

ARTICLE

Poly(ω -Bromoalkylnorbornenes-co-norbornene) by ROMP-Hydrogenation: a Robust Support Amenable to Post-Polymerization Functionalization

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The ring opening metathesis copolymerization of norbornene and ω -bromoalkylnorbornenes NB-(CH₂)_nBr (n = 1, 4) by Grubbs' 2nd generation catalyst, followed by hydrogenation, gives insoluble saturated polynorbornenes (ROMPH-PNBs) that have pendant ω -bromoalkyl chains (**4a**, **b**). These materials can be functionalized by nucleophilic substitution of bromide to give a variety of substituted polymers (ROMPH-PNB-(CH₂)_nNu where Nu = CN, SPh, OOCMe, N₃, SnR₃). The stannylated polymers were tested in a Pd-catalyzed reaction, the Stille coupling. The azido polynorbornenes ROMPH-PNB-(CH₂)_nN₃ easily undergo the click 1,3-dipolar cycloaddition with alkynes, which could be a useful strategy to anchor other functionalities of interest. The aliphatic nature of the ROMPH-PNB-(CH₂)_nBr backbone makes robust supports and the presence of the bromo substituent imparts versatility so they are good candidates to be used as a general starting material to anchor a group required for a specific synthetic purpose.

Introduction

Polymeric supports are becoming increasingly important in the context of sustainable synthetic chemistry, since they are used to anchor catalysts or reagents that could be better separated from the products and reused.¹ They are also fundamental tools in solid phase organic synthesis.² Polystyrene and polyethylene glycol are widespread scaffolds for immobilizing a specific functionality. They combine good physical properties and low reactivity and are commercially available, so they can be purchased as conveniently functionalized resins and easily transformed by the chemical practitioner, usually working outside the polymer chemistry area, to attach the reactive group needed. The enormous success of these polymers has obscured other polymeric scaffolds that can be also very useful. In particular, aliphatic saturated carbon chains would make very attractive supports for most applications since, being chemically very robust, they would increase the chances of getting reusable materials. A saturated support is suitable for reactions that may be risky for polystyrene where aromatic and benzylic groups are present, such as aromatic substitutions or radical processes. Few completely saturated polymeric scaffolds have been used in the literature as supports. Polyethylene based FibreCat supported palladium catalysts,³ or imidazolium salts attached to a polyethylene backbone can be found.⁴ Some examples of polyisobutylene materials have also been reported.^{1d,5} The availability of aliphatic saturated scaffolds comparable to the well known and versatile halo- or

hydroxymethyl functionalized polystyrene resins is very limited.⁶ We have previously done some work on the vinylic addition copolymerization of haloalkylsubstituted norbornenes and norbornene (VA-PNB, Figure 1), which gives a saturated polycyclic polymeric material easy to functionalize by nucleophilic substitution of the halogen group.⁷ These polymers have been used, for example, as precursors of supported stannyl reagents in the Stille reaction,⁸ or of supported organocatalysts,⁹ and they can be recycled. With the aim to develop versatile saturated polymeric scaffolds for a variety of applications, we rationalized that a halo-substituted polymer obtained by ring opening metathesis polymerization of the above-mentioned norbornenyl monomers (ROMP-PNB, Figure 1) could be an excellent precursor to obtain a variety of materials by post-polymerization reactions.¹⁰ However, ROMP leads to unsaturated polymer skeletons which contain double bonds as potential reactive centers, so the support may be unstable for certain applications such as catalysis. A way to avoid this drawback is reduction of the polymeric main chain to a saturated one, and this can be achieved by stoichiometric reagents such as hydrazides,¹¹ or by metal catalyzed hydrogenation (ROMPH-PNB, Figure 1).¹² The ROMP-hydrogenated polynorbornene main chain is polycyclic, but the cyclopentenyl units are linked by ethyl groups so, overall, the main chain is expected to be more flexible than the vinylic addition polymer. It has also good optical properties suitable for industrial applications.¹³ Both types of polynorbornenes (VA-PNB and ROMPH-PNB) have the advantage of being saturated

robust scaffolds, so the reactive center lays exclusively on the supported functionality of choice.

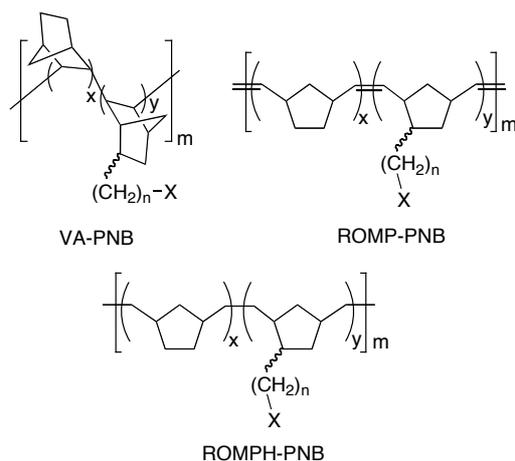


Fig. 1. Polymers derived from norbornene and norbornene derivatives.

Ring opening metathesis polymerization of cyclic olefins is applicable to different types of substituted monomers since the reaction tolerates the presence of many functional groups.¹⁴ Among those cyclic olefins the strained norbornene is a convenient monomer due to its easy polymerization and many different substituted norbornenes have been polymerized to ROMP-PNB materials with pendant groups that introduce interesting physical properties,^{12b,15} or have a use as catalysts,¹⁶ or reagent support.^{1d,17} As mentioned before, all these materials have an unsaturated polymeric main chain but few attempts have been made at transforming them on the saturated analogue. Clapham, Janda et al. described a saturated ROMPH polynorbornene resin by ROM emulsion copolymerization of norbornene, 5-hydroxymethyl norbornene and a norbornenyl crosslinker.¹⁸ The hydrogenation of the ROMP material was achieved under very harsh conditions, and they used the saturated resin in solid phase organic synthesis by functionalization of the hydroxo group in the polymer. They demonstrated that the saturated ROMPH resin is more resistant than the common polystyrene beads to solid phase Friedel Crafts acylation reactions and gives better yields. Despite this potential advantage, the use of ROMPH scaffolds has not been extended. A reason for that may be that some functional groups on the ROMP polymer may not survive the reduction conditions that lead to a saturated main chain. Thus, the combination of a saturated inert support with a given substitution pattern may not be accessible by direct polymerization of the functionalized monomer and subsequent hydrogenation. The introduction of the target groups by post-polymerization functionalization of a suitable and general saturated scaffold may be more convenient.¹⁹ We describe here new saturated polymeric materials obtained by ROMP of norbornene and ω -bromoalkyl norbornenes followed by hydrogenation. These materials have pendant ω -bromoalkyl chains which can be functionalized in a variety of ways and can be used as general precursors to support a specific group of

interest. It is noteworthy that, even if a large variety of substituted norbornenes have been polymerized by ROMP, halogenated or haloalkyl substituted norbornenes have rarely been used as monomers and only a few examples have been reported.²⁰

Experimental Section

Materials and General Considerations

NMR spectra in solution were recorded at 293 K using Bruker AV-400 and Agilent MR-500 and MR-400 instruments. Chemical shifts (δ) are reported in ppm and referenced to SiMe_4 (^1H and ^{13}C) and CFCl_3 (^{19}F) and SnMe_4 (^{119}Sn). The solid state NMR spectra were recorded at 293 K under magic angle spinning (MAS) in a Bruker AV-400 spectrometer using a Bruker BL-4 probe with 4mm diameter zirconia rotors spinning at 8 kHz. ^{13}C CP MAS NMR spectra were measured at 100.61 MHz and recorded with proton decoupling (tppm), with a 90° pulse length of 4.5 μs and a contact time of 3 ms and recycle delay of 3 s. The ^{13}C NMR spectra were referred to glycine (CO signal at 176.1 ppm). IR spectra were collected on the solid samples using a Perkin-Elmer FT/IR SPECTRUM FRONTIER spectrophotometer with CsI + ATR diamond accessory. The bromo content in the polymers was determined by oxygen-flask combustion of a sample and analysis of the residue by mercurimetric titration of the bromide.²¹ The ratios NB:1 (x/y , Scheme 1) in the ROMP-PNB copolymers were determined from these values. Considering that $[\text{M}_w(\mathbf{1}) + x/y \text{M}_w(\text{NB})]$ g of copolymer contains 1 mol of Br, x/y is given by the formula $x/y = [1000 - \alpha \text{M}_w(\mathbf{1})] / [\alpha \text{M}_w(\text{NB})]$ where $\alpha = \text{mmol Br/g copolymer}$, $\text{M}_w(\mathbf{1})$ and $\text{M}_w(\text{NB})$ molecular weight of monomers $\mathbf{1}$ and norbornene. Size exclusion chromatography (SEC) was carried out on a Waters SEC system using a three-column bed (Styragel 7.8 \times 300 mm columns: 50–100.000 D, 5000–500.000 D and 2.000–4.000.000 D) and Waters 410 differential refractometer. SEC samples were run in CHCl_3 at 313 K and calibrated to polystyrene standards. Residual tin in the Stille coupling product was determined by ICP-MS using Agilent 7500i equipment; the sample was dissolved in a mixture of $\text{HNO}_3/\text{H}_2\text{SO}_4 = 7:3$ using an ETHOS SEL Milestone microwave oven. Solvents used in the reactions and to prepare solutions of the reagents were dried using a Solvent Purification System (SPS PS-MD-5) or distilled from appropriate drying agents, de-oxygenated and kept under nitrogen, prior to use. Norbornene, 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), tetrabutylammonium cyanide, sodium azide, thiophenol, dimethylacetylenedicarboxylate, the terminal alkynes, the organic halides and the ruthenium complex $\mathbf{2}$ were purchased from Aldrich, Acros, Merck or Lancaster. ω -bromoalkyl norbornenes $\mathbf{1}$,⁷ and $\text{SnHBU}_2(p\text{-C}_6\text{H}_4\text{OMe})$,²² were prepared according to procedures reported in the literature.

