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Versatile Route to Functionalized Vinylic Addition Polynorbornenes

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ABSTRACT: Vinylic addition polynorbornenes bearing functional groups can be obtained in a versatile way by nucleophilic substitution of a halogen in new vinylic haloalkyl polynorbornenes. The latter are obtained by vinylic homo and copolymerization of norbornene and haloalkyl norbornenes catalyzed by $[Ni(C_6F_5)_2(SbPh_3)_2]$. This method circumvents the problem of catalyst deactivation encountered in classical copolymerizations with polar monomers. The content of substituted monomer in the copolymers is in the range 26−59%, depending on the monomer ratio in the feed. Nucleophilic substitution reactions afford polymers with ester, cyano, phenylthio, or azido groups in the same wide range of composition. Click chemistry on the azido polynorbornenes give polynorbornenes with pendant triazole groups.

Introduction

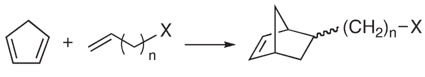
The vinylic polymerization of norbornene affords materials with a saturated aliphatic backbone. They exhibit a combination of properties, such as high stability and transparency, that make them ideal for many electronic, optical, and other applications.[1,2] However, the absence of polar groups in the polymer lead to low adherence to surfaces, which is a drawback in the use of the polymers for the construction of devices. Polynorbornenes with polar groups could be accessed by addition polymerization of functionalized norbornenes or by copolymerization of these monomers with norbornene, but these are difficult reactions, and many catalytic systems that work very well in the polymerization of norbornene have produced only poor to modest results when tested for substituted norbornenes. For instance, early transition metal catalysts are deactivated by the presence of a polar substituent (usually an oxygen containing functionality) in the monomer.[3] On the other hand, late transition metal complexes such as Ni or Pd derivatives have proved more resistant to deactivation,[2c,4] but they afford low polymer yields.[5] When copolymerization takes place with other alkenes, the incorporation of the polar monomer, a norbornylene ester, alcohol, or aldehyde, is often low.[6,7]

In addition to the physical properties induced by the presence of functions in the polymer, there is also an interest in functionalized polymers related to supported transition-metal catalysis. In this respect, it is desirable to have easy and versatile laboratory methods to prepare polymers with different flexibility. The polynorbornene skeleton is a chemically stable structure that could be used, provided an appropriate methodology for functionalization is made available.

Here, we have developed an interesting approach to vinylic addition polynorbornenes with polar functionalities that circumvents the problems of the classical polymerization synthetic approach. We have found out that norbornene derivatives with a halogen group can be easily homopolymerized and, more interestingly, copolymerized with norbornene to give copolymers with a wide range of incorporation of the functional monomer. Subsequent halogen substitution in the halogenated polymer leads easily to functionalized polynorbornenes with pendant functional groups that are difficult or impossible to access by catalytic polymerization of the substituted monomers, at least with the existing catalytic systems.

Results and Discussion

Synthesis of the Halogenated Polynorbornenes. The haloalkyl substituted norbornenes **1**−**4** (eq 1) were synthesized by Diels−Alder reactions of cyclopentadiene and the corresponding terminal 1-haloalkenes. All the NB derivatives are a mixture of endo (major) and exo (minor) isomers in a ratio close to endo:exo = 85:15.



(1)

n = 1, X = Cl, **1**; n = 1, X = Br, **2**;
n = 2, X = Br, **3**; n = 4, X = Br, **4**.

Catalysts $[Ni(R_f)_2L_2]$ (R_f = $C_6Cl_2F_3$, C_6F_5; L = $AsPh_3$, $SbPh_3$) are very active in the polymerization of norbornene,[8] and active in the copolymerization of stannylated norbornenes with NB.[9] Other $[Ni(R_f)_2L_2]$ complexes (L = THF, toluene, 1,2-dme) have also been used in the polymerization of norbornene.[10] In this case, the homopolymerization and copolymerization reactions of monomers **1**−**4** with norbornene were carried out using $[Ni(C_6F_5)_2(SbPh_3)_2]$ (**5**) as catalyst and afforded polymers **6**−**9** (Scheme 1). Table 1 collects relevant data for the polymerization reactions. The molar ratio of monomers in the copolymer is given as a/b = $NB/NBCH_2X$. Although halogenated norbornenes are sometimes included in the broad general formulations of potential monomers in the patent literature regarding the polymerization of norbornenes, this is, to our knowledge, the first reported halogenated vinylic addition polynorbornenes with variable content of the halo-containing functionality.

