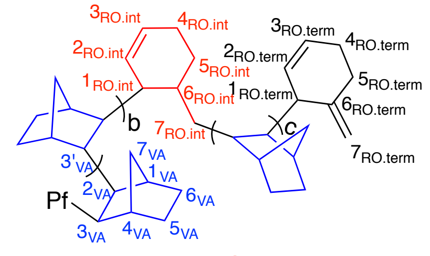


VA/RO-PNB

Pf = C_6F_5

1.5- Synthesis of a short VA/RO-PNB (NB_{VA}/NB_{RO} = 2.3/1).

$[Ni(C_6F_5)_2(AsPh_3)_2]$ (**2**, 100 mg, 0.0995 mmol) was placed in a Schlenk tube under N_2. The yellow solid was dissolved in 4 mL of dry CH_2Cl_2 followed by the addition of acetophenone (0.174 mL, 1.49 mmol). The yellow solution was stirred for 5 min at room temperature. A solution of norbornene (0.13 mL, 0.494 mmol; 3.8 M; $[NB]_o$ = 0.115 M) was added to the mixture and the solution was stirred for 24 h at 25 ºC. MeOH (10 mL) was added to the solution and the resulting suspension was stirred for 20 min at room temperature. The white solid was filtered off, washed with MeOH (2 x 5 mL) and Et_2O (5 mL). The white powder was air dried for 6 h (30 mg, 64% yield). NB_{VA}/NB_{RO} = 2.3/1. M_w = 2270; Đ = 1.5. ^1H NMR (500.13 MHz, δ, $CDCl_3$): 5.8-5.25 (b, $H^{3RO.int}$, $H^{3RO.term}$, $H^{2RO.int}$, $H^{2RO.term}$), 4.75, 4.74 ($H^{7RO.term}$), 3.25 (H^{3VA}), 2.7-1.6 (b, $H^{6RO.int}$, $H^{5RO.int}$, $H^{5RO.term}$, $H^{4RO.int}$, $H^{4RO.term}$, H^{4VA}, $H^{3'VA}$, H^{2VA}, H^{1VA}, $H^{1RO.int}$, $H^{1RO.term}$), 1.6-0.55 (b, H^{7VA}, H^{6VA}, H^{5VA}, $H^{7RO.int}$). $^{13}C\{^1H\}$ NMR (125.66 MHz, δ, $CDCl_3$): 146.9-143.9 (C_{ortho}, C_6F_5), 139.9-135.8 ($C_{meta,para}$, C_6F_5), 132-125 ($C^{3RO.int}$, $C^{3RO.term}$, $C^{2RO.int}$, $C^{2RO.term}$), 116.75 (C_{ipso} C_6F_5), 107.2 ($C^{7RO.term}$), 54.3-36.6 ($C^{6RO.int}$, C^{4VA}, C^{3VA}, $C^{3'VA}$, C^{2VA}, C^{1VA}, $C^{1RO.int}$, $C^{1RO.term}$), 36.6-26.6 ($C^{7RO.int}$, C^{7VA}, C^{6VA}, C^{5VA}, $C^{5RO.term}$, $C^{4RO.term}$), 25.4-22.6 ($C^{5RO.int}$, $C^{4RO.int}$). ^{19}F NMR (500.13 MHz, δ, $CDCl_3$): -132 to -140 (multiple signals, F_{ortho}), -157 to -158.5 (b, F_{para}), -162 to -163.5 (b, F_{meta}).



VA/RO-PNB

Pf = C_6F_5

1.6- Polymerization experiments quenched by carbonylation.

*VA/RO-polymerization of norbornene using a mol ratio NB:**2**:acetophenone = 5:1:15).* $[Ni(C_6F_5)_2(AsPh_3)_2]$ (**2**, 160 mg, 0.159 mmol) was placed in a Schlenk tube under N_2. The yellow solid was dissolved in 8.1 mL of dry CH_2Cl_2 followed by the addition of acetophenone (0.278 mL, 2.38 mmol). The yellow solution was stirred for 5 min at room temperature. A solution of norbornene (0.205 mL, 0.8 mmol; 3.9 M; $[NB]_0$ = 0.093 M) was added to the mixture and the yellow solution was stirred for 1.5 h at 25 °C. After this time, a solution of NaOMe (10 mg, 0.165 mmol) in 4 mL of dry MeOH was added and CO was bubbled through the suspension for 40 min. 10 mL of MeOH was added to the suspension to ensure the complete precipitation of the polymer and it was stirred for 20 min at room temperature. The greyish solid was filtered off, washed with MeOH (2 x 5 mL) and Et_2O (5 mL). The polymer was recrystallized by dissolving it in 5 mL of $CHCl_3$, adding activated carbon to the solution and filtering it through a plot of kieselguhr. MeOH (15 mL) was added to the colorless filtrate to induce the precipitation of the polymer. The white solid was filtered off, washed with MeOH (2 x 5 mL) and Et_2O (5 mL) and air dried for 6 h (40 mg, 53% yield). NB_{VA}/NB_{RO} = 3.7/1. M_w = 3895 Da; Đ = 1.6.

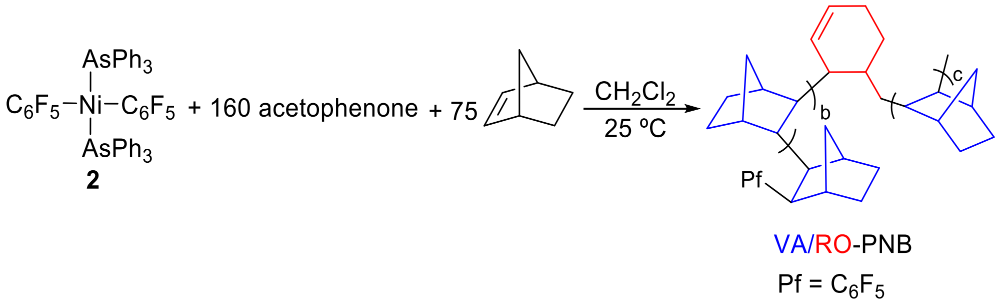
The polymer obtained is a short VA/RO-PNB, which showed the same NMR spectra detailed above with additional characteristic signals of the -COOMe termination moiety: 3.68 ppm in the ^1H NMR (Figure S11) and a carbonyl signal at 174.1 (*C*OOMe) as a cross peak in the long range ^1H-^{13}C gHMBCAD NMR experiment.

A polymerization carried out under the conditions of Table 1, entry 1 was quenched after 15 min in a similar way as described above. The -COOMe termination group was also visible in the ^{1}H NMR of the polymer (3.68 ppm, Figure S16).

1.7- Dependence of the formation of ring opened units in the chain of VA/RO-PNB on the conversion and the initial NB concentration.

[Ni(C_6F_5)$_2$(AsPh$_3$)$_2$] (**2**) (10 mg, 0.00994 mmol) was placed in a Schlenk tube under N_2. The yellow solid was dissolved in 12 mL of dry CH_2Cl_2 followed by the addition of acetophenone (0.185 mL, 1.6 mmol) and a solution of norbornene in CH_2Cl_2 (0.196 mL, 0.745 mmol; 3.8 M, $[NB]_0$ = 0.061 M). The polymerization was quenched by adding 10 mL of MeOH to the reaction mixture at the times collected in Table S1. The solid was filtered off and washed with MeOH (2 x 10 mL) and Et_2O (5 mL). The white powder was air dried for 6 h.

Table S1. Polymerization of norbornene with the combination NB:**2**:acetophenone (mol ratio 75:1:160) at different reaction times.[a]

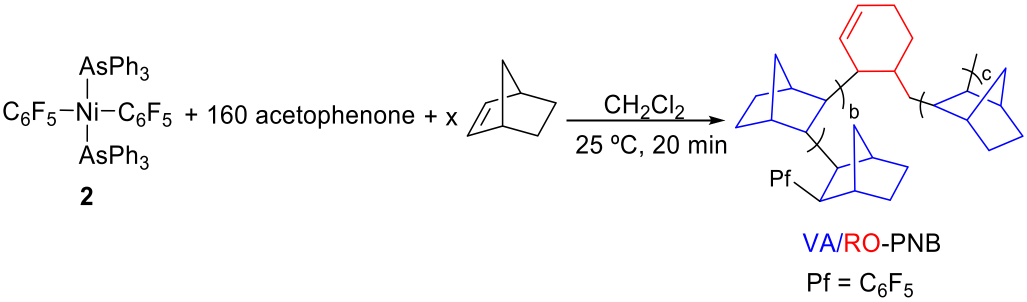


Entry	Time (min)	NB_{VA}/NB_{RO}[b]	% NB_{RO}[c]	Yield (%)	M_n[d]	M_w[d]
1	5	32.3/1	3.0%	3.5%	5788	6688
2	10	15.7/1	6.0%	10.6%	6044	7261
3	20	12.7/1	7.3%	19.8%	6242	7398
4	40	10.0/1	9.1%	38.6%	6949	8457
5	120	7.5/1	11.8%	60.9%	8827	11829

a) Reaction conditions: $[NB]_0$ = 0.061 M, mol ratio NB:Ni:acetophenone = 75:1:160, CH_2Cl_2, 25 ºC, under N_2. b) The mol ratio NB_{VA}/NB_{RO} was calculated by comparison of the integral of the ^{1}H NMR signals (olefinic vs aliphatic) of a solution of the polymer in dry $CDCl_3$ (see above, Figure S1). c) The molar % was calculated from the mol ratio NB_{VA}/NB_{RO}. d) M_n and M_w (Da) determined by GPC in $CHCl_3$ using polystyrene standards.

The polymerization experiments with different initial concentrations of norbornene were carried out in the same way described above, using an initial concentration of catalyst $[\mathbf{2}]_0 = 7.6 \times 10^{-4}$ M and the corresponding initial concentration of NB. The polymerization reaction time was 20 min. The results are collected in Table S2.

Table S2. Polymerization of norbornene with the combination NB:**2**:acetophenone (mol ratio 75:1:160) using different initial norbornene concentrations.[a]



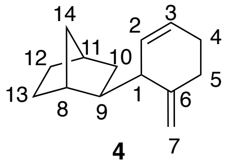
Entry	$[NB]_0$ (M)	NB_{VA}/NB_{RO}[b]	% NB_{RO}[c]	Yield
1	0.142	45.4/1	2.15%	67%
2	0.114	29.2/1	3.3%	45.7%
3	0.0856	18.3/1	5.2%	32.4%
4	0.057	12.5/1	7.4%	23.1%
5	0.028	8.1/1	11%	10.5%
6	0.015	4.8/1	17.2%	1.4%

a) Reaction conditions: $[\mathbf{2}]_0 = 7.6 \times 10^{-4}$M, mol ratio Ni:acetophenone = 1:160, 20 min, CH_2Cl_2, 25 ºC, under N_2. b) The mol ratio NB_{VA}/NB_{RO} was calculated by comparison of the integral of the ^{1}H NMR signals (olefinic vs aliphatic) of a solution of the polymer in dry $CDCl_3$ (see above, Figure S1). c) The molar % was calculated from the mol ratio NB_{VA}/NB_{RO}.

1.8- Synthesis and characterization of the norbornene dimer **4**.

Compound **4** was synthesized following a previous reported method.[3]

In a 100 mL Schlenk tube was placed [$NiCl_2$dppe] (0.58 g, 1 mmol) in a N_2 atmosphere. Norbornene (2.82 g, 30 mmol) and 50 mL of dry MeOH were added. Finally, $NaBH_4$ (0.038 g, 1 mmol) was added and the brown suspension was heated for 23 h at 80 ºC. After this time, the suspension was evaporated to dryness and 5 mL of Et_2O were added to the residue. The solid was filtered off and the yellow solution was evaporated to dryness. The yellow oil was distilled at 100 ºC and 1.2 mbar. Finally, the colorless oil was purified by chromatography using silica gel and n-hexane as eluent (25 mg, 26.5 % yield).* ^{1}H NMR (500.13 MHz, δ, $CDCl_3$): 5.69 (m, 2H, H^3, H^2), 4.81 (m, 1H, H^7), 4.61 (m, 1H, $H^{7'}$), 2.29-2.11 (m, 7H, H^{11}, H^8, H^5, $H^{5'}$, H^4, $H^{4'}$, H^1), 1.52-1.32 (m, 6H, H^{14}, H^{13}, H^{12}, H^{10}, $H^{10'}$, H^9) 1.18-1.06 (m, 3H, $H^{14'}$, $H^{13'}$, $H^{12'}$). ^{13}C{^{1}H} NMR (125.66 MHz, δ, $CDCl_3$): 149.1 (C^6), 129.7, 126.8 (C^3, C^2), 108.7 (C^7), 48.5 (C^1), 47.5 (C^9), 39.2 (C^8), 37.2 (C^{11}), 36.4 (C^{10}), 35.25 (C^{14}), 30.3, 29.03 (C^{13}, C^{12}), 28.85 (C^5), 28.5 (C^4). MS (EI, 70 eV): m/z (%) 188.14 (20), 95.08 (100), 77.03 (92), 67.05 (100).