Synthesis of ROMP-PNB-NBCH₂Br (**3a**, $x/y = 4.85$)

A solution of norbornene in CH_2Cl_2 (1.22 mL, 3.49 M, 4.26 mmol) was mixed with $\mathbf{1a}$ (0.15 mL, 1.07 mmol) and CH_2Cl_2 (6

mL) under a nitrogen atmosphere. A solution of **2** in CH_2Cl_2 (0.24 mL, 8.96×10^{-4} M, 2.1×10^{-4} mmol) was added dropwise and CH_2Cl_2 was added to get a total volume of 8 mL. The reaction mixture was stirred for 4 h at room temperature. The solution became darker and increased its viscosity as the reaction progressed. The reaction mixture was poured onto MeOH and a solid precipitated, which was crushed, stirred with MeOH, filtered, washed with MeOH (3 x 15 mL) and air-dried. Off-white gum-like solid. 0.52 g, 86% yield. ^1H NMR (CDCl_3 , 500.13 MHz): δ 5.35 (b, $\text{H}^2_{\text{trans}} + \text{H}^3_{\text{trans}}$, NB + **1a**), 5.20 (b, $\text{H}^2_{\text{cis}} + \text{H}^3_{\text{cis}}$, NB + **1a**), 3.49, 3.34 (b, $\text{H}^8_{\text{cis}} + \text{H}^8_{\text{trans}}$), 3.40, 3.24 (b, $\text{H}^8_{\text{trans}} + \text{H}^8_{\text{trans}}$), 3.06 (b, $\text{H}^1 + \text{H}^4$, **1a**), 2.79 (b, $\text{H}^1_{\text{cis}} + \text{H}^4_{\text{cis}}$, NB; $\text{H}^1 + \text{H}^4$, **1a**), 2.44 (b, $\text{H}^1_{\text{trans}} + \text{H}^4_{\text{trans}}$, NB; $\text{H}^1 + \text{H}^4 + \text{H}^5$, **1a**), 2.05 (b, $\text{H}^6 + \text{H}^7$, **1a**), 1.85 (b, H^7 , NB), 1.80, 1.35 (b, $\text{H}^5 + \text{H}^6$, NB), 1.25 (b, $\text{H}^6 + \text{H}^7$, **1a**), 1.03 (m, H^7 , NB). ^{13}C NMR (CDCl_3 , 125.76 MHz): δ 134.0, 133.9, 133.8, 133.7 ($\text{C}^2_{\text{cis}} + \text{C}^3_{\text{cis}}$, NB + **1a**), 133.1, 133.0, 132.8 ($\text{C}^2_{\text{trans}} + \text{C}^3_{\text{trans}}$, NB + **1a**), 46.0 (C^5 , **1a**), 43.6, 43.3, 42.9 ($\text{C}^1_{\text{trans}} + \text{C}^4_{\text{trans}}$, NB), 42.3 (C^7 , NB), 41.5 (C^6 or C^7 , **1a**), 42.7, 41.8, 40.4, 37.1 ($\text{C}^1 + \text{C}^4$, **1a**), 39.8 (C^6 or C^7 , **1a**), 38.8, 38.6 ($\text{C}^1_{\text{cis}} + \text{C}^4_{\text{cis}}$, NB), 38.6 (C^8_{cis}), 36.8 ($\text{C}^8_{\text{trans}}$), 33.3, 33.1, 32.6, 32.5 ($\text{C}^5 + \text{C}^6$, NB). IR (neat, cm^{-1}), $\nu(\text{=CH})$: 972 (s), 750 (m); $\nu(\text{C-Br})$: 640 (m). The copolymer contains 124.07 mg (1.553 mmol) of Br/g of polymer, which indicates a monomer ratio in the polymer of NB:**1a** = 4.85 ($x/y = 4.85$).

The polymers collected in Tables 1, 2 and 3 were prepared in the same way by just using the corresponding bromoalkylnorbornene and changing the amount of norbornene or CTA (Table 2) to reach the appropriate ratio in the feed, and the catalyst amount used (Table 3).

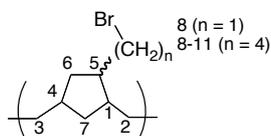


Chart 1. Numbering scheme for the repeating norbornene-derived units in both the ROMP and ROMPH polymers (only the ROMPH repeating **1a** or **1b** units are shown).

ROMP-PNBCH₂Br (**3a**, $x/y = 0$)

Off-white gum-like solid. 87% yield. ^1H NMR (CDCl_3 , 500.13 MHz): δ 5.37 (b, $\text{H}^2_{\text{trans}} + \text{H}^3_{\text{trans}}$), 5.22 (b, $\text{H}^2_{\text{cis}} + \text{H}^3_{\text{cis}}$), 3.46, 3.30 (b, $\text{H}^8_{\text{cis}} + \text{H}^8_{\text{trans}}$), 3.36, 3.26 (b, $\text{H}^8_{\text{trans}} + \text{H}^8_{\text{trans}}$), 3.05, 2.83, 2.72, 2.49 (b, $\text{H}^1 + \text{H}^4$), 2.44 (b, H^5), 2.07 (b, $\text{H}^6 + \text{H}^7$), 1.23 (b, $\text{H}^6 + \text{H}^7$). ^{13}C NMR (CDCl_3 , 125.76 MHz): δ 135.9, 133.1, 131.4, 128.7 ($\text{C}^2_{\text{cis}} + \text{C}^3_{\text{cis}}$), 135.7, 134.1, 130.6, 129.1 ($\text{C}^2_{\text{trans}} + \text{C}^3_{\text{trans}}$), 45.9 (C^5), 45.5, 45.4, 45.2, 42.0, 41.8, 41.5, 39.9, 37.4, 37.3, 37.1 ($\text{C}^1 + \text{C}^4$), 40.8, 40.2, 40.1, 39.7, 39.5, 38.9, 38.5 ($\text{C}^6 + \text{C}^7$), 36.7 (C^8). IR (neat, cm^{-1}), $\nu(\text{=CH})$: 968 (s), 746 (m); $\nu(\text{C-Br})$: 635 (m). It contains 399.70 mg (5 mmol) of Br/g of polymer.

ROMP-PNB-NB(CH₂)₄Br (**3b**, $x/y = 5.74$)

A monomer feed ratio NB:**1b** = 4:1 was used. Off-white gum-like solid. 97% yield. ^1H NMR (CDCl_3 , 500.13 MHz): δ 5.35

(b, $\text{H}^2_{\text{trans}} + \text{H}^3_{\text{trans}}$, NB + **1b**), 5.21 (b, $\text{H}^2_{\text{cis}} + \text{H}^3_{\text{cis}}$, NB + **1b**), 3.39 (b, H^8), 2.93 (b, $\text{H}^1 + \text{H}^4$, **1b**), 2.79 (b, $\text{H}^1_{\text{cis}} + \text{H}^4_{\text{cis}}$, NB; $\text{H}^1 + \text{H}^4$, **1b**), 2.54 (b, $\text{H}^1 + \text{H}^4$, **1b**), 2.44 (b, $\text{H}^1_{\text{trans}} + \text{H}^4_{\text{trans}}$, NB; $\text{H}^1 + \text{H}^4$, **1b**), 1.99 (H^7 , **1b**), 1.86, 1.80 (b, H^5 or $\text{H}^6 + \text{H}^7$, NB; $\text{H}^5 + \text{H}^8 + \text{H}^{10}$, **1b**), 1.36 (b, H^5 or H^6 , NB; $\text{H}^6 + \text{H}^9$, **1b**), 1.14 (b, $\text{H}^6 + \text{H}^7$, **1b**), 1.03 (m, H^7 , NB). ^{13}C NMR (CDCl_3 , 125.76 MHz): δ 134.2, 134.1, 134.0, 133.9 ($\text{C}^2_{\text{cis}} + \text{C}^3_{\text{cis}}$, NB + **1b**), 133.3, 133.1, 133.0 ($\text{C}^2_{\text{trans}} + \text{C}^3_{\text{trans}}$, NB + **1b**), 43.6, 43.3 ($\text{C}^1_{\text{trans}} + \text{C}^4_{\text{trans}}$, NB), 42.9 (C^5 , **1b**), 42.2 (C^7 , NB), 41.5 (C^7 , **1b**), 45.4, 41.0, 40.4, 39.8, 37.6 ($\text{C}^1 + \text{C}^4$, **1b**), 38.8, 38.6 ($\text{C}^1_{\text{cis}} + \text{C}^4_{\text{cis}}$, NB), 34.2 (C^{11}), 33.3, 33.1, 32.5, 32.4 ($\text{C}^5 + \text{C}^6 + \text{C}^{10}$, NB), 31.0 (C^6 , **1b**), 27.4 (C^9), 27.2 (C^8). IR (neat, cm^{-1}), $\nu(\text{=CH})$: 971 (s), 740 (m); $\nu(\text{C-Br})$: 637 (w), 557 (w). It contains 103.69 mg (1.30 mmol) of Br/g of polymer, which indicates a monomer ratio in the polymer of NB:**1b** = 5.74:1.