The polymerization or copolymerization reactions were carried out using a molar amount of catalyst **5** between 1% and 0.5%. Although **5** is extremely active in the polymerization of NB, it is less effective in the polymerization of substituted norbornenes. Catalyst loadings below 0.5% of the total molar amount of monomers used are not recommended (cf. entries 4, 7, and 8, Table 1).

The halogenated monomers undergo homopolymerization (entries 1 and 9−11, Table 1) with moderate or good

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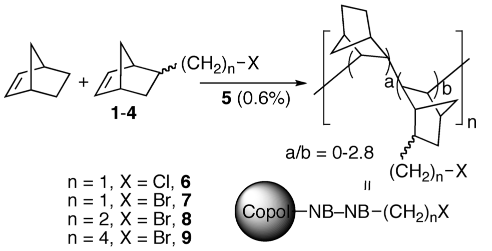
yields. The yield improves as the carbon bearing the halogen substituent is farther away from the bicyclic unit, so the homopolymerization is very efficient for **3** and **4**.

The copolymerization reaction conditions with norbornene were explored for the halogenated monomer **2**. The incorporation of the haloalkyl monomers in the copolymer can be roughly controlled by the monomer ratio in the feed, as shown in Table 1 for the copolymerization of NB and **2** (entries 2−6). The NB content in the copolymer is always higher than in the initial monomer feed showing its expected higher reactivity. According to the data in Table 1 (entries 2−5) the reactivity ratios of NB and **2** can be determined as r_{NB}, 1.11, and $r_{\mathbf{2}}$, 0.29. On the other hand, the analysis of the remaining unreacted monomers **2**, after copolymerization is finished, shows that the original percentage of 85% endo has increased to 90−97%, depending on the actual experiment. This change indicates a preference for incorporation of the exo isomer, as found for other substituted norbornenes,[11] not as large as observed for norbornene copolymers with oxygen functionalities such as esters or aldehydes, where the coordination of the endo isomers to the metal center as an η^2-alkene, O-donor chelating ligand blocks the metal center and halts further polymer growth.[11b] In our case, comparison of the yields in copolymer with the initial masses and the copolymer final composition, shows that a quantitative conversion of NB has occurred. Copolymers containing percentages of incorporation of the halogenated monomer **2** in the range between 59% (a/b = 0.7, entry 2, Table 1) and 26% (a/b = 2.8, entry 5, Table 1) could be obtained by tuning the composition of the feed. The copolymers are white solids, soluble in CH_2Cl_2 or THF. They show unimodal distributions in GPC and a polydispersity in the range 1−2. As observed in other copolymerization reactions of norbornene monomers,[9] the molecular weight of the copolymers increases with the NB content (cf. entries 2 to 6, Table 1). Monomers **1**, **3**, and **4** can be copolymerized with NB similarly as **2** (entries 12−14, Table 1). For the longer chain monomers, a higher incorporation of the bromoalkylnorbornene is observed compared to **2** (cf. entries 4, 13, and 14). A rough estimation of the reactivity ratios for both couples NB/**3** and NB/**4** give similar values around r_{NB}, 0.7, and $r_{NB\text{-}Br}$, 0.4, which show a higher incorporation rate of **3** or **4** vs **2** when reacted with NB.

Scheme 1. Polymerization of Haloalkylnorbornenes



As for the morphology of the polymers and copolymers, the ^1H and $^{13}C\{^1H\}$ NMR spectra show characteristic $-CH_2X$ signals and broad resonances for the NB skeleton. The absence of resonances in the olefinic region supports a vinylic polymerization mechanism. The $^{13}C\{^1H\}$ NMR spectra point to an exo norbornene enchained polymer, as they do not show signals around 20 ppm.[12] The ^{13}C resonance assignments were made with the help of $^1H-^{13}C$ HMQC experiments and previous literature data.[10,12] The polymers show $C-C_6F_5$ end groups (in the ^{19}F NMR spectra, F_{ortho} region).[13] This suggests an insertion mechanism of polymerization initiated by insertion of NB or the halogenated norbornene into the $Ni-C_6F_5$ bond, as reported before for related systems.[8−10] DSC measurements did not show a clear heat capacity change for all the polymers, so T_g could not be determined in all cases. In the few cases that T_g could be measured the values were high (around 250 °C), as it is the case for other polynorbornenes.[5a,6c,10]

Functionalization of the Halogenated Polynorbornenes. Different nucleophilic substitution reactions were carried out on the haloalkyl polynorbornenes, as shown in Scheme 2, producing new polynorbornenes with ester, cyano, thio, or azido substituents.