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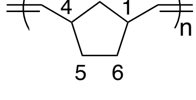
*Minor signals for other oligomers are detected in the ^{1}H NMR.

1.9- Synthesis of ROMP-PNB.

In a Schlenk tube under N_2 was placed a solution of norbornene in CH_2Cl_2 (0.415 mL, 1.577 mmol; 3.8 M) and 7.5 mL of dry CH_2Cl_2. A solution of the 2nd generation Grubbs' catalyst $[RuCl_2(CHPh)(PCy_3)(IMesH_2)]$ ($IMesH_2$ = 1,3-bis(mesityl)-2-imidazolidinylidene) was added (0.175 mL, 3.154×10^{-3} mmol; 1.80×10^{-3} M). The solution was stirred for 4 h at 25 ºC. MeOH (20 mL) was added to the solution and the suspension was stirred for 30 min at room temperature. The white solid was filtered off and washed with MeOH (2 x 10 mL). The white powder was air dried for 12 h (0.14 g, 94.5% yield). ^{1}H NMR (500.13 MHz, δ, $CDCl_3$): 5.35 (b, H^3, H^2 *trans*), 5.21 (b, H^3, H^2 *cis*), 2.81 (b, H^4, H^1 *cis*), 2.45 (b, H^4, H^1 *trans*), 1.86, 1.78 (b, H^7, H^6, H^5), 1.36 (b. $H^{6'}$, $H^{5'}$), 1.02 (m, $H^{7'}$). ^{13}C{^{1}H} NMR (125.66 MHz, δ, $CDCl_3$): 134.1-132.6 (C^3, C^2), 43.4, 43.1, 38.6, 38.4 (C^4, C^1), 42.7, 42.1, 41.4 (C^7), 33.1, 32.9, 32.3, 32.1 (C^6, C^5).



ROMP-PNB

1.10- Monitorization of the VA/RO norbornenene polymerization and microkinetic modeling.

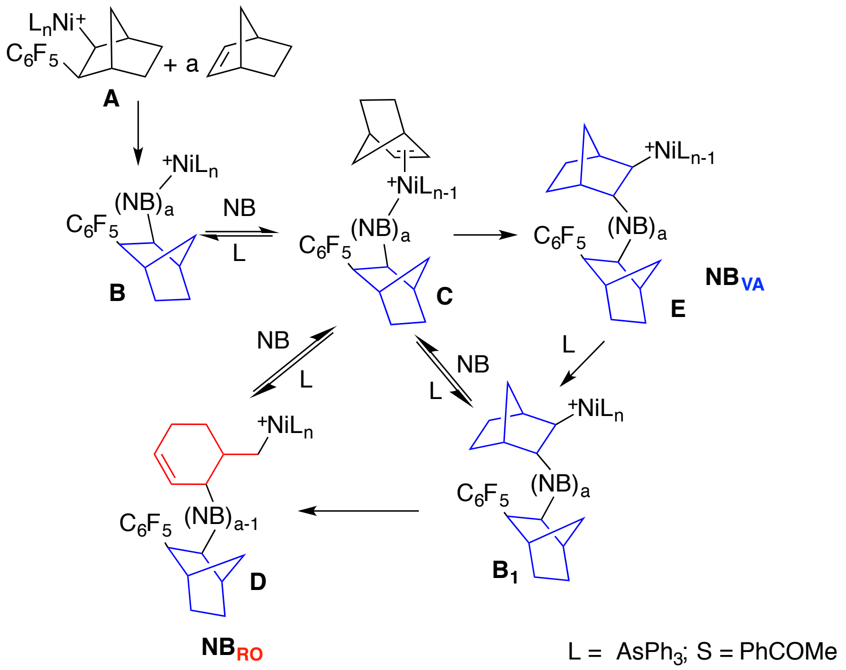
In an NMR tube in a N_2 atmosphere was placed $[Ni(C_6F_5)_2(AsPh_3)_2]$ (**2**, 12 mg, 0.0119 mmol). The complex was dissolved in 0.6 mL of CD_2Cl_2. Then, acetophenone (21 μL, 0.18 mmol) and tribromobenzene as internal standard (10.1 mg, 0.032 mmol) were added to the yellow solution. The solution was cooled to -10 ˚C and a solution of norbornene in CD_2Cl_2 (21 μL, 0.057 mmol, 2.73 M) was added to the cooled solution. The polymerization was followed by ^{1}H NMR spectroscopy at 298 K. The results are collected in Table S3.

Table S3. Experimental data for the monitorization of a VA/RO norbornene polymerization. Initial concentrations: $[Ni]_0$ = 0.01853 M; $[NB]_0$ = 0.089 M; [PhCOMe] = 0.28 M

Time (s)	$[NB]_t$	Mol ratio NB_{VA}/NB_{RO}	Mol fraction NB_{RO}
85	0.08416	12.5902	0.0736
170	0.07974	10.6094	0.0861
255	0.07420	9.5909	0.0944
340	0.07011	8.7362	0.1027
425	0.06676	7.6335	0.1158
510	0.06323	7.2369	0.1214
595	0.06014	6.8332	0.1277
680	0.05754	6.2520	0.1379
765	0.05482	5.9302	0.1443
850	0.05173	5.9221	0.1445
935	0.04951	5.6761	0.1498
1020	0.04720	5.5467	0.1527
1105	0.04547	5.3628	0.1572
1190	0.04331	5.2067	0.1611
1275	0.04169	5.0855	0.1643
1360	0.03989	5.0545	0.1652
1445	0.03868	4.9003	0.1695
1530	0.03735	4.8465	0.1710
1615	0.03595	4.7696	0.1733
1700	0.03431	4.7811	0.1730
1785	0.03330	4.7105	0.1751
1870	0.03216	4.6323	0.1775
1955	0.03120	4.5565	0.1800
2040	0.03012	4.5583	0.1799
2125	0.02929	4.4623	0.1831
2210	0.02821	4.4748	0.1827
2295	0.02749	4.4524	0.1834
2380	0.02662	4.3789	0.1859
2465	0.02575	4.4008	0.1852

2550	0.02516	4.3636	0.1864
2635	0.02440	4.3434	0.1871
2720	0.02391	4.2804	0.1894
2805	0.02337	4.2140	0.1918
2890	0.02261	4.2385	0.1909
2975	0.02197	4.2433	0.1907
3060	0.02128	4.2352	0.1910
3145	0.02105	4.2014	0.1923
3230	0.02049	4.1600	0.1938
3315	0.01992	4.1974	0.1924
3400	0.01917	4.1952	0.1925
3485	0.01899	4.1347	0.1948
3570	0.01840	4.1500	0.1942

Kinetic simulation of the VA/RO-PNB formation was carried out using the COPASI software.[4] The kinetic model used for the propagation of the polymerization (NB_{VA} and NB_{RO} formation) and the nomenclature for the different species are depicted in Scheme S1. Experimental concentrations were used.



Scheme S1.

Kinetic equations and rate constants.

$\mathbf{B} + \mathrm{NB} \underset{k_{-1NB}}{\overset{k_{1NB}}{\rightleftharpoons}} \mathbf{C} + \mathrm{L}$ $k_{1NB} = 0.1\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$; $k_{-1NB} = 0.35\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$

$\mathbf{C} \xrightarrow{k_2} \mathbf{NB}_{\mathbf{VA}} + \mathbf{E}$ $k_2 = 0.09\ \mathrm{s}^{-1}$

$\mathbf{E} + \mathrm{L} \xrightarrow{k_3} \mathbf{B}_1$ $k_3 = 100\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$

$\mathbf{B}_1 + \mathrm{NB} \underset{k_{-1NB}}{\overset{k_{1NB}}{\rightleftharpoons}} \mathbf{C} + \mathrm{L}$ $k_{1NB} = 0.1\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$; $k_{-1NB} = 0.35\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$

$\mathbf{B}_1 \xrightarrow{k_4} \mathbf{NB}_{\mathbf{RO}} + \mathbf{D}$ $k_4 = 5 \times 10^{-4}\ \mathrm{s}^{-1}$

$\mathbf{D} + \mathrm{NB} \underset{k_{-1NB}}{\overset{k_{1NB}}{\rightleftharpoons}} \mathbf{C} + \mathrm{L}$ $k_{1NB} = 0.1\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$; $k_{-1NB} = 0.35\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$

Initial concentrations:

$[\mathbf{B}]_0 = [\mathrm{Ni}]_0 = 0.01853$ M;

$[\mathrm{NB}]_0 = 0.089$ M; $[\mathrm{L}]_0 = [\mathrm{PhCOMe}] = 0.28$ M

$[\mathbf{C}]_0 = [\mathbf{D}]_0 = [\mathbf{E}]_0 = [\mathbf{B}_1]_0 = [\mathbf{NB}_{\mathbf{VA}}]_0 = [\mathbf{NB}_{\mathbf{RO}}]_0 = 0$

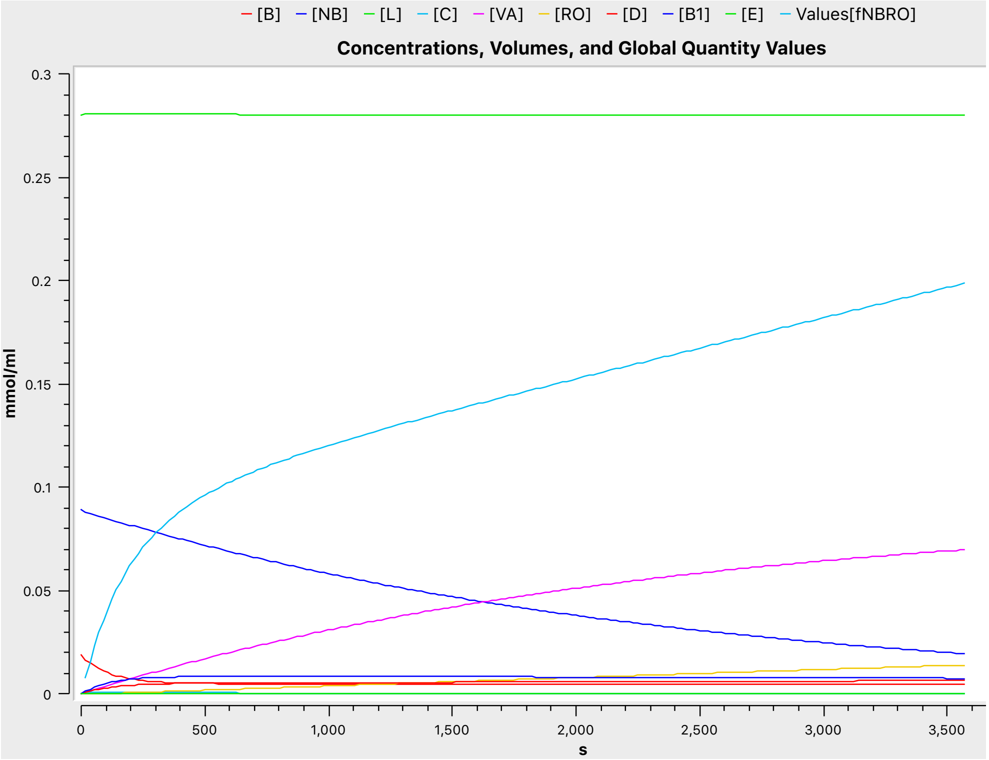
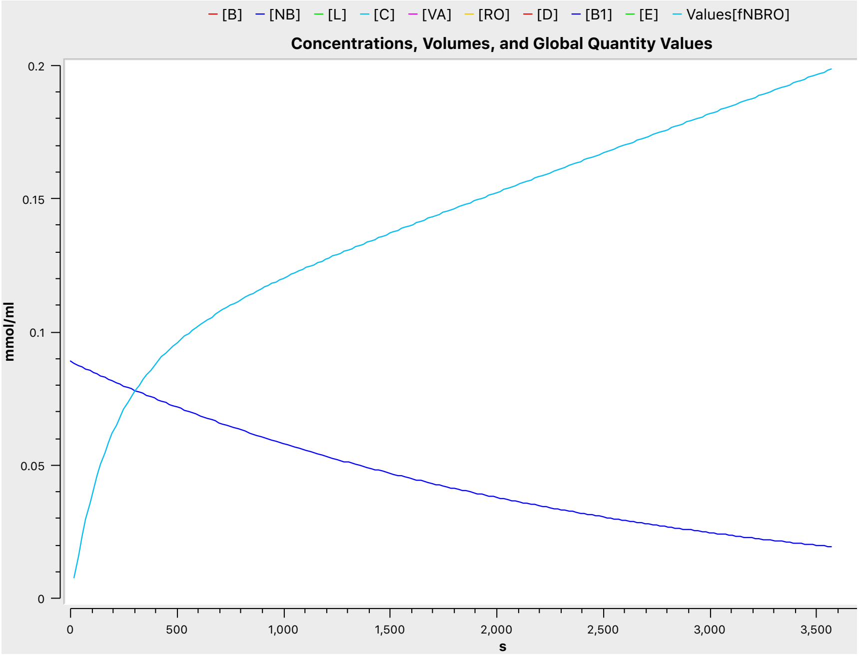