ROMP-PNB(CH₂)₄Br (**3b**, $x/y = 0$)

Off-white gum-like solid. 93% yield. ^1H NMR (CDCl_3 , 500.13 MHz): δ 5.30 (b, $\text{H}^2_{\text{trans}}$, $\text{H}^3_{\text{trans}}$), 5.20 (b, H^2_{cis} , H^3_{cis}), 3.40 (b, H^8), 2.92, 2.77, 2.57, 2.44 (b, $\text{H}^1 + \text{H}^4$), 1.91 (b, $\text{H}^5 + \text{H}^7$), 1.84 (b, $\text{H}^8 + \text{H}^{10}$), 1.38 (b, $\text{H}^6 + \text{H}^9$), 1.14 (b, $\text{H}^6 + \text{H}^7$). ^{13}C NMR (CDCl_3 , 125.76 MHz): δ 134.8, 133.5, 131.9, 130.4 ($\text{C}^2_{\text{cis}} + \text{C}^3_{\text{cis}}$), 134.8, 134.5, 131.2, 130.8 ($\text{C}^2_{\text{trans}} + \text{C}^3_{\text{trans}}$), 45.8, 45.4, 42.4, 40.9, 37.5 ($\text{C}^1 + \text{C}^4$), 43.5 (C^5), 40.3 (C^7), 34.2 (C^{11}), 33.2 (C^{10}), 31.1 (C^6), 27.4 (C^9), 27.2 (C^8). IR (neat, cm^{-1}), $\nu(\text{=CH})$: 969 (s), 736 (m); $\nu(\text{C-Br})$: 641 (s), 558 (s). It contains 309.70 mg (3.9 mmol) of Br/g of polymer.

Synthesis of ROMPH-PNB-NBCH₂Br (**4a**)

Chlorobenzene (450 mL) was added to a mixture of ROMP-PNB-NBCH₂Br (**3a**, $x/y = 7.9$, 6.76 g, 64.63 double bond equiv.) and p-toluensulfonylhydrazide (48.19 g, 258.93 mmol) under a nitrogen atmosphere. The polymer swelled in the solvent after 10-15 min at room temperature. The reaction mixture was refluxed for 5 h and the formation of foam was observed. After this time, the mixture was poured onto MeOH (300 mL) and the beige gum-like solid was filtered, washed with MeOH (4 x 50 mL) and air-dried. 6.65 g, 96% yield. If needed, the polymer can be swollen in CH_2Cl_2 and then precipitated onto MeOH to facilitate the elimination of residual chlorobenzene. ^1H NMR (CDCl_3 , 400.13 MHz): δ 3.52 (m, H^8), 3.27 (m, H^8), 2.35 (b, H^5_{endo} , **1a**), 2.04 (b, H^6_{endo} , **1a**), 1.91 (b, H^7 , NB; $\text{H}^1 + \text{H}^5_{\text{exo}} + \text{H}^7$, **1a**), 1.71 (b, $\text{H}^1 + \text{H}^4 + \text{H}^5$ or H^6 , NB; $\text{H}^4 + \text{H}^6_{\text{exo}}$, **1a**), 1.42 (b, $\text{H}^2 + \text{H}^6_{\text{exo}}$, **1a**), 1.26 (b, $\text{H}^2 + \text{H}^3$, NB; H^3 , **1a**), 1.13 (b, H^5 or H^6 , NB), 1.07 (b, $\text{H}^2 + \text{H}^6_{\text{endo}}$, **1a**), 0.88 (m, H^7 , **1a**), 0.61 (m, H^7 , NB). ^{13}C NMR (CDCl_3 , 100.61 MHz): δ 44.7 (C^5 , **1a**), 42.4 (C^1 , **1a**), 40.9 (C^7 , NB), 40.5 ($\text{C}^1 + \text{C}^4$, NB), 39.1 (C^4 , **1a**), 38.8 (C^7 , **1a**), 38.6 (C^6 , **1a**), 37.6 (C^8), 36.2, 35.6 (C^3 , **1a**), 35.9 ($\text{C}^2 + \text{C}^3$, NB), 31.9 ($\text{C}^5 + \text{C}^6$, NB), 29.5 (C^2 , **1a**). IR (neat, cm^{-1}), $\nu(\text{C-Br})$: 638 (m). The copolymer contains 79.89 mg (1 mmol) of Br/g of polymer. All the saturated ROMPH polymers were prepared in the same way.

ROMPH-PNBCH₂Br (**4a**)

Prepared from **3a**, $x/y = 0$. Off-white gum-like solid. 54% yield. ^1H NMR (CDCl_3 , 500.13 MHz): δ 3.51 (m, H^8), 3.27 (m, H^8),

2.36 (b, H⁵_{endo}), 2.05 (b, H⁶_{endo}), 1.95 (b, H¹ + H⁵_{exo} + H⁷), 1.79 (b, H⁴), 1.71 (b, H⁶_{exo}), 1.50, 1.44 (b, H² + H⁶_{exo}), 1.32 (b, H³), 1.07 (b, H² + H⁶_{endo}), 0.89 (b, H⁷). ¹³C NMR (CDCl₃, 100.61 MHz): 46.9 (C⁵_{exo}), 44.4 (C⁵_{endo}), 42.5, 42.1 (C¹), 39.6 (C⁸_{exo}), 38.8 (C⁴), 38.6 (C⁷), 38.4 (C⁶_{endo}), 37.7 (C⁶_{exo}), 37.2 (C⁸_{endo}), 35.9, 35.7 (C³), 29.2 (C²). IR (neat, cm⁻¹), ν(C-Br): 638 (m).

ROMPH-PNB-NB(CH₂)₄Br (4b)

Prepared from **3b**, x/y = 10.48. Off-white gum-like solid. 88% yield. ¹H NMR (CDCl₃, 400.13 MHz): δ 3.41 (b, H¹¹), 1.88 (b, H⁷, NB; H⁷_{exo} + H⁷_{endo} + H¹⁰, **1b**), 1.71 (b, H¹ + H⁴ + H⁵ or H⁶, NB; H¹ + H⁴ + H⁵ + H⁸, **1b**), 1.45–1.20 (b, H² + H³, NB; H² + H³ + H⁶ + H⁹, **1b**), 1.13 (b, H⁵ or H⁶, NB; H⁶, **1b**), 0.82 (b, H⁷_{endo}, **1b**), 0.63 (b, H⁷, NB; H⁷_{exo}, **1b**). ¹³C NMR (CDCl₃, 100.61 MHz): δ 44.7 (C⁵_{exo}, **1b**), 43.0, 42.2, 41.8 (C¹ + C⁴, **1b**), 40.9 (C⁷, NB; C⁷_{exo}, **1b**), 40.5 (C¹ + C⁴, NB), 39.2 (C⁵_{endo}, **1b**), 38.7 (C⁷_{endo}, **1b**), 38.3 (C⁸, **1b**), 36.6 (C² + C³, **1b**), 35.9 (C² + C³, NB), 34.2 (C¹¹), 33.3 (C¹⁰), 31.9 (C⁵ + C⁶, NB), 30.2, 30.0 (C⁶_{exo} + C⁶_{endo}, **1b**), 27.3 (C⁹). IR (neat, cm⁻¹), ν(C-Br): 651(m), 564 (m). The copolymer obtained contains 55.32 mg (0.69 mmol) of Br/g of polymer.