Table 2 collects the new polymers obtained from copolymers **7** of different composition. The bromoalkyl polynorbornenes were chosen for these reactions, as they undergo the reactions more readily than the chloroalkyl derivatives. For instance, the reaction of a chloroalkyl polynorbornene of composition NB:**1** = 1.7:1 in the same conditions used for the bromo copolymer in entry 4 of Table 2, lead to only 35% of Cl substitution vs 95% for Br substitution. The nucleophiles were generated by *in situ* deprotonation of the corresponding

Scheme 2. Synthesis of Functionalized Polynorbornenes

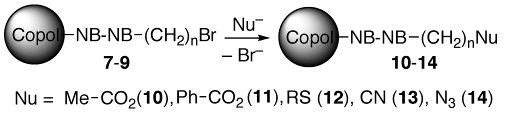


Table 1. Homo and Copolymerization Reactions of Monomers 1−4 and Norbornene to give polymers 6−9.[a]

entry	feed composition NB:NBCH$_2$X:[Ni][b]	isolated yield (%)[c]	copolymer, a/b[d] (a/b = NB/NBCH$_2$X)	M_w[e]	M_w/M_n[e]
1	NB:**2**:[Ni] = 0:75:1	50	**7**, 0	13 655	1.54
2	NB:**2**:[Ni] = 25:75:1	75	**7**, 0.7	32 210	1.75
3	NB:**2**:[Ni] = 50:75:1	70	**7**, 1.2	40 578	2.12
4	NB:**2**:[Ni] = 75:75:1	74	**7**, 1.7	54 074	1.40
5	NB:**2**:[Ni] = 150:75:1	86	**7**, 2.8	71 020	1.45
6	NB:**2**:[Ni] = 225:75:1	76	**7**, 2.8	63 007	1.55
7[f]	NB:**2**:[Ni] = 100:100:1	55	**7**, 2.1	49 221	1.54
8[f]	NB:**2**:[Ni] = 150:150:1	2			
9	NB:**1**:[Ni] = 0:75:1	55	**6**, 0	60 951	1.00
10	NB:**3**:[Ni] = 0:75:1	83	**8**, 0	77 750	1.04
11	NB:**4**:[Ni] = 0:75:1	94	**9**, 0	189 941	1.63
12	NB:**1**:[Ni] = 75:75:1	77	**6**, 1.6	116 048	1.19
13	NB:**3**:[Ni] = 75:75:1	80	**8**, 1.3	728 988	1.63
14	NB:**4**:[Ni] = 75:75:1	78	**9**, 1.4	856 839	1.89

[a] The reactions were carried out using CH_2Cl_2 as solvent (6.25 mL total volume of the reaction mixture) at 28 °C for 24 h. [b] Molar ratio in the feed; [Ni] = $[Ni(C_6F_5)_2(SbPh_3)_2]$ (**5**), 0.0356 mmol, unless otherwise noted. [c] Yields are referred to the total monomer mass. [d] a/b was determined by quantitative analyses of halogen in the copolymer. [e] Determined by GPC using polystyrene standards. [f] [Ni] = 0.0267 mmol for entry 7 and [Ni] = 0.0178 mmol for entry 8.

Table 2. Functionalization of Copol−NB−NBCH$_2$Br according to Scheme 2

entry	Copol−NB−NBCH$_2$Br (**7**), NB:**2** (**2**, mol %) in copolymer[a]	isolated yield (%)	Copol−NB−NBCH$_2$Nu, Nu (mol %)[b]	M_w	M_w/M_n
1	0:1 (100)	74	**11**, PhCOO (94.4)	15 767	1.54
2	0.7:1 (58.8)	79	**11**, PhCOO (53.0)	34 436	1.87
3	1.2:1 (45.4)	94	**11**, PhCOO (40.3)	37 114	2.24
4	1.7:1 (37.0)	84	**11**, PhCOO (35.3)	43 808	2.05
5	2.8:1 (26.3)	85	**11**, PhCOO (22.8)	51 576	1.50
6	2:1 (33.3)	83	**10**, MeCOO (29.9)	80 337	2.47
7	2:1 (33.3)	91	**12**, PhS (27.7)	95 952	1.49
8	2:1 (33.3)	82	**13**, CN (30.4)	82 763	1.39
9	2:1 (33.3)	85	**14**, N$_3$ (27.7)[c]		

[a] The polymers in entries 1−5 correspond to those in Table 1. [b] The differences in the content of **2** (mol %) in the starting copolymer **7** and Nu (mol %) in the final copolymer indicate that the bromo substitution is not complete. [c] Insoluble polymer.