Figure S2. Evolution of concentration (M) over time (s) for the VA/RO-PNB formation from the mikrokinetic model (COPASI simulation).

a)



b)

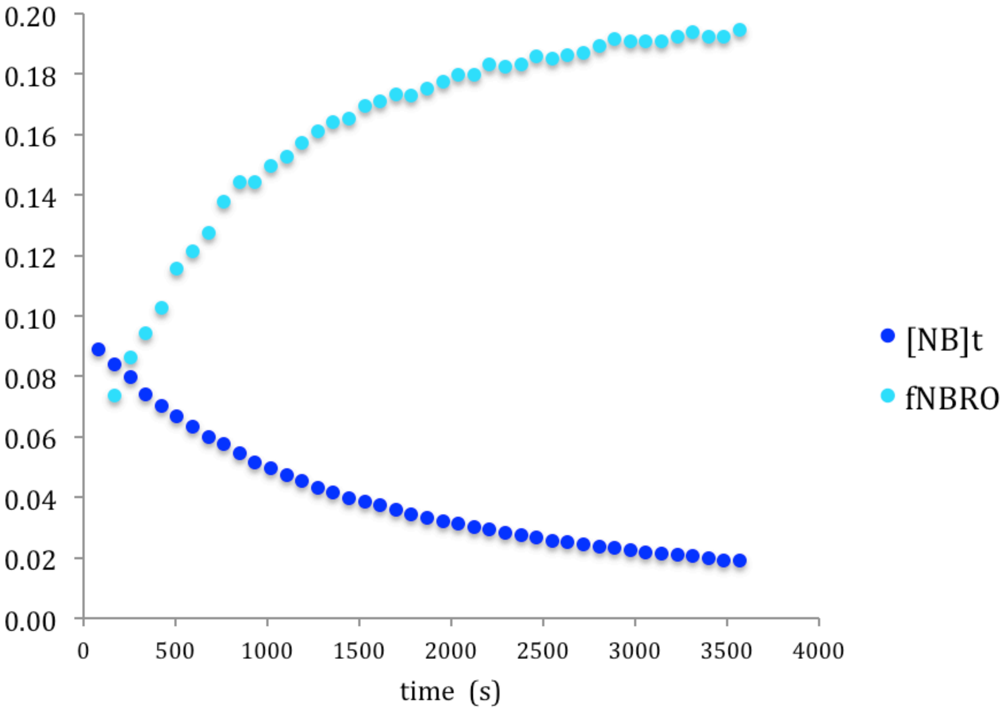


Figure S3. Evolution of NB concentration (M) and mol fraction of NB_{RO} over time (s) for the VA/RO-PNB formation: a) COPASI simulation; b) experimental data.

2. Selected NMR spectra for polymers and dimer 4.

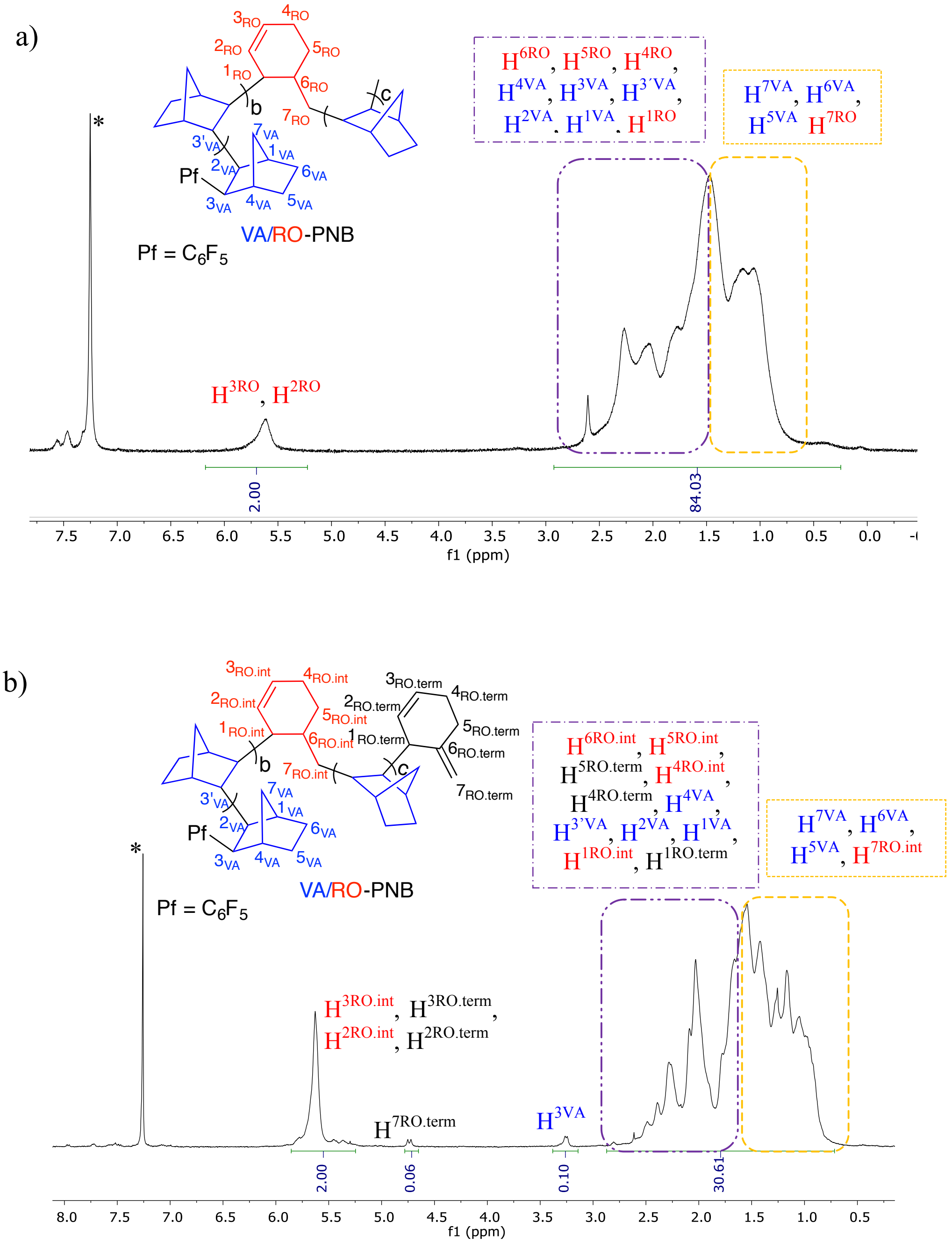


Figure S4. ^{1}H NMR (500.13 MHz, CDCl$_3$) at 298 K of: a) VA/RO-PNB polymer with a mol ratio NB$_{VA}$/NB$_{RO}$ = 7.6/1 (initial mol ratio NB:Ni:acetophenone = 75:1:160, M$_w$ = 17391 Da, Đ = 1.5; entry 5, Table 2). b) short VA/RO-PNB polymer with a mol ratio NB$_{VA}$/NB$_{RO}$ = 2.3/1 (initial mol ratio NB:Ni:acetophenone = 5:1:15, M$_w$ = 2270 Da, Đ = 1.5). *Signal corresponding with the solvent.

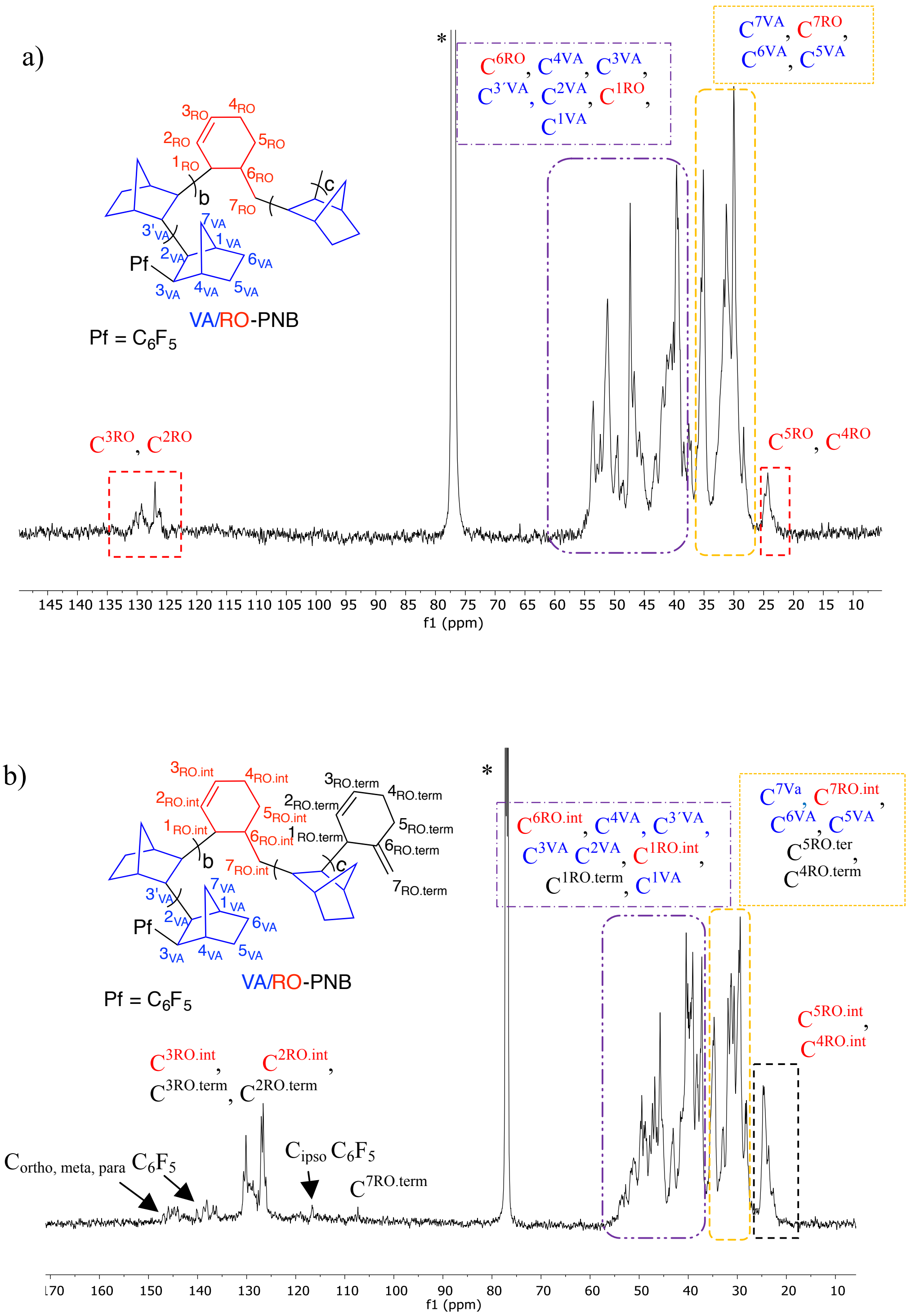


Figure S5. $^{13}C\{^{1}H\}$ NMR (125.758 MHz, $CDCl_3$) at 298 K of: a) VA/RO-PNB with a mol ratio NB_{VA}/NB_{RO} = 7.6/1 (initial mol ratio NB:Ni:acetophenone = 75:1:160, M_w = 17391 Da, Đ = 1.5; entry 5, Table 2). b) short VA/RO-PNB with a mol ratio NB_{VA}/NB_{RO} = 2.3/1 (mol ratio NB:Ni:acetophenone = 5:1:15, M_w = 2270 Da, Đ = 1.5). *Signal corresponding to the solvent.