ROMPH-PNB(CH₂)₄Br (4b)

Prepared from **3b**, x/y = 0: Off-white gum-like solid. 72% yield. ¹H NMR (CDCl₃, 500.13 MHz): δ 3.42 (t, H¹¹), 1.97 (b, H⁷_{exo}), 1.90 – 1.65 (m, H¹ + H⁴ + H⁵_{endo} + H⁷_{endo} + H⁸ + H¹⁰), 1.47 (b, H⁹), 1.40 – 1.20 (b, H² + H³ + H⁵_{exo} + H⁶_{exo} + H⁶_{endo} + H⁹), 1.07 (m, H⁶_{endo}), 0.94 (b, H⁶_{exo}), 0.81 (b, H⁷_{endo}), 0.67 (b, H⁷_{exo}). ¹³C NMR (CDCl₃, 100.61 MHz): δ 44.7 (C⁵_{exo}), 42.7, 42.2, 41.7 (C¹ + C⁴), 40.8 (C⁷_{exo}), 39.3 (C⁵_{endo}), 38.8 (C⁷_{endo}), 38.3 (C⁸), 36.7, 36.5 (C² + C³), 34.3 (C¹¹), 33.3 (C¹⁰), 30.1 (C⁶_{exo} + C⁶_{endo}), 27.3 (C⁹). IR (neat, cm⁻¹), ν(C-Br): 647 (m), 563 (s).

Determination of reactivity ratios

Copolymerizations of norbornene and **1a** were carried out at monomer feed ratios $f = \text{NB}/\mathbf{1a} = 0.94, 1.87, 3.80$ and 7.61 using 0.10 mL (0.72 mmol) of **1a** in each experiment and following the conditions of Table 1. After 60 min the reactions were quenched by pouring the mixture onto methanol. The composition of the copolymers was determined by quantitative analysis of the bromo content in the material. The composition data of the copolymers (F) obtained for the copolymerization at different monomer feed ratios (f) were fitted to the Finemann-Ross equation.²³ The reactivity ratios for the copolymerization of NB and **1b** were determined in a similar way. Details can be found in the ESI.

Synthesis of ROMPH-PNB-NBCH₂CN (5a)

Polymer **4a** (0.2 g, 0.28 mmol of Br), tetrabutylammonium cyanide (0.12 g, 0.42 mmol) and dry THF (35 mL) were mixed in a flask under nitrogen. The polymer swelled and the reaction mixture was stirred for 24 h at reflux. The mixture was poured onto MeOH (100 mL) and a white gum-like solid precipitated, which was filtered, washed with MeOH (3 x 15 mL), air-dried and kept overnight at 35 °C in vacuo. 0.18 g, 98% yield. ¹H

NMR (CDCl₃, 500.13 MHz): δ 2.37 (m, H⁸), 2.14 (m, H⁸), 1.89 (m, H⁷, NB; H¹ + H⁷, NB-CH₂CN), 1.71 (b, H¹ + H⁴ + H⁵ or H⁶, NB; H⁴ + H⁶, NB-CH₂CN), 1.26 (b, H² + H³, NB; H² or H³, NB-CH₂CN), 1.13 (b, H⁵ or H⁶, NB; H⁵, NB-CH₂CN), 0.87 (m, H⁷, NB-CH₂CN), 0.63 (m, H⁷, NB). ¹³C NMR (CDCl₃, 100.61 MHz): δ 120.4 (CN), 40.9 (C⁷, NB), 40.5 (C¹ + C⁴, NB), 38.4 (C⁵, NB-CH₂CN), 35.7 (C² + C³, NB), 31.9 (C⁵ + C⁶, NB), 29.7 (C² or C³, NB-CH₂CN), 19.6 (C⁸). IR (neat, cm⁻¹), ν(CN): 2254 (w). The copolymer contains 3.32 mg (0.041 mmol) of Br/g, which indicates a 97% of bromine substitution.

Synthesis of ROMPH-PNB-NBCH₂OCOME (6a)

Polymer **4a** (0.2 g, 0.28 mmol of Br), acetic acid (0.040 mL, 0.70 mmol), DBU (0.10 mL, 0.70 mmol) and toluene (30 mL) were mixed in a flask under nitrogen. The reaction was stirred for 24 h at reflux. The solution was poured onto MeOH (100 mL) and a white gum-like solid precipitated. The solid was filtered, washed with MeOH (3 x 15 mL), air-dried and kept overnight at 35 °C in vacuo. 0.16 g, 85% yield. ¹H NMR (CDCl₃, 500.13 MHz): δ 4.09 (b, H⁸), 3.88 (b, H⁸), 2.22 (b, H⁵, NB-CH₂OCOME), 2.04 (b, Me), 1.89 (b, H⁷, NB; H¹ + H⁷, NB-CH₂OCOME), 1.71 (b, H¹ + H⁴ + H⁵ or H⁶, NB; H⁴ + H⁶, NB-CH₂OCOME), 1.26 (b, H² + H³, NB; H² or H³, NB-CH₂OCOME), 1.13 (b, H⁵ or H⁶, NB), 0.86 (b, H⁷, NB-CH₂OCOME), 0.62 (m, H⁷, NB). ¹³C NMR (CDCl₃, 100.61 MHz): δ 170.9 (CO), 66.6 (C⁸), 41.0 (C⁷, NB), 40.6 (C¹ + C⁴, NB), 40.2 (C⁵, NB-CH₂OCOME), 39.3 (C⁴, NB-CH₂OCOME), 35.9 (C² + C³, NB), 31.9 (C⁵ + C⁶, NB), 29.8 (C² or C³, NB-CH₂OCOME), 21.3 (Me). IR (neat, cm⁻¹), ν(C=O): 1744 (s); ν(C–O): 1240 (s). The copolymer contains 19.58 mg (0.245 mmol) of Br/g of Cop, which indicates 83% of substitution.

Synthesis of ROMPH-PNB-NBCH₂SPh (7a)

Polymer **4a** (0.2 g, 0.28 mmol of Br), thiophenol (0.060 mL, 0.56 mmol), DBU (0.086 mL, 0.56 mmol) and toluene (30 mL) were mixed in a flask under nitrogen. The reaction was stirred for 24 h at reflux. The mixture was poured onto MeOH (100 mL) and a white gum-like solid precipitated. The solid was filtered, washed with MeOH (3 x 15 mL), air-dried and kept overnight at 35 °C in vacuo. 0.20 g, 97% yield. ¹H NMR (CDCl₃, 500.13 MHz): δ 7.31 (b, H_{ortho}, H_{meta}), 7.15 (b, H_{para}), 3.08 (dd, $J = 11, 5$ Hz, H⁸), 2.69 (t, $J = 11$ Hz, H⁸), 2.15 (b, H⁵, NB-CH₂SPh), 2.03 (m, H⁶, NB-CH₂SPh), 1.90 (m, H⁷, NB; H¹ + H⁷, NB-CH₂SPh), 1.71 (b, H¹ + H⁴ + H⁵ or H⁶, NB; H⁴, NB-CH₂SPh), 1.45 (b, H², NB-CH₂SPh), 1.27 (b, H² + H³, NB; H³, NB-CH₂SPh), 1.14 (b, H⁵ or H⁶, NB; H⁶, NB-CH₂SPh), 0.86 (m, H⁷, NB-CH₂SPh), 0.63 (m, H⁷, NB). ¹³C NMR (CDCl₃, 125.76 MHz): δ 137.7 (C_{ipso}), 129.0, 128.9 (C_{ortho}, C_{meta}), 125.7 (C_{para}), 42.4 (C¹, NB-CH₂SPh); 41.0 (C⁷, NB; C⁵, NB-CH₂SPh), 40.6 (C¹ + C⁴, NB), 39.1 (C⁴, NB-CH₂SPh), 38.8 (C⁷, NB-CH₂SPh), 38.7 (C⁶, NB-CH₂SPh). 36.5 (C⁸), 35.9, 35.7 (C² + C³, NB; C³, NB-CH₂SPh), 31.9 (C⁵ + C⁶, NB), 29.9 (C², NB-CH₂SPh). IR (neat, cm⁻¹), 1584 (w), 734 (s), 690 (s), 473 (m). The copolymer contains 3.53 mg (0.044 mmol) of Br/g of Cop, which indicates 97% of substitution.

Synthesis of ROMPH-PNB-NBCH₂N₃ (**8a**)

Polymer **4a** (6.5 g, 6.5 mmol of Br) and NaN₃ (2.54 g, 39 mmol) were mixed in DMF (200 mL) under nitrogen. The suspension was refluxed for 24 h and then it was poured onto MeOH (200 mL). The solid was filtered, washed with MeOH (3 x 50 mL and 3 x 15 mL), air-dried and kept overnight at 35 °C in vacuo. Off-white spongy solid. 6.12 g, 98% yield. ¹³C CP-MAS NMR (100.61 MHz): 43.2 (b), 37.9 (b), 32.9 (b). IR (neat, cm⁻¹), ν(N≡N): 2091 (vs); ν(N=N): 1269 (vs). The polymer contains no Br which indicates 100 % of substitution. ROMPH-PNB-(CH₂)₄N₃ (**8b**) was prepared following the same procedure, but using polymer **4b** (0.45g, 0.71 mmol of Br). Ochre spongy polymer. 0.40 g, 96% yield. ¹³C CP-MAS NMR (100.61 MHz): 42.8 (b), 38.0 (b), 33.2 (b). The copolymer contains no Br, which indicates 100% of substitution. IR (neat, cm⁻¹), ν(N≡N): 2090 (vs); ν(N=N): 1254 (vs).