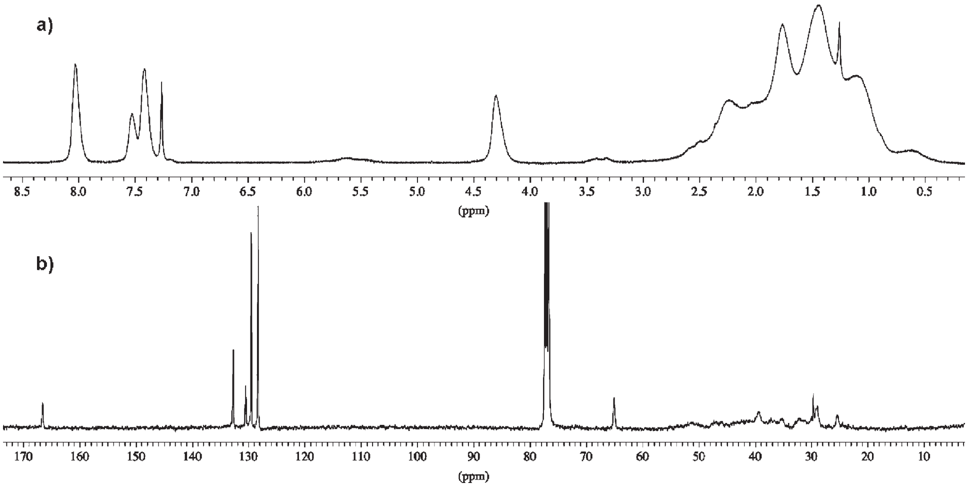


Figure 1. ^{1}H (a) and ^{13}C{^{1}H} (b) NMR spectra of polymer **11** (n = 4; Nu = PhCO$_2$).

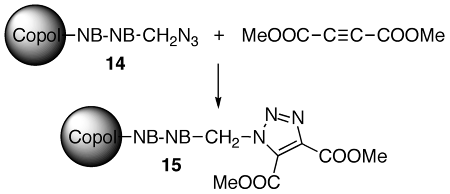
conjugated acids (carboxylates and sulfide) or used as salts (cyanide and azide).[14,15]

The extent of substitution was determined by quantitative analysis of residual halide in the polymer; in general, about 10% of the initial CH$_2$Br groups remain unreacted in the new polymer. The incorporation of the functional groups was confirmed spectroscopically. Characteristic IR absorption bands for the ester, nitrile or azido groups were found whereas the C−Br absorption at 636 cm^{-1} was almost absent (see Experimental Section and Supporting Information). Moreover, the ^{1}H and ^{13}C NMR resonances of methylene group attached to the new functionality showed noticeable different chemical shifts compared to the parent −CH$_2$Br group. Figure 1 shows the ^{1}H and ^{13}C{^{1}H} NMR for the benzoate substituted polymer **11** (n = 4) resulting from ester substitution in **9**, where the chemical shift of the −CH$_2$Br methylene signal is 3.4 ppm.

Starting from bromoalkyl polynorbornenes with different composition, these substitution reactions provide new polynorbornenes with variable content of the polar groups, as exemplified for the benzoate derivatives (entries 1−5, Table 2). This method gives access to substituted polynorbornenes that cannot be prepared by vinylic addition polymerization of the corresponding monomers. For instance, it has been reported that the polymer with cyano groups **13** (entry 8, Table 2) could not be synthesized by vinylic polymerization or copolymerization of norbornylene nitrile because the presence of a cyano group deactivated the Ni catalysts that had been useful for the polymerization of other substituted norbornenes.[6d]

Interestingly the reaction of the azido derivative Copol−NB−NBCH$_2$N$_3$ (**14**) with alkynes leads to new polynorbornenes where complete transformation of the azido groups to triazole groups has occurred (Scheme 3). This click reaction gives access to new polymers with pendant triazoles and illustrates the versatility of these new polynorbornenes for further functionalization. Click chemistry has been used successfully to attach catalysts to commercial polystyrene resins through a triazole link,[16] so the polynorbornenes prepared here are good candidates for use as a new type of matrix support in these applications.

Scheme 3. Synthesis of Polynorbornenes with Pendant Triazole Groups



Conclusion

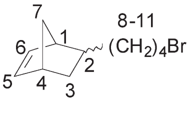
New vinylic addition functionalized polynorbornenes with polar groups can be achieved by a different route starting from haloalkyl polynorbornenes that