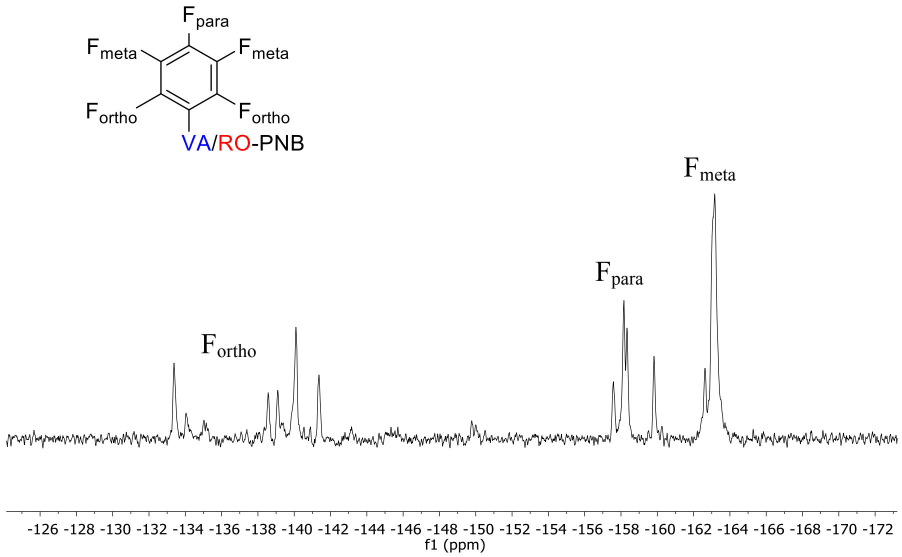


Figure S6. ^{19}F NMR (470.592 MHz, CDCl$_3$) of a VA/RO-PNB with NB$_{VA}$/NB$_{RO}$ mol ratio = 7.6/1 (initial mol ratio NB:Ni:acetophenone = 75:1:160, M$_w$ = 17391 Da, Đ = 1.5; entry 5, Table 2) at 298 K.

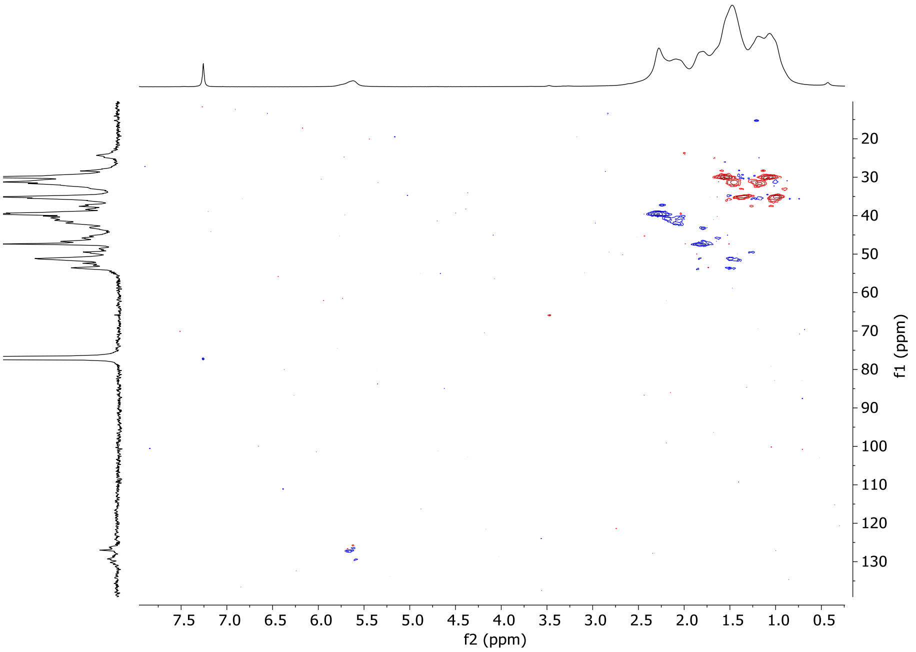


Figure S7. ^{1}H-^{13}C g-HSQCAD NMR (500.13 MHz, CDCl$_3$) of a VA/RO-PNB with NB$_{VA}$/NB$_{RO}$ mol ratio = 7.6 (initial mol ratio NB:Ni:acetophenone = 75:1:160, M$_w$ = 17391 Da, Đ = 1.5; entry 5, Table 2) at 298 K. Blue cross peaks correspond to methine groups and red cross peaks to methylene groups.

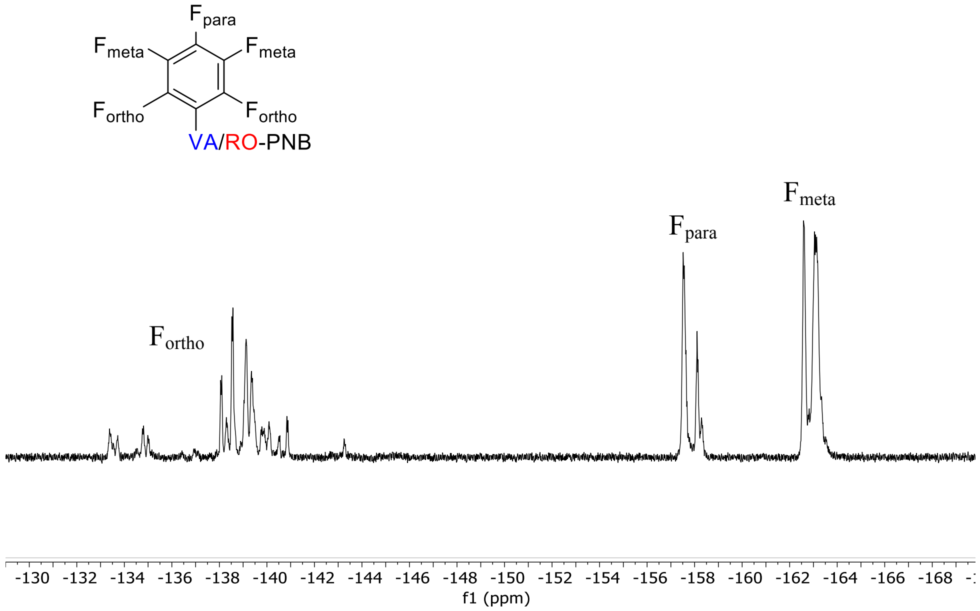


Figure S8. ^{19}F NMR (500.13 MHz, CDCl$_3$) for a short VA/RO-PNB with NB$_{VA}$/NB$_{RO}$ mol ratio = 2.3/1 (mol ratio NB:Ni:acetophenone = 5:1:15, M$_w$ = 2270 Da, Đ = 1.5) at 298 K.

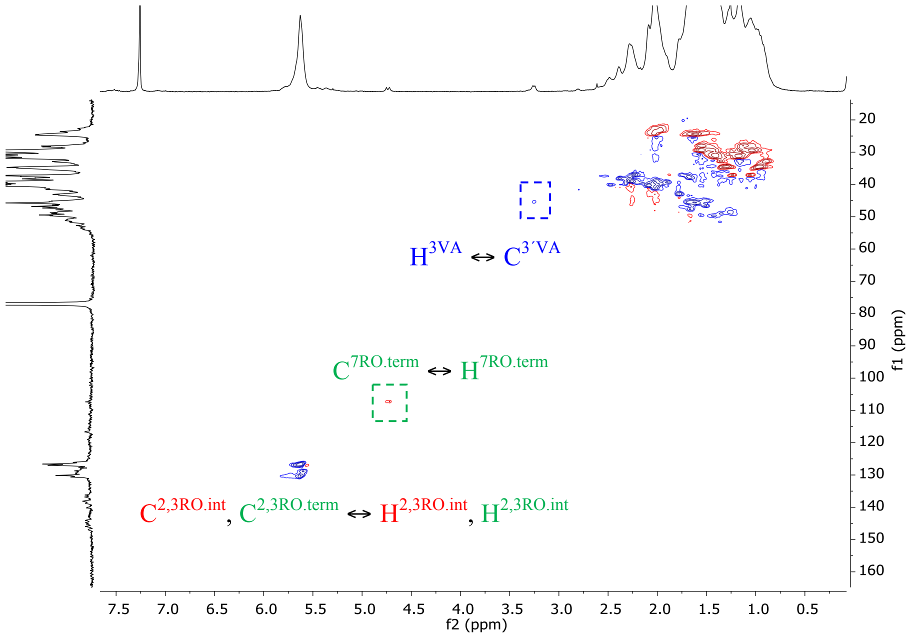


Figure S9. ^{1}H-^{13}C gHSQCAD NMR (500.13 MHz, CDCl$_3$) of a short VA/RO-PNB with a mol ratio NB$_{VA}$/NB$_{RO}$ = 2.3/1 (mol ratio NB:Ni:acetophenone = 5:1:15, M$_w$ = 2270 Da, Đ = 1.5) at 298 K. Blue cross peaks correspond to methine groups and red cross peaks to methylene groups.

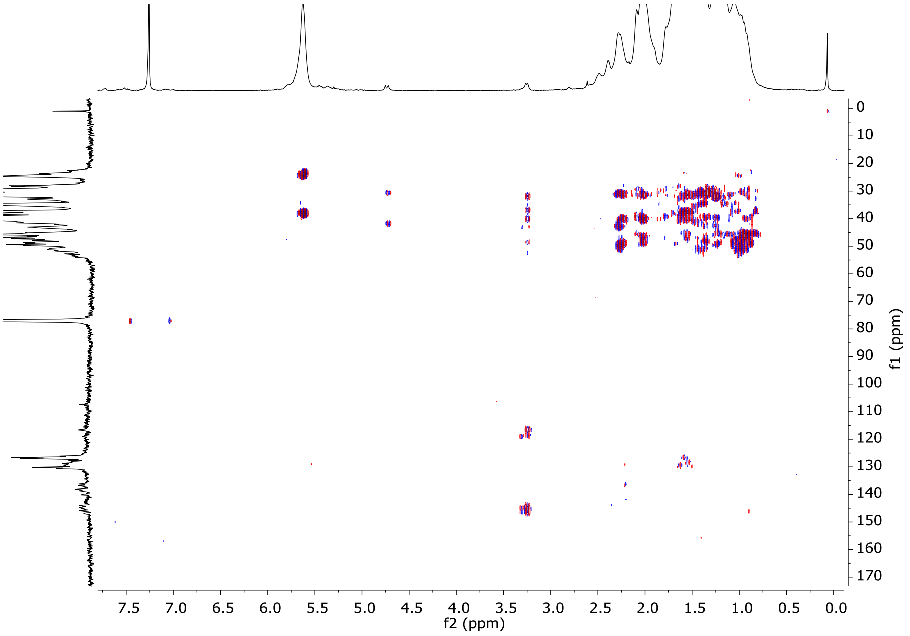


Figure S10. ^{1}H-^{13}C gHMBCAD NMR (500.13 MHz, CDCl$_3$) for a short VA/RO-PNB with a mol ratio NB$_{VA}$/NB$_{RO}$ = 2.69/1 (mol ratio NB:Ni:acetophenone = 5:1:15, M$_w$ = 2270 Da; Đ = 1.5) at 298 K.