Synthesis of ROMPH-PNB-NB(CH₂)₄SnBu₂(*p*-C₆H₄OMe) (**9b**)

Diisopropylamine (4.23 mL, 29.94 mmol) was dissolved in THF (40 mL) under a nitrogen atmosphere and set at -78 °C. Butyl lithium (18.71 mL, 1.6 M, 29.94 mmol) was added dropwise and stirred for 90 min at -78 °C. Dibutyltinhydride (10.21 g, 29.94 mmol) dissolved in THF (5 mL) was added dropwise and stirred during 60 min at -78 °C. The solution turned dark yellow. Polymer **4b** (4.90 g, 6.67 mmol of Br) was swelled in THF (120 mL) under a nitrogen atmosphere and cooled to -78 °C. The solution of LiSnBu₂(*p*-C₆H₄OMe) was added to the polymer via canula. The mixture was stirred for 24 h and the temperature was slowly risen during this time to room temperature. The mixture was poured onto MeOH and a solid precipitated; it was filtered, crushed, washed with MeOH (3 x 50 mL and 3 x 20 mL), air-dried and kept overnight in vacuo at 35 °C. Off-white gum-like solid. 6.08 g, 92% yield. ¹H NMR (CDCl₃, 500.13 MHz): δ 7.37 (m, H_{ortho}), 6.90 (m, H_{meta}), 3.80 (b, OCH₃), 1.88 (b, H⁷, NB + NB(CH₂)₄SnR₂R'), 1.71 (b, H¹ + H⁴ + H⁵ or H⁶, NB; H¹ + H⁴ + H⁵, NB(CH₂)₄SnR₂R'), 1.54 (b, CH₂CH₂Sn), 1.33 (m, CH₂(CH₂)₂Sn), 1.26 (b, H² + H³, NB + NB(CH₂)₄SnR₂R'), 1.13 (b, H⁵ or H⁶, NB), 1.02 (m, CH₂Sn), 0.88 (t, *J* = 7.3 Hz, CH₃(Bu); H⁷, NB(CH₂)₄SnR₂R'), 0.62 (m, H⁷, NB). ¹³C NMR (CDCl₃, 100.61 MHz): δ 137.4 (C_{ortho}), 114.1 (C_{meta}), 55.3 (OCH₃), 42.0 (C⁵, NB(CH₂)₄SnR₂R'), 41.0 (C⁷, NB + NB(CH₂)₄SnR₂R'), 40.6 (C¹ + C⁴, NB + NB(CH₂)₄SnR₂R'), 35.9 (C² + C³, NB + NB(CH₂)₄SnR₂R'), 31.9 (C⁵ + C⁶, NB), 29.3 (CH₂CH₂Sn), 27.0 (CH₂(CH₂)₂Sn), 13.9 (CH₃(Bu)), 9.8 (CH₂Sn). ¹¹⁹Sn NMR (CDCl₃, 149.21 MHz): δ -42.08. IR (neat, cm⁻¹), 1587 (m), 1494 (m), 1276 (s), 1242 (s), 1180 (s), 1035 (m), 805 (m), 514 (m). The copolymer contains no Br, which indicates 100 % of substitution.

Synthesis of ROMPH-PNB-NBCH₂triazole (**10a**)

Polymer **8a** (0.2 g, 0.21 mmol of azide), dimethyl acetylenedicarboxylate (0.1 mL, 0.82 mmol) and toluene (12 mL) were mixed in a flask. The reaction mixture was stirred at reflux for 8 h, and poured onto MeOH. The solid was filtered,

washed with MeOH (3 x 15 mL), air-dried and kept overnight at 35 °C in vacuo. Ochre-white solid. 0.21g, 95% yield. ¹³C CP-MAS NMR (100.61 MHz): δ 161.0 (OCOR); 140.2, 130.8 (C=C); 53.6 (OCH₃); 42.9, 37.8, 33.1 (polymeric backbone). IR (neat, cm⁻¹), ν(C=O): 1734 (vs); ν(C-O st. as): 1216 (s); ν(C-O st. sim): 1059 (m).

General synthesis of ROMPH-PNB-NBCH₂triazoles **11a-15a**

Polymer **8a** (0.2 g, 0.208 mmol of azide), CuI (0.0779 g, 0.41 mmol), DIPEA (1.78 mL, 10.2 mmol), the corresponding alkyne (0.82 mmol) and THF (20 mL) were mixed in a flask and stirred at the appropriate temperature for 24 h under nitrogen (see Table 6). The resulting mixture was poured onto MeOH (20 mL) and a cloudy yellow suspension was obtained. Aqueous NH₃ (30 mL, 32% w/w) was added, and the mixture turned blue. The solid was filtered, washed with 16.7 M aqueous NH₃ (3 x 15 mL), H₂O (3 x 15 mL), a H₂O:MeOH = 1:1 mixture (3 x 15 mL), air-dried and kept overnight at 35 °C in vacuo. The product was a solid insoluble in most common organic solvents.

11a. Yellowish white solid. 0.22 g, quantitative yield. ¹³C CP-MAS NMR (100.61 MHz): δ 157.5 (C=CR), 120.0 (C=CR); 43.0, 37.8, 32.9 (polymeric backbone + ^tBu). IR (neat, cm⁻¹): 1223 (m), 1045 (m).

12a. Yellowish white solid. 0.21 g, 95% yield. ¹³C CP-MAS NMR (100.61 MHz): δ 149.9 (C=CR), 129.8 (C=C cyclohexenyl), 126.8-112.7 (C=C cyclohexenyl; C=CR); 42.9, 37.8, 33.0 (polymeric backbone + aliphatic cyclohexenyl). IR (neat, cm⁻¹): 1044 (m).

13a. Ochre solid. 0.22 g, quantitative yield. ¹³C CP-MAS NMR (100.61 MHz): δ 148.6 (C=CR), 138.5 – 124.5 (C_{ph} + C=CR); 43.0, 37.8, 33.1 (polymeric backbone). IR (neat, cm⁻¹): 1636 (w), 758 (s), 692 (s).

14a. Beige solid. 0.22 g, 99% yield. ¹³C CP-MAS NMR (100.61 MHz): δ 147.1 (C=CR), 136.2 (C_{ipso}), 130.9 (C_{para}), 126.7 (C=CR, C_{ortho}, C_{meta}), 124.5 (CF₃); 42.9, 37.8, 33.1 (polymeric backbone). ¹⁹F MAS NMR (376.5 MHz): δ -60.4. IR (neat, cm⁻¹), ν(C-F st.): 1321 (vs); 1171 (s), 1129 (vs), 1059 (s).

15a. Yellow solid. 0.23 g, quantitative yield. ¹³C CP-MAS NMR (100.61 MHz): δ 160.2 (C_{para}-OCH₃), 148.5 (C=CR), 122.4–110.6 (C=CR, C_{ortho}, NC-C_{ipso}), 114.7 (C_{meta}), 56.5 (OCH₃); 42.8, 37.8, 33.0 (polymer backbone). IR (neat, cm⁻¹): 1500 (m), 1248 (s), 1174 (m), 1031 (m), 828 (m), 541 (m).

ROMPH-PNB-NB(CH₂)₄triazole (**15b**) was synthesized in the same way from polymer **8b** (1.7 mmol azide/g). Quantitative yield. ¹³C CP-MAS NMR (100.61 MHz): δ 160.4 (C_{para}-OCH₃), 149.0 (C=CR), 137.4–111.4 (C=CR, C_{ortho}, NC-C_{ipso}, C_{meta}), 56.8 (OCH₃); 42.9, 38.6, 33.8 (polymeric backbone). IR (neat, cm⁻¹): 1601 (m), 1500 (s), 1290 (s), 1251 (vs), 1167 (vs), 1031 (vs), 817 (vs), 534 (s), 450 (s).

General procedure for the Stille reactions using **9b**. Synthesis of 4-methoxy-4'-trifluoromethyl-1,1'-biphenyl

Polymer **9b** (0.81 g, 0.82 mmol) was placed in a flask under nitrogen and swollen in 40 mL of toluene. 4-

iodotrifluorobenzene (0.98 mL, 0.65 mmol) and [Pd(PPh₃)₄] (0.19 mg, 0.016 mmol) were added to the polymer. The mixture was kept at 100 °C for 40 h and then it was cooled down to room temperature. MeOH (100 mL) was added to the mixture and the polymer precipitated. It was filtered, washed with MeOH (3 x 20 mL), air-dried and kept overnight at vacuo at 40 °C. The solvents in the filtrate were distilled to ca. 1 mL, and the resulting liquid residue was treated with activated carbon and filtered through a silica column using CH₂Cl₂ as eluent. Evaporation of the solvent afforded the coupling product as a solid (119.2 mg, 73% yield). It was characterized by ¹H and ¹⁹F NMR and the spectra compared to those reported in the literature.²⁴ The amount of residual tin in the product was 0.216 mg Sn/g. The yields and conditions of other experiments are collected in Table 5.

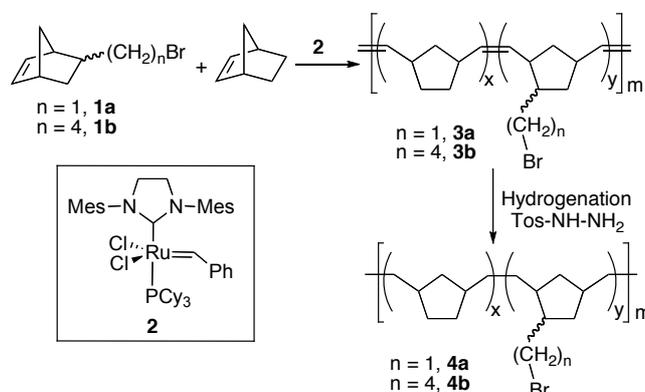
Results and Discussion

Synthesis of the ROMP and ROMPH ω-bromoalkyl polynorbornenes.

Bromoalkylnorbornenes **1a** and **1b** were synthesized by the Diels-Alder reaction of commercially available dicyclopentadiene and allyl bromide or 6-bromo-1-hexene respectively, as described before.⁷ Either monomer has a potential advantage in the synthesis of polymeric support materials. The synthesis of **1a** is less expensive but, on the other hand, the longer alkyl chain in **1b** may be of interest to place a functional group away from the polymeric backbone in order to improve reactivity. Both **1a** and **1b** are a mixture of endo and exo isomers in a ratio endo:exo close to 85:15, and this mixture was used in the polymerization experiments. The ROM homopolymerization of **1a** or **1b** and also de ROM copolymerization of either monomer and norbornene were carried out using Grubbs' 2nd generation catalyst **2** (Scheme 1). An amount of catalyst 0.02% mol of the functionalized monomer **1** is enough to achieve high polymerization yields in 4 hours (Table 1) and this amount of catalyst and reaction time were used in all the experiments. Similar good yields can also be obtained if the amount of catalyst is reduced to 0.01% mol but the reaction time needs to be extended to 15 h. Lower catalyst loadings (0.004% mol of the amount of monomer **1**) decreased the yield of the reaction dramatically (1.5% yield for a 1:1 copolymerization of **1a** and norbornene in 15 h). CH₂Cl₂ was the solvent of choice since it gives better yields than toluene (45% yield for an experiment analogous to entry 3, Table 1) or more coordinating solvents such as acetonitrile or THF (about 10% yield in both cases). The polymers obtained are off-white gum-like solids which are not soluble in most organic solvents, so their molecular weight and polydispersity could not be determined. The copolymer composition was determined by quantitative analysis of the bromo content in the polymer.

As it can be observed in Table 1, the composition of the copolymers does not reproduce the monomer feed ratio and the amount of norbornene in the resulting polymer is always higher. A rough determination of the reactivity ratios for these

copolymerizations is consistent with this observation and for the copolymerization of NB/**1a** the results are $r_{NB} = 1.58$ and $r_{1a} = 0.65$, which correspond to an almost ideal random copolymer richer in norbornene. The copolymerization of NB/**1b** shows $r_{NB} = 1.78$ and $r_{1b} = 0.84$, and thus a non-ideal random copolymer again richer in norbornene should be expected. By varying the monomer feed ratio, polymers with a functionalization roughly between 1 to 5 mmol of Br/g of polymer can be obtained.



Scheme 1. Synthesis of the polymeric ROMPH-PNB supports **4**.

Table 1. ROMP reactions of ω-bromoalkylnorbornenes and norbornene (NB).^a

Entry	Monomer	Feed Ratio ^b NB:1:2	Yield (%) ^c	Copolymer, x/y ^d	mmol Br/g in 3
1	1a	0:5000:1	87	3a , 0	5.3
2	1a	5000:5000:1	93	3a , 1.05	3.5
3	1a	10000:5000:1	84	3a , 2.8	2.2
4	1a	20000:5000:1	91	3a , 6.2	1.3
5	1a	40000:5000:1	97	3a , 11.3	0.8
6	1b	0:5000:1	93	3b , 0	4.4
7	1b	5000:5000:1	94	3b , 1.35	2.8
8	1b	10000:5000:1	96	3b , 3.1	1.9
9	1b	20000:5000:1	96	3b , 5.1	1.4
10	1b	40000:5000:1	96	3b , 10.8	0.8

^a The reactions were carried out under nitrogen in CH₂Cl₂ (total volume 8 mL for 4 h at room temperature using 0.7 mmol of **1a** or 0.5 mmol of **1b**). ^b Molar ratio in the feed. ^c Yields are referred to the total monomer mass. ^d x/y ratio was determined by quantitative analyses of the bromo content in the polymer (see Experimental Section).

The polymers swell in solvents such as THF, dichloromethane and chloroform by a volume factor between 2 and 3, enough to allow the characterization of these polymers by NMR of the viscous samples. Assignments were made with the help of NMR homo- and heteronuclear correlation experiments and previous literature characterization data (see Experimental Section).²⁵ The ¹H NMR spectra of the homo- and copolymers show signals in the olefinic region for the trans (δ 5.3) and cis (δ 5.2) stereochemistry of the double bonds. Both arrangements in the polymers are closely represented, with trans:cis ratios that range from 70:30 to 40:60, as it has been observed before for other polymerizations with this type

of catalysts.^{11j,12d} The bromoalkyl substituents show characteristic resonances for the bromomethyl group around 3.5-3.2 ppm. A complicated stereochemistry can be anticipated for these polymers and besides the inherent complex tacticity of ROMP polynorbornene,^{11j,25} different arrangements of the bromoalkyl monomers are expected (head to head, head to tail, tail to tail) which are visible in the ¹³C NMR spectra of homopolymers **3a** and **3b** (x/y = 0) (see ESI).^{25c} Also, the presence of both configurations for C⁵ (due to the exo/endo configuration in **1**) complicate the structural assignments. Thus, no attempts were made at analyzing the fine structure of the spectra in detail. The IR spectra of the solid polymer samples also show characteristic absorptions for the double bond, $\nu(\text{=CH})$ about 970 (trans) and 740 (cis) cm⁻¹,²⁶ and the bromo substituent, $\nu(\text{C-Br})$ in the region 640-550 cm⁻¹.

The insolubility of the polymers is an advantage if they are to be used as solid supports but it prevented their molecular weight and polydispersity index (PDI) determination by GPC. We carried out some polymerizations using ethyl vinyl ether as chain transfer agent (CTA) in a feed ratio 1:CTA = 50:1. In this way, shorter polymer chains are expected, hopefully soluble enough to perform a GPC analysis, which could give a minimum value for the molecular weight of the polymers obtained in Table 1. Indeed, the polymers prepared in this way were soluble and showed unimodal distributions in GPC although they are quite polydisperse materials (Table 2).

Table 2. ROMP reactions of ω -bromoalkylnorbornenes and norbornene in the presence of a CTA.^a

Entry	Monomer	NB:1:CTA:2 ^b	3 , x/y ^c	Yield (%) ^d	M _n (x 10 ⁻³)	M _w /M _n
1	1a	0:5000:100:1	3a , 0	74	22.2	2.12
2	1b	0:5000:100:1	3b , 0	83	36.8	2.23
3	1a	20000:5000:100:1	3a , 4.81	91	29.1	3.47
4	1b	20000:5000:100:1	3b , 4.88	93	54.2	6.57

^a CTA: ethyl vinyl ether. The reactions were carried out under nitrogen in CH₂Cl₂ (total volume 8 mL) for 4 h at room temperature using 0.7 mmol of **1a** or 0.5 mmol of **1b**. ^b Molar ratio in the feed. ^c x/y ratio was determined by quantitative analyses of the bromo content in the polymer (see Experimental Section). ^d Yields are referred to the total monomer mass.

The molecular weights are larger for the copolymers than for the homopolymers and also for the polymerizations involving **1b**. It is reasonable to assume that the insoluble polymers obtained without the use of a CTA, suitable to be used as supports, are larger and also very polydisperse.