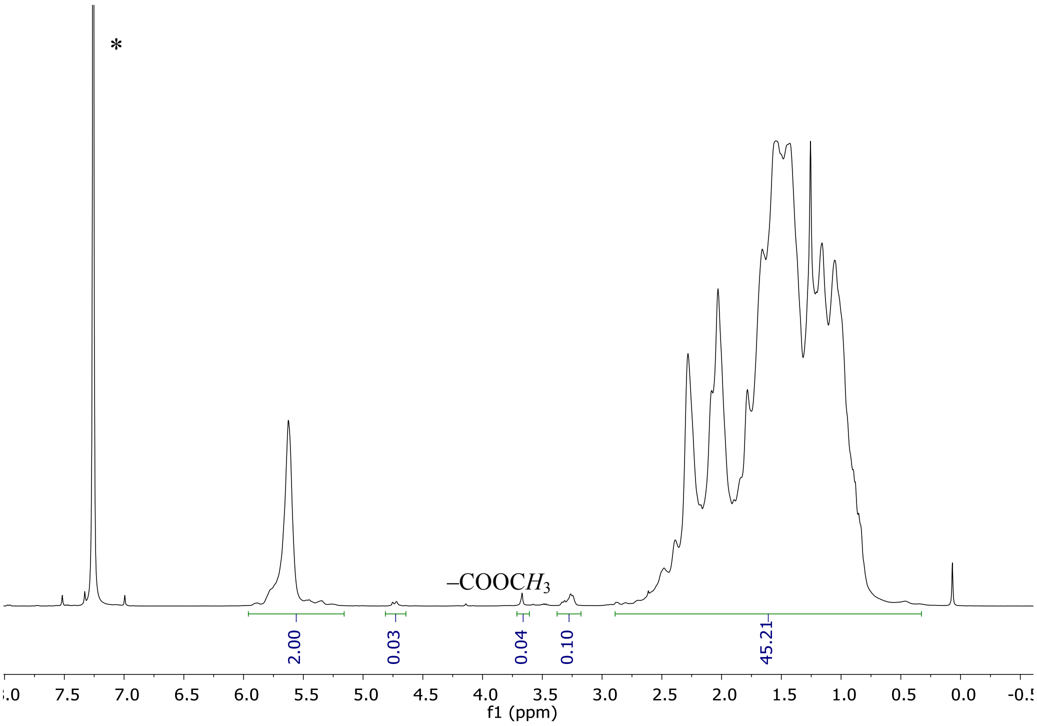


Figure S11. ^{1}H NMR (500.13 MHz, CDCl$_3$) at 298 K of VA/RO-PNB polymer with a mol ratio NB$_{VA}$/NB$_{RO}$ = 3.7/1 (initial mol ratio NB:Ni:acetophenone = 5:1:15, M$_w$ = 3895 Da; Đ = 1.6). Polymerization quenched by carbonylation. *Signal corresponding with the solvent.

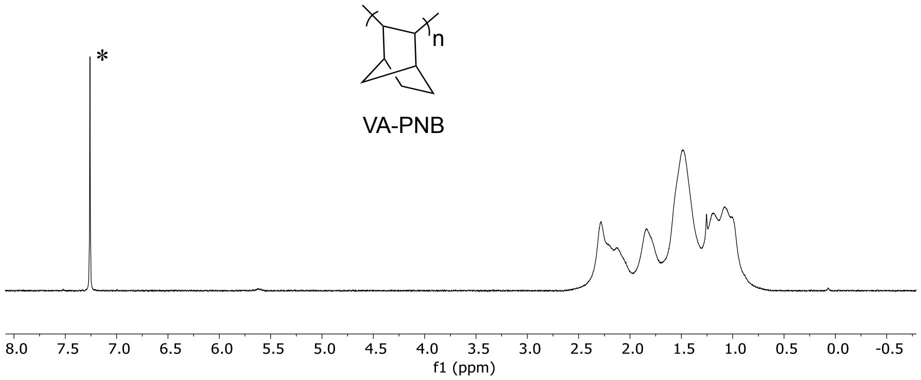


Figure S12. ^{1}H NMR (500.13 MHz, $CDCl_3$) of VA-PNB (initial mol ratio NB:Ni = 75:1; entry 3, Table 1) at 298 K. *Signal corresponding to the solvent.

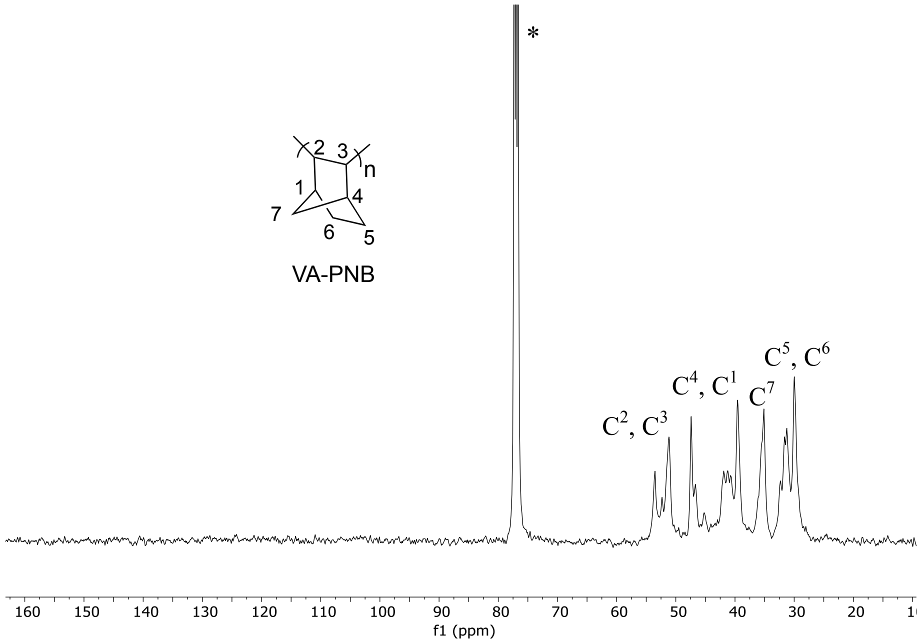


Figure S13. $^{13}C\{^1H\}$ NMR (125.758 MHz, $CDCl_3$) of VA-PNB (initial mol ratio NB:Ni = 75:1; entry 3, Table 1) at 298 K. *Signal corresponding to the solvent.

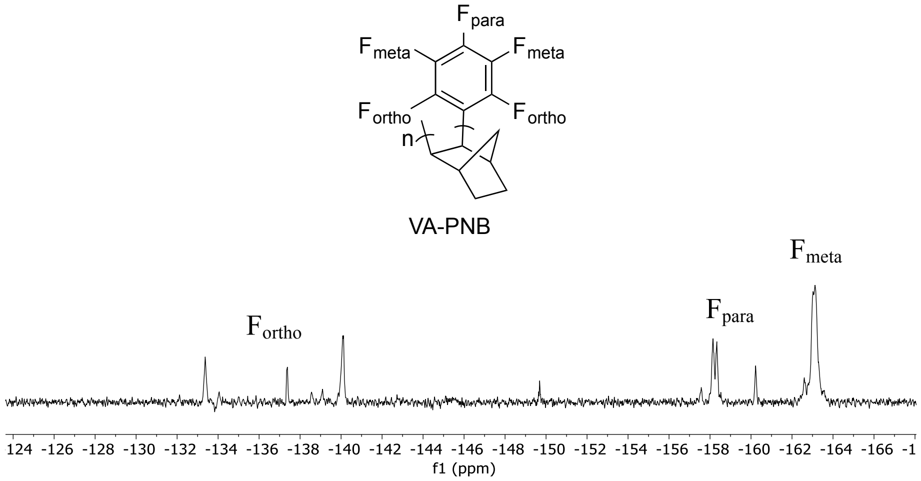


Figure S14. ^{19}F NMR (470.592 MHz, $CDCl_3$) of VA-PNB (initial mol ratio NB:Ni = 75:1; entry 3, Table 1) at 298 K.

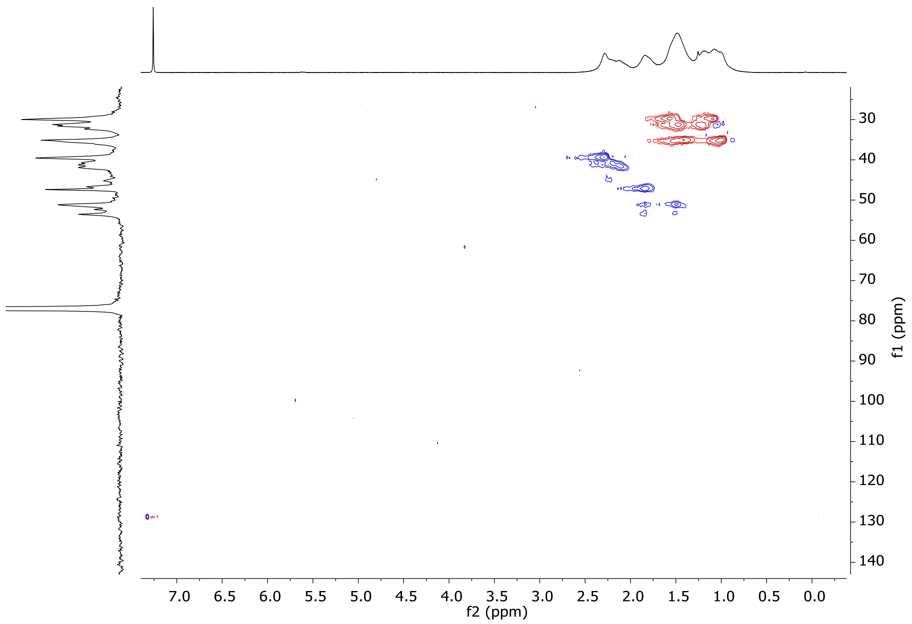


Figure S15. ^{1}H-^{13}C gHSQCAD NMR (500.13 MHz, $CDCl_3$) of VA-PNB (initial mol ratio NB:Ni = 75:1; entry 3, Table 1) at 298 K. Blue cross peaks correspond to methine groups and red cross peaks to methylene groups.

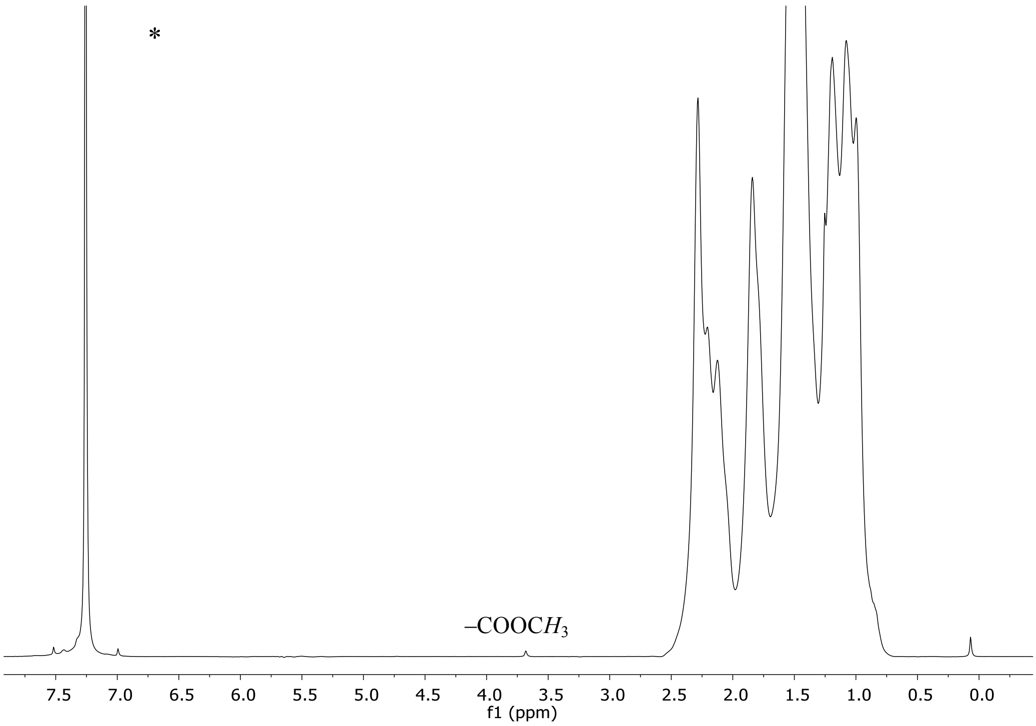


Figure S16. ^{1}H NMR (500.13 MHz, $CDCl_3$) at 298 K of VA-PNB (initial mol ratio NB:Ni: = 75:1; conditions of entry 1, Table 1). Polymerization quenched by carbonylation. *Signal corresponding with the solvent.