It has been shown that the second-generation Grubbs' catalyst is very active and, the rate of propagation being larger than the rate of initiation, leads to non-living polymerizations and secondary metathesis processes that increase the polydispersity of the obtained materials.^{14c,27} We carried out several experiments using a higher amount of catalyst in order to obtain soluble polymers which could give information about the prevalence of secondary metathesis reactions in the polymerization of **1** with complex **2** and/or other cross-linking

pathways. Several homopolymerizations of **1a** in a **1a**:**2** = 100:1 ratio were carried out changing the reaction times (entries 1-4, Table 3). A clear decrease in molecular weight is observed along with an increase in the polydispersity and the trans to cis alkene ratio in the polymer, upon increasing the reaction time. These are indications of secondary metathesis on the polymer chains (chain transfer, depolymerization and backbiting) that do not allow to obtain the well-defined polymers characteristic of a living polymerization.^{12c,28}

An additional experiment was performed that led to similar conclusions. First, the homopolymerization reaction of **1a** in a **1a**:**2** = 100:1 ratio was carried out and, after 40 min, the reaction mixture was split in two batches. The first one was poured onto methanol and a polymer precipitated which was filtered and kept for further analysis (entry 5A, Table 3). The second batch was stirred for a longer time (4 h total time) and then poured onto methanol where a second polymer sample was

Table 3. ROMP reactions of ω -bromoalkylnorbornenes with lower monomer : catalyst ratio.^a

Entry	Monomer	NB:1:2 ^b	Reaction time (min)	M _n (x 10 ⁻³)	M _w /M _n	Trans:cis ratio ^c
1	1a	0:100:1	15	13.9	2.80	2.23
2	1a	0:100:1	30	14.3	2.80	2.35
3	1a	0:100:1	60	6.6	3.26	2.61
4	1a	0:100:1	240	3.9	3.16	2.84
5A	1a	0:100:1	40	14.9	2.83	2.28
5B	1a	0:100:1	240	7.1	2.87	2.45
6	1a	0:1000:1	240	24.8	2.09	2.31
7 ^d	1a	100:100:1	240	3.8	3.5	1.79
8 ^d	1a	1000:1000:1	240	38.5	3.39	1.21
9 ^d	1b	100:100:1	240	5.4	6.57	1.23
10 ^d	1a	200:100:1	240	4.52	4.57	1.50

^a The reactions were carried out under nitrogen in CH₂Cl₂ (total volume 8 mL) at room temperature using 0.1 mL of **1** (0.09 M for **1a** and 0.07 M for **1b**); the yields obtained range from 65 to 85% in the homopolymerization reactions and > 89% for the copolymerizations. ^b Molar ratio in the feed. ^c Alkene trans/cis ratio in the polymer was determined by ¹H NMR. ^d Composition of copolymers x/y: 1 (entry 7), 1.1 (entry 8), 0.95 (entry 9), 1.9 (entry 10).

obtained (entry 5B, Table 3). Again the change in M_n, PDI and trans to cis alkene ratio upon catalyst exposure shows that secondary metathesis is taking place.^{27,29,30} The additional polymerization reactions collected in Table 3 show that the NB/1 copolymers are generally more polydisperse than the homopolymers (cf. entries 4, 7 and 10, Table 3). The increase of the monomer:catalyst ratio leads to polymers with higher molecular weight (cf. entries 4 and 6 or 7 and 8, Table 3). In every polymer synthesized or used for the abovementioned experiments, the -CH₂Br ¹H NMR region shows exactly the same pattern, and the ratio of the integrals for the alkene:CH₂Br signals in the homopolymers is invariably 1:1, showing that the bromo functionality does not change and it is not lost in the

polymerization process. Thus, it is unlikely that the bromoalkyl chains are involved in cross-linking processes and the lower solubility of the polymers collected in Table 1, where a larger monomer:catalyst ratio is used, must be mostly determined by their large molecular weight along with the effect of secondary metathesis on the polymer chains.

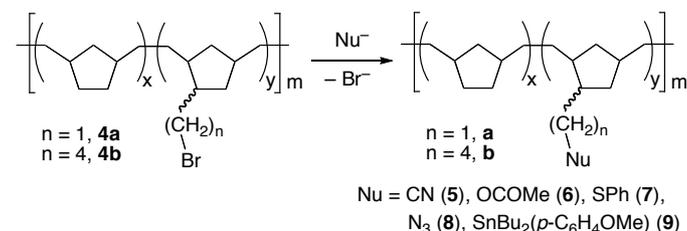
Saturated ω -bromoalkyl ROMPH-PNBs (**4**, Scheme 1) were obtained by hydrogenation of the double bonds of the ROMP-PNBs **3**. The reduction with excess *p*-toluenesulfonylhydrazide worked well, and complete disappearance of the olefinic signals were observed in the NMR spectra of the new materials. The polymers were obtained as gum-like off-white solids, insoluble in most organic solvents, which swell in chloroform, CH_2Cl_2 and THF by a volume swelling factor between 1.2-1.4 for **4a** and 1.3-1.9 for **4b**. Thus, the extent of swelling of these materials is small, certainly smaller than that observed for polymers **3**, but enough to allow the NMR characterization of the viscous samples. Resonances for the bromomethyl group in the NMR spectra (δ 3.5-3.2) and the $\nu(\text{C-Br})$ absorption between 640-560 cm^{-1} in IR spectroscopy are characteristic features for **4**. The amount of bromo in the ROMPH-PNBs was determined by quantitative analysis and, starting from the different copolymers **3**, saturated materials with a functionalization degree between 1 and 5 mmol Br/gr can be obtained.

In some reduction experiments, a small loss of bromide (5-15%) was observed in polymers **4** when compared with the calculated amount considering the functionalization of the starting ROMP-PNBs **3**, and the slight weight change upon hydrogenation. This decrease in the amount of bromide could be due to a selective loss of bromo-enriched polymeric chains in the reaction workup. Nonetheless, we checked if it was linked to the introduction of an additional undesired functionality in the polymer. An independent experiment treating 1-bromo-3-methylbutane as a model compound with excess *p*-toluenesulfonylhydrazide, in the same conditions used for the reduction of **3**, did not show the loss of the bromo substituent. A HBr elimination in the polymer does not occur since it would result in a methyl generated from the hydrogenation of the new terminal double bond formed, which was not present in the polymer, as checked by ^1H and ^{13}C NMR spectroscopy. Thus, the reduction process does not introduce any new reactive center in the polymer which remains a saturated scaffold with bromo as the only functional group present.

Functionalization of the ROMPH ω -bromoalkyl polynorbornenes **4**.

The versatility of the ROMPH scaffolds was tested by subjecting **4** to several transformations that can be useful in post-polymerization attachment of a functional group of interest. First, the synthesis of saturated polymers with pendant functionalized alkyl chains was possible by nucleophilic substitution of bromide in polymers **4**. Different nucleophiles have been introduced which lead to polymeric materials bearing cyano, azido, thio or ester groups (Scheme 2). Even a bulky

nucleophile such as a stannyl group can be introduced. Table 4 collects the polymers prepared by this route. The bromo content of the final polymers was determined to check the efficiency of the substitution, which is very high in most reactions (97-100%), with the exception of the ester substitution (83%, entry 2, Table 4). In the latter case, HBr elimination is also observed as shown by the presence of small olefinic signals in the ^1H NMR spectrum of **6a** (4.82 and 4.72 ppm). The other nucleophiles collected in Table 4 undergo faster bromo substitution and HBr elimination does not compete.



Scheme 2. Nucleophilic substitution reactions on the ω -bromoalkyl ROMPH polynorbornenes.

Table 4. Functionalization of polymers **4** by nucleophilic substitution.^a

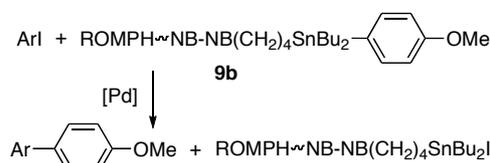
Entry	4 (mmol Br/g)	ROMPH-PNB-NB(CH ₂) _n Nu, Nu	Residual mmol Br/g	Isolated yield %, (Br substitution %) ^f
1 ^b	4a (1.4)	5a , CN	0.041	98 (97)
2 ^c	4a (1.4)	6a , OCOMe	0.245	85 (83)
3 ^c	4a (1.4)	7a , SPh	0.044	97 (97)
4 ^d	4a (1)	8a , N ₃	0	98 (100)
5 ^d	4b (1.58)	8b , N ₃	0	96 (100)
6 ^e	4b (1.36)	9b , SnBu ₂ An	0	92 (100)

^a Reaction time 24 h, using the appropriate solvent at reflux. ^b THF. ^c Toluene. ^d DMF. ^e THF, room temperature. ^f Calculated considering the residual Br content in the polymer and the weight change upon substitution of Br by Nu (see ESI).

As their parent materials, the polymers are not soluble in common organic solvents. With the exception of **8**, they swell in chloroform or THF, enough to allow their characterization by NMR in the viscous mixture. A shift of the methylene protons of the $-\text{CH}_2\text{Nu}$ groups when compared to the $-\text{CH}_2\text{Br}$ parent groups is observed, as well as the presence of the characteristic signals of Nu groups. The IR spectra show the disappearance of the $\nu(\text{C-Br})$ absorption along with new absorptions of the Nu groups (see Experimental Section). The azido ROMPH polymers **8** could not be characterized by solution NMR and the CP-MAS ^{13}C NMR spectra do not show a distinct $-\text{CH}_2\text{N}_3$ resonance, which overlaps with the broad signals of the polymer. Nonetheless, the IR spectra is very informative and clearly shows the presence of the strong $\nu(\text{N=N})$ resonances at 2090 cm^{-1} .

Our former experience with stannylated polymers of different backbones, specially vinylic addition polynorbornenes (VA-PNBs),^{8,22a,31} led us to introduce a stannyl group on **4b**. As shown in Table 4 (entry 6) the substitution works well leading

to a polymeric material that can be used as reagent in the Stille reaction. **4b** was chosen for this application since polymers with longer pendant alkyl chains have proved to be more reactive.⁸ Polymer **9b** was used in the Stille reaction for the formation of biphenyls in good or moderate yields (Scheme 3 and Table 5). Stille couplings using polymeric materials are generally slower and need longer reaction times than those using monomeric tin derivatives. However, this is counterbalanced by the easy separation of the coupling products from the polymeric halogenated tin byproduct which can be precipitated and filtered in a very convenient way. Using **9b**, 4-methoxy-4'-trifluoromethyl-1,1'-biphenyl (entry 2, Table 5) was prepared in a larger scale in a 73% isolated yield with a contamination of only 0.022 % weight of tin (see Experimental). This amount is about 200 times lower than the residual tin found in the preparations using a tributyltin derivative and a more cumbersome work up.^{31b} This reaction shows that ROMPH-PNBs are robust enough to be used in catalysis at high temperature (100 °C in this case). Their performance in this reaction is comparable to the vinylic addition polynorbornenes (VA-PNBs) we reported before.^{8,31b}



Scheme 3. Stille coupling using **9b** as reagent.

Table 5. Use of polymer **9b** as reagent in Stille couplings.^a

Entry	ArI	t (h)	R-An, Yield (%) ^b
1	C ₆ H ₅ I	20	C ₆ H ₅ -p-C ₆ H ₄ OMe, 55
2	p-CF ₃ C ₆ H ₄ I	40	p-CF ₃ C ₆ H ₄ -p-C ₆ H ₄ OMe, 81
3	p-FC ₆ H ₄ I	40	p-FC ₆ H ₄ -p-C ₆ H ₄ OMe, 74
4	o-MeC ₆ H ₄ I	40	o-MeC ₆ H ₄ -p-C ₆ H ₄ OMe, 38
5	p-MeC ₆ H ₄ I	40	p-MeC ₆ H ₄ -p-C ₆ H ₄ OMe, 62

^a Reaction conditions: toluene, 100 °C, 0.1 g **9b** (0.1 mmol SnBu₂An), 0.08 mmol ArI, [Pd(PPh₃)₄] as catalyst (2.5% mol). ^b Crude yield determined by integration of ¹H or ¹⁹F NMR signals.

A saturated scaffold is very attractive for a polymeric support in Pd-catalyzed reactions. The parent ROMP polymers, with an unsaturated backbone, are less convenient in these reactions, since alkene insertion into Pd-C bonds is a well-known process that can alter the nature of the ROMP skeleton. This was clearly shown when the soluble copolymer **3a** (x/y = 1.11, entry 8, Table 3) was mixed with [PdBrPf(NCMe)₂] (Pf = C₆F₅), a model complex analogous to the palladium aryl species formed in many Pd-catalyzed C-C coupling reactions.³² We have previously shown that alkenes insert into the Pd-C bond of this complex, and the formation of the new C-Pf bond can be clearly seen by ¹⁹F NMR where the F_{ortho} signal of the Pf group undergoes a strong shift from around -120 ppm (Pd-Pf) to -140 ppm (C-Pf).³³ As can be seen in Figure 2 the ROMP copolymer

reacts with the palladium aryl complex and the pentafluorophenyl group (Pf) is incorporated to the polymeric backbone.

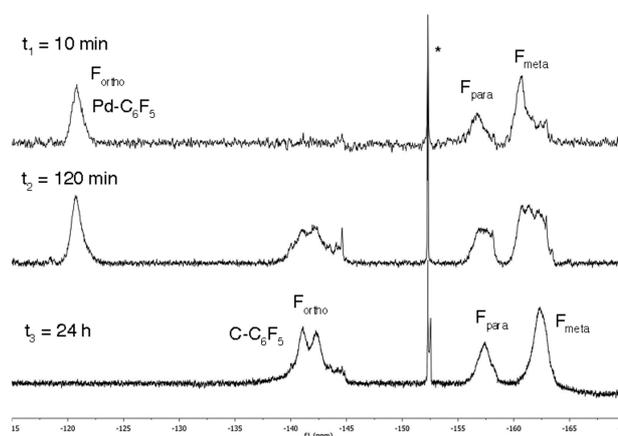
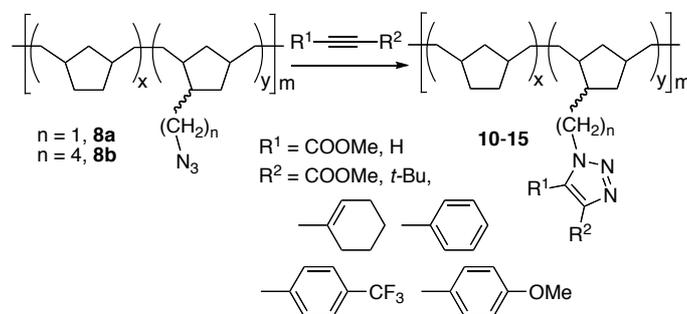


Fig. 2. ¹⁹F NMR spectra for the reaction of [PdBr(C₆F₅)(NCMe)₂] with ROMP copolymer **3a** (x/y = 1.1) in CDCl₃ at different times. * BF₄⁻ impurity from the synthesis of the complex.

The alkyne-azide cycloaddition reaction is one of the most popular and versatile click reactions. The copper-catalyzed version (CuAAC) allows the cycloaddition of a wide variety of substrates,³⁴ and it has been applied to polymer and macromolecule functionalization,^{34c,35} including ROMP polynorbornenes.³⁶ Thus, we checked the CuAAC reactions on the azido polymers **8** since this route of functionalization opens up a way to anchor a large variety of groups through a 1,2,3-triazole link by selecting the appropriate alkyne (Scheme 4). We checked the reaction with alkynes with different substituents from the diester dimethyl acetylenedicarboxylate, which does not need copper catalysis to form the triazole, to enynes (Table 6). In all cases the triazole is formed and this is shown by the disappearance of the strong azide absorption in the IR spectra (2090 cm⁻¹) and the appearance of characteristic bands for the substituents of the alkyne. All the triazole substituted polymers are insoluble solids and they were characterized by ¹³C CP-MAS solid state NMR. Resonances for the triazole C=C bond are shown in the spectra along with other resonances of the specific substituents (see Experimental Section).



Scheme 4. Click functionalization of the azido ROMPH polynorbornenes.

Table 6. Triazole functionalization of polymers **8** by CuAAC reactions according to Scheme 4.^a

Entry	8 , (mmol N ₃ /g)	R ¹ , R ²	Polymer	Isolated yield (%)
1 ^b	8a (1)	COOMe, COOMe	10a	93
2 ^c	8a (1)	H, <i>t</i> -Bu	11a	100
3 ^c	8a (1)	H, cyclohexenyl	12a	97
4 ^d	8a (1)	H, C ₆ H ₅	13a	100
5 ^c	8a (1)	H, <i>p</i> -C ₆ H ₄ CF ₃	14a	96
6 ^d	8a (1)	H, <i>p</i> -C ₆ H ₄ OMe	15a	100
7 ^d	8b (1.7)	H, <i>p</i> -C ₆ H ₄ OMe	15b	100

^a The reactions were carried out in THF for 24 h; molar ratio **8**:alkyne:CuI:DIPEA = 1:4:2:50. ^b Without CuI; toluene at reflux. ^c At room temperature. ^d At reflux.

Conclusions

New bromosubstituted polymeric materials with a saturated polymeric backbone are available to be used as manifold supports by introducing the appropriate functionality by post-polymerization functionalization. The support is a copolymer of norbornene and a ω -bromoalkyl norbornene which has been synthesized by ring opening metathesis polymerization followed by hydrogenation. The bromo functionality is attached to the saturated polymeric backbone by an alkyl chain tether of different length and nucleophilic substitution of this bromide by different reagents is possible. Among the reactions tested, an azido polymer has been prepared which opens up the possibility to use the alkyne-azide cycloaddition reaction as a tool to link a variety of groups and this has been demonstrated. A stannylated polymer has also been synthesized and used in the Stille coupling to give biphenyls, a Pd-catalyzed reaction that is carried out at high temperature.

Thus, a more robust, saturated version of the frequently used ROMP polynorbornene is now available that allows different types of functionalization but does not require the synthesis of the polymer from scratch, i.e. from the prefunctionalized monomer. Not many all-aliphatic polymeric supports are available that can be used by the synthetic chemist, working outside the polymer field. In resemblance to what occurs for the popular and useful functionalized polystyrenes, the ω -bromoalkyl polynorbornenes described here have the potential to be part of the toolbox to devise efficient and green synthetic procedures, specially if the support has to be subjected to reaction conditions not compatible with a more reactive polymer skeleton.

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