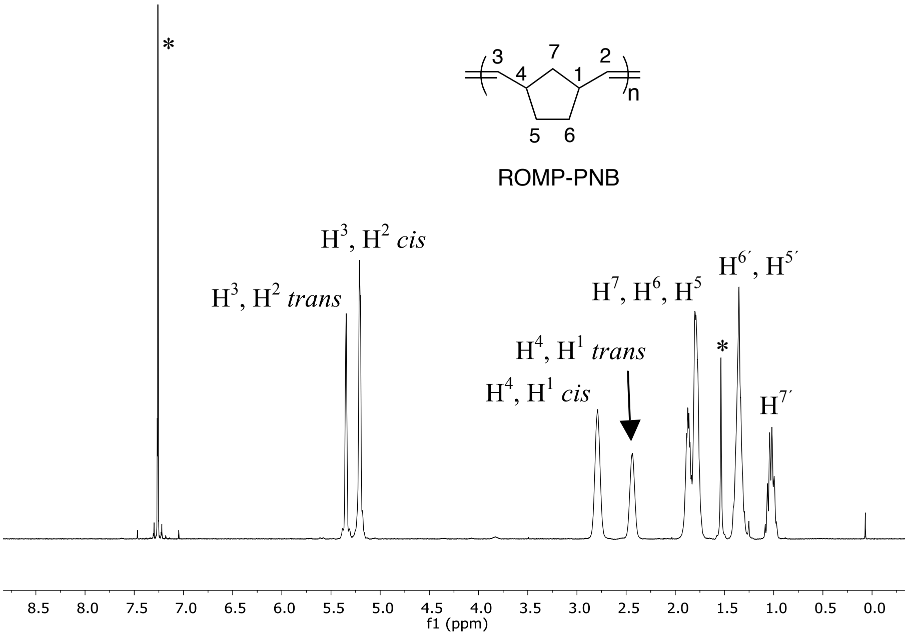


Figure S17. ^{1}H NMR (500.13 MHz, $CDCl_3$) of ROMP-PNB. *Signal corresponding to the solvent and water.

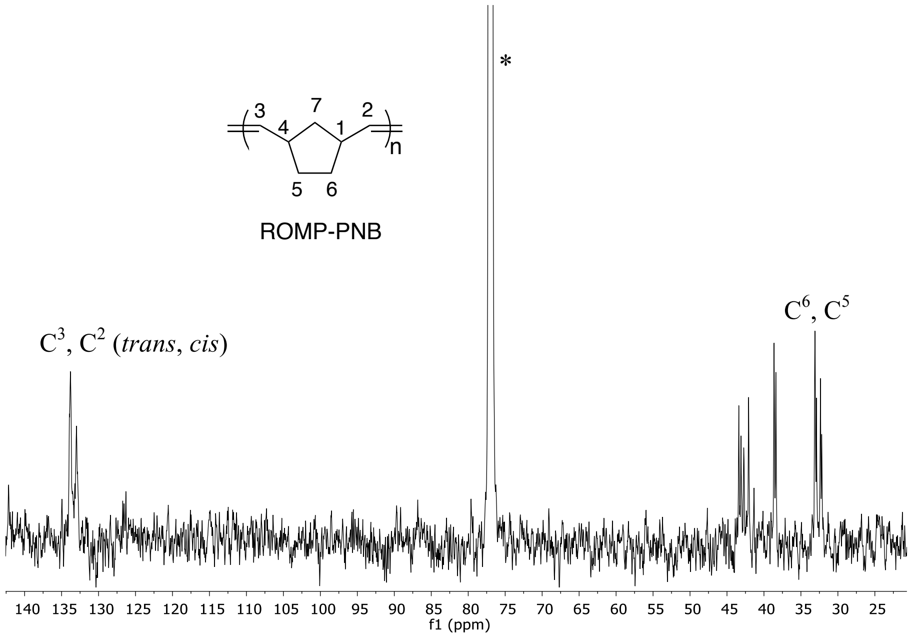


Figure S18. $^{13}C\{^1H\}$ NMR (125.758 MHz, $CDCl_3$) of the ROMP-PNB. *Signal corresponding to the solvent.

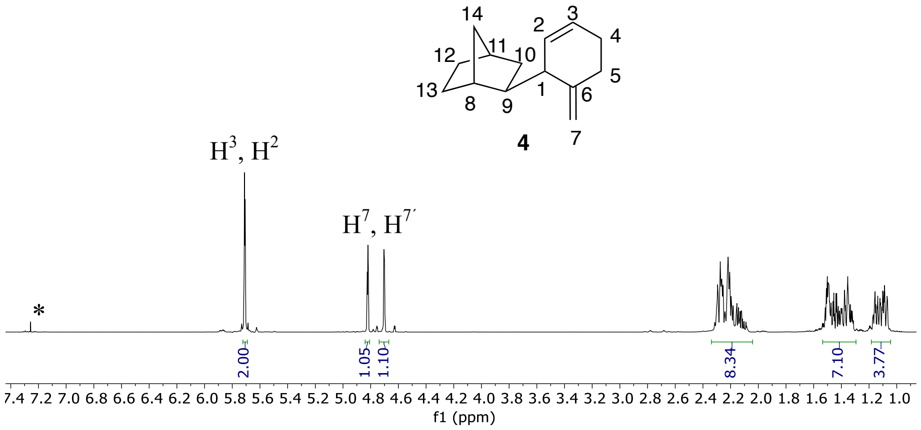


Figure S19. ^1H NMR (500.13 MHz, $CDCl_3$) of dimer **4**. *Signal corresponding to the solvent.

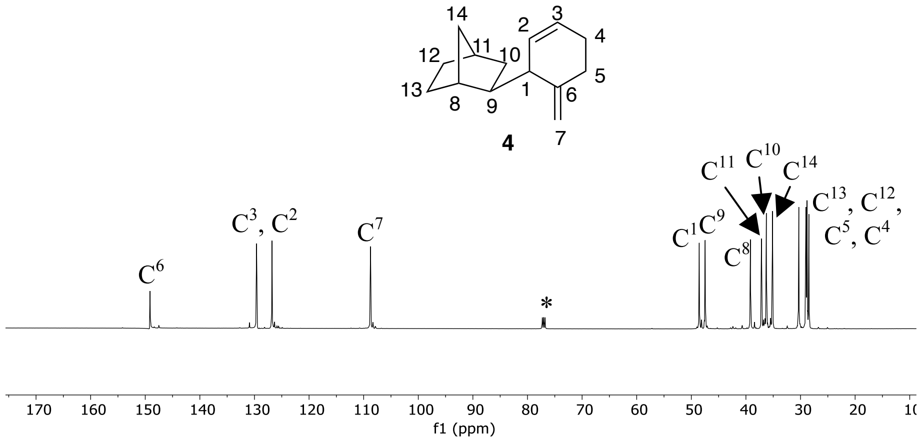


Figure S20. $^{13}C\{^1H\}$ NMR (125.758 MHz, $CDCl_3$) of dimer **4**. *Signal corresponding to the solvent.

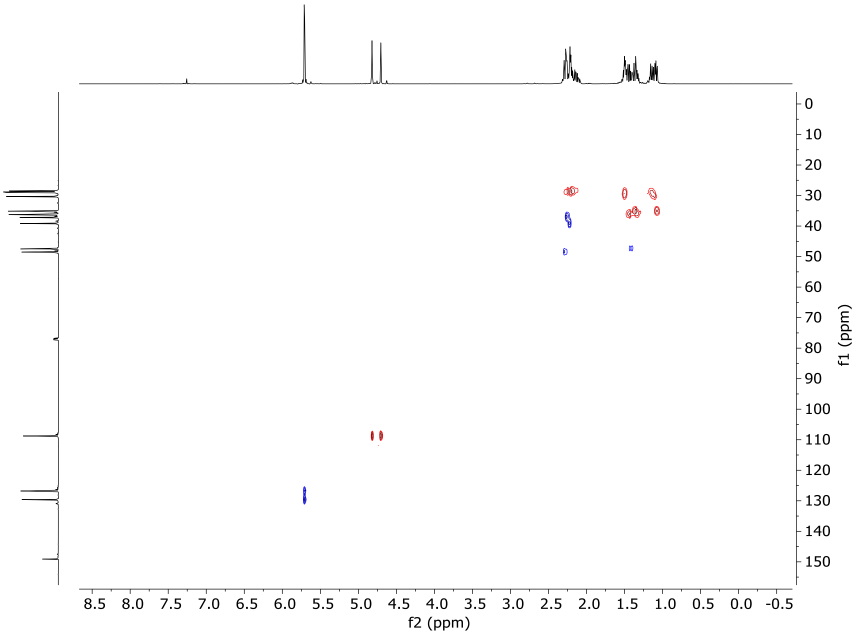


Figure S21. ^1H-^{13}C gHSQCAD NMR (500.13 MHz, $CDCl_3$) of dimer **4**. Blue cross peaks correspond to methine groups and red cross peaks to methylene groups.

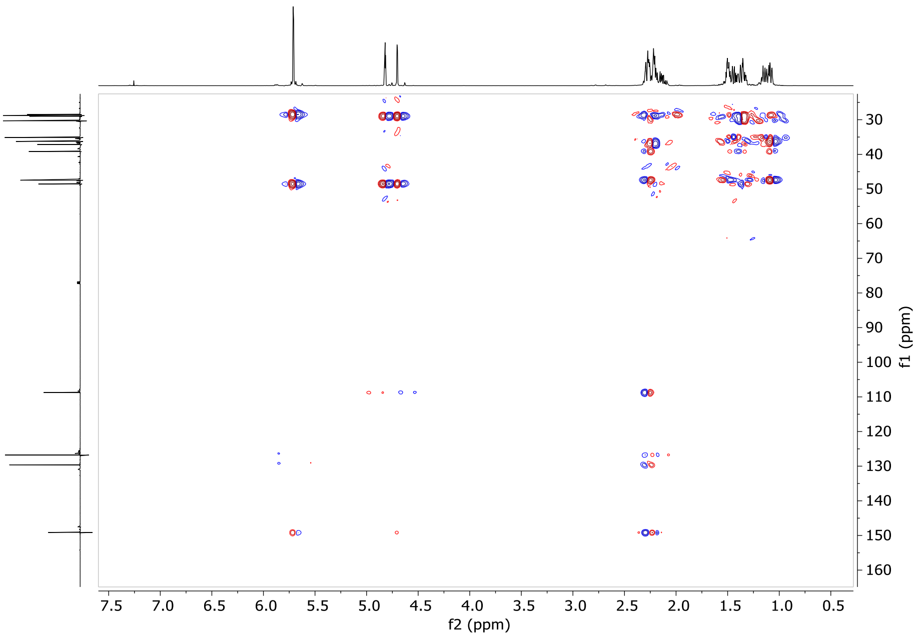


Figure S22. ^{1}H-^{13}C gHMBCAD NMR (500.13 MHz, $CDCl_3$) of dimer **4**.

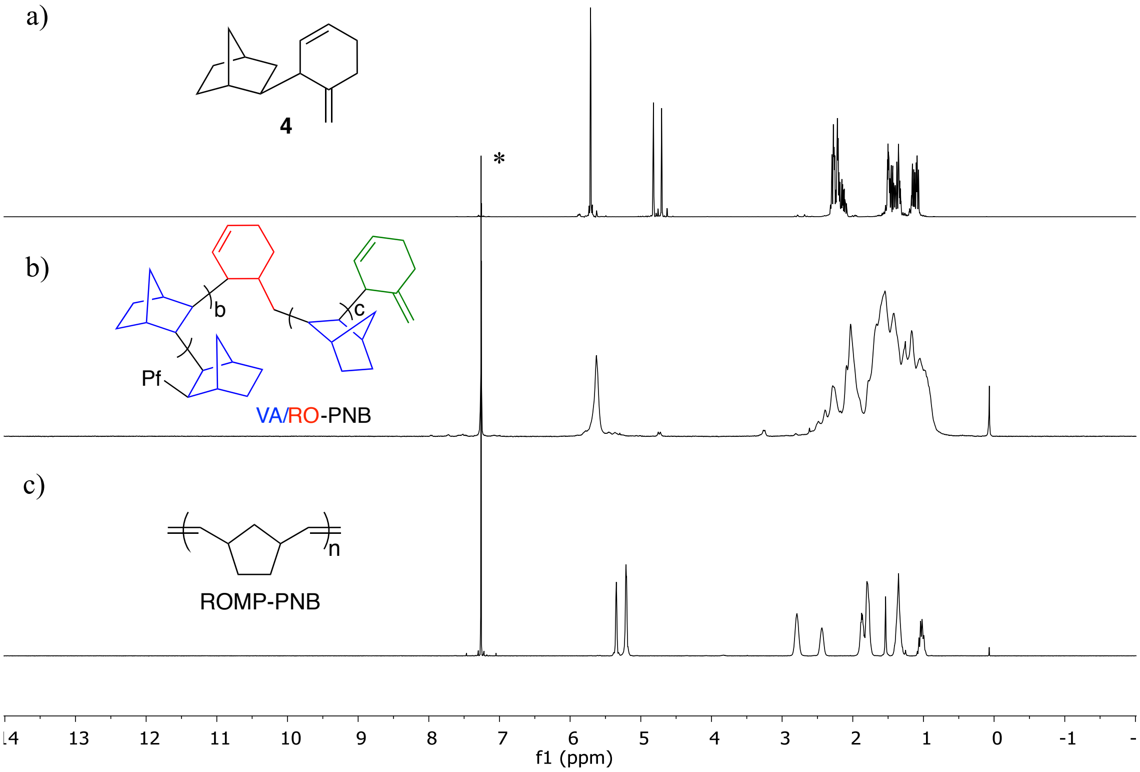


Figure S23. ^{1}H NMR (500.13 MHz, $CDCl_3$) at 298 K of: a) dimer **4**; b) a VA/RO-PNB with $NB_{VA}/NB_{RO} = 2.3/1$; c) ROMP-PNB;. *Signal corresponding to the solvent.

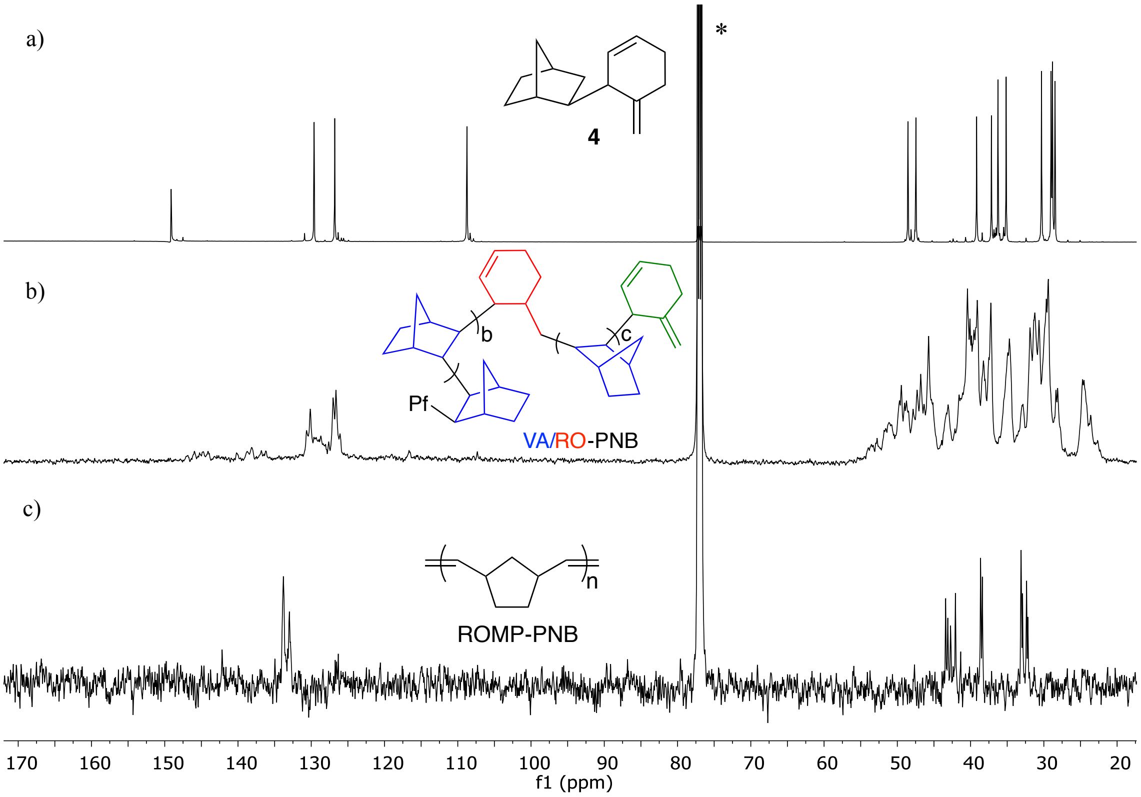
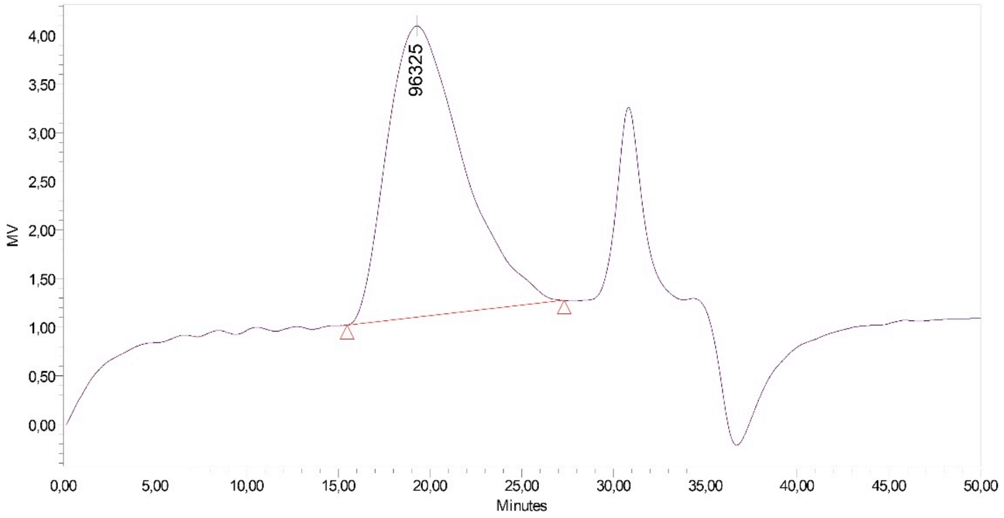


Figure S24. $^{13}C\{^{1}H\}$ NMR (125.758 MHz, $CDCl_3$) at 298 K of: a) dimer **4**; b) a VA/RO-PNB with NB_{VA}/NB_{RO} = 2.3/1; c) ROMP-PNB. *Signal corresponding to the solvent.

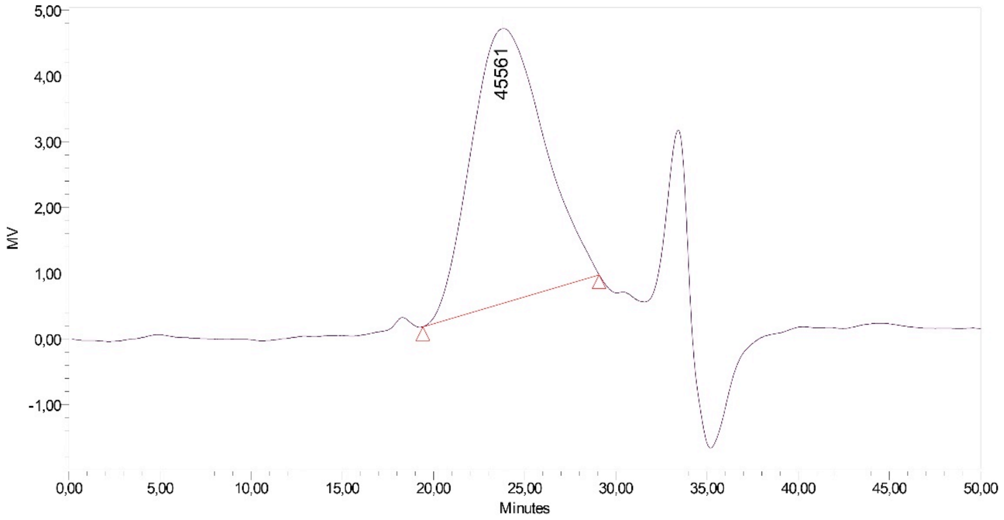
3. Selected GPC chromatograms.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		19,283	19,283	19,283	36627	162090	96325	981293	2970086	6,053990
2			26,217							

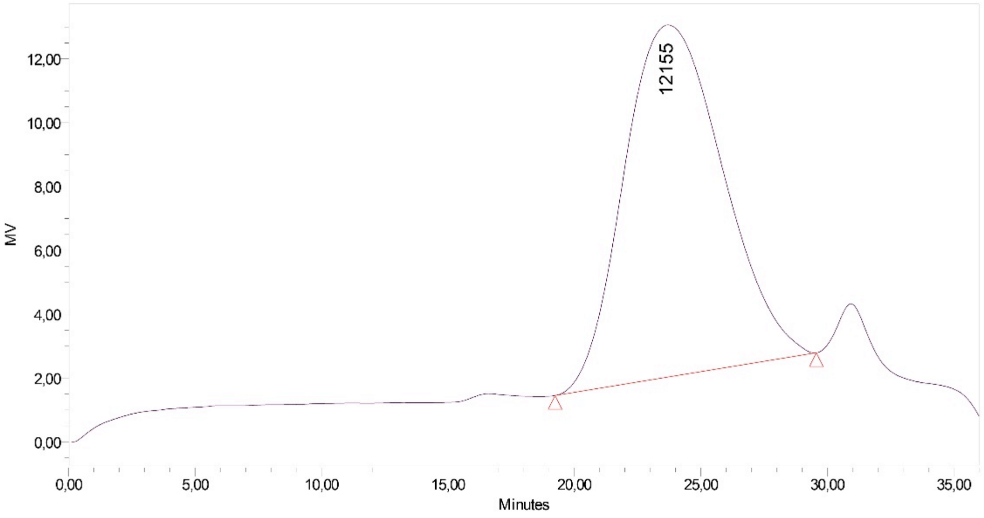
Figure S25. GPC chromatogram in $CHCl_3$ of VA-PNB generated with catalyst **1** (mol ratio NB:Ni = 75:1, $[NB]_0$ = 0.34 M; M_w = 162090 Da, entry 1, Table 1; main text).



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		23,767	23,767	23,767	26232	49065	45561	78666	112866	1,603306

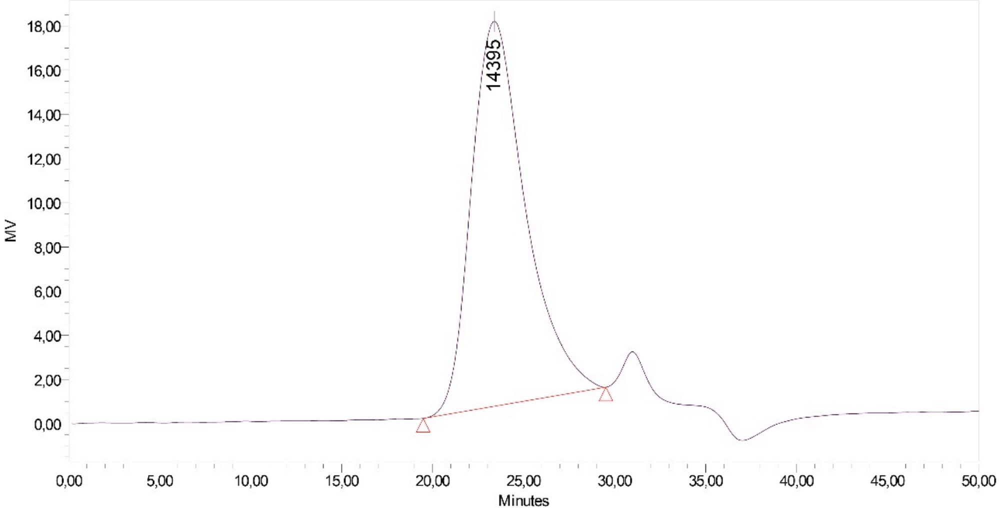
Figure S26. GPC chromatogram in $CHCl_3$ of VA/RO-PNB generated with catalyst **1** (mol ratio NB:Ni = 75:1, $[NB]_0$ = 0.061 M; % NB_{RO} = 1.5 %; M_w = 49065 Da, entry 2, Table 1; main text).



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		23,667	23,667	23,667	4326	14071	12155	25945	35169	1,843878	2,499385

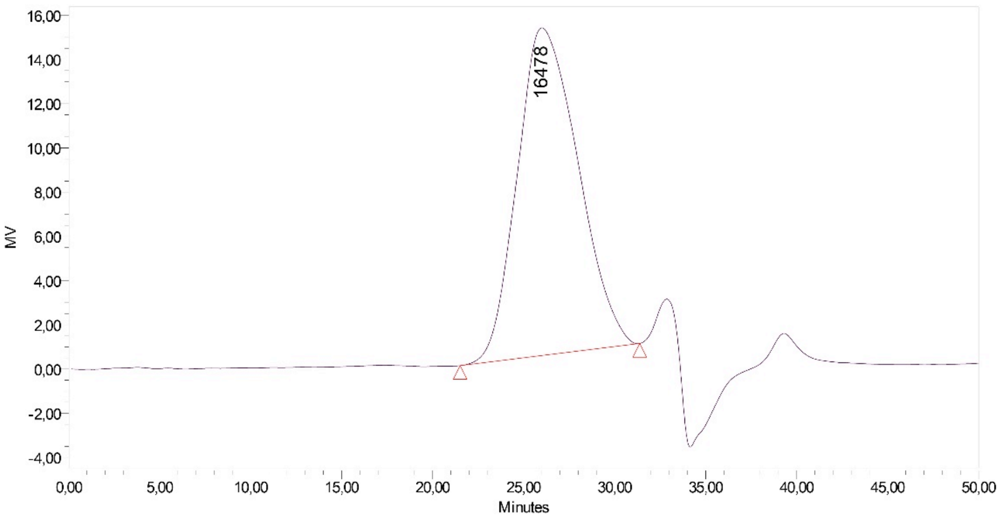
Figure S27. GPC chromatogram in $CHCl_3$ of VA/RO-PNB generated with catalyst **2** (mol ratio NB:Ni = 75:1, $[NB]_0$ = 0.061 M; % NB_{RO} = 6.5 %; M_w = 14071 Da, entry 4, Table 1; main text).



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		23,403	23,403	23,403	5414	14302	14395	22481	28802	1,571902	2,013896

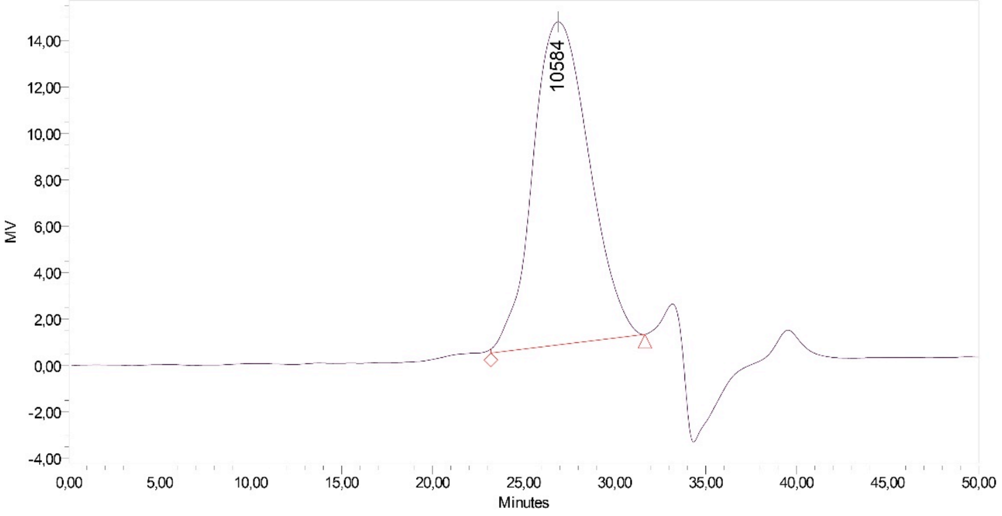
Figure S28. GPC chromatogram in $CHCl_3$ of VA/RO-PNB generated with catalyst **2** in the presence of Me_2CO (mol ratio NB:Ni:Me_2CO = 75:1:160, $[NB]_0$ = 0.061 M; % NB_{RO} = 7.6 %; M_w = 14302 Da, entry 2, Table 2; main text).



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		26,007	26,007	26,007	11541	17391	16478	25002	33224	1,437646

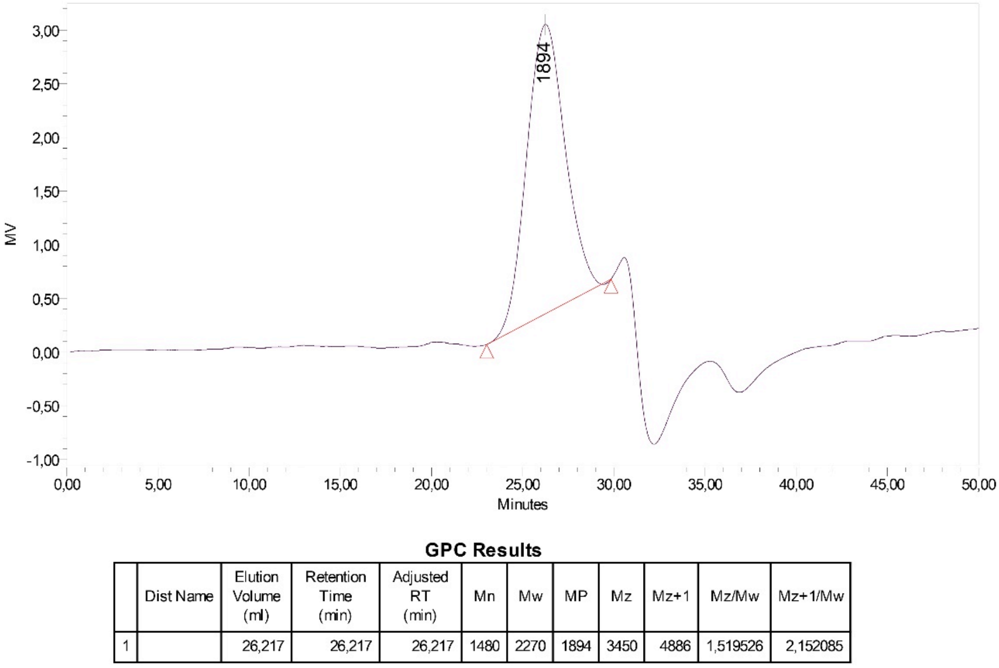
Figure S29. GPC chromatogram in $CHCl_3$ of VA/RO-PNB generated with catalyst **2** in the presence of PhMeCO (mol ratio NB:Ni:PhMeCO = 75:1:160, $[NB]_0$ = 0.061 M; % NB_{RO} = 11.6 %; M_w = 17391 Da, entry 5, Table 2; main text).



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		26,903	26,903	26,903	9109	12570	10584	17467	23333	1,389657	1,856332

Figure S30. GPC chromatogram in $CHCl_3$ of VA/RO-PNB generated with catalyst **2** in the presence of DMA (mol ratio NB:Ni:DMA = 75:1:20, $[NB]_0$ = 0.061 M; % NB_{RO} = 12.5 %; M_w = 12570 Da, entry 6, Table 2; main text).



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		26,217	26,217	26,217	1480	2270	1894	3450	4886	1,519526	2,152085

Figure S31. GPC chromatogram in $CHCl_3$ of a short VA/RO-PNB generated with catalyst **2** in the presence of PhMeCO (mol ratio NB:Ni:PhMeCO = 5:1:15, $[NB]_0 = 0.115$ M; % $NB_{RO} = 30.3$ %; $M_w = 2270$ Da).

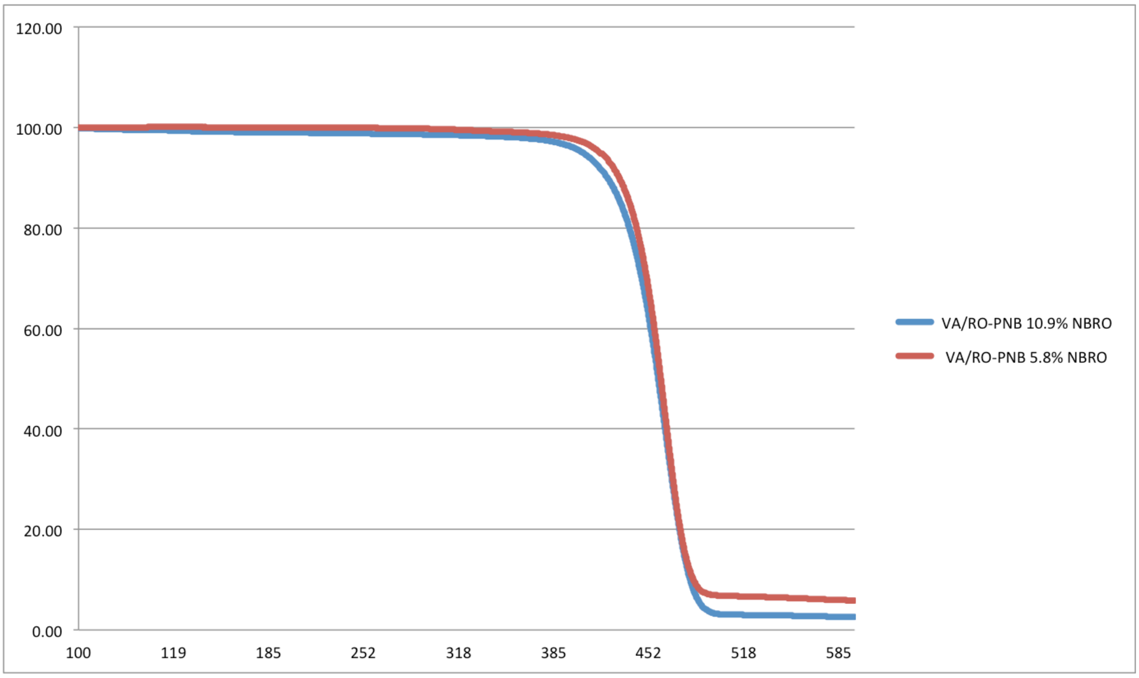


Figure S32. Thermogravimetric curves at 10 ˚C min^{-1} for VA/RO-PNBs: a) % $NB_{RO} = 10.9$, $M_w = 12141$ Da, entry 6, Table 2 (blue); 436-480 ˚C, 97% weight loss. b) % $NB_{RO} = 5.8$, $M_w = 19297$ Da, entry 7, Table 2 (red); 438-478 ˚C, 94% weight loss.

4. References

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[1] a) A. Arcas, P. Royo, *Inorg. Chim. Acta* 1978, **30**, 205–207; b) J. A. Casares, P. Espinet, J. M. Martín-Alvarez, J. M. Martínez-Ilarduya, G. Salas, *Eur. J. Inorg. Chem.* 2005, 3825-3831.

[2)] For characterization of VA-PNBs see: a) W. Kaminsky, A. Bark, M. Arndt, *Makromol. Chem. Macromol. Symp.* 1991, **41**, 83-93; b) M. Arndt, R. Engenhausen, W. Kaminsky, K. Zoumis, *J. Mol. Catal. A Chem.* 1995, **101**, 171-178; c) D. A. Barnes, G. M. Benedikt, B. L. Goodall, S. S. Huang, H. A. Kalamarides, S. Lenhard, L. H. McIntosh, K. T. Selvy, R. A. Shick, L. F. Rhodes, *Macromolecules* 2003, **36**, 2623-2632.

[3] A. Tenaglia, A. Terranova, B. Waegell, *J. Mol. Cat.* 1987, **40**, 281-287.

[4] COmplex PAthway Simulator (COPASI) is an easily available free software: S. Hoops, S. Sahle, R. Gauges, C. Lee, J. Pahle, N. Simus, M. Singhal, L. Xu, P. Mendes and U. Kummer, *Bioinformatics*, 2006, **22**, 3067–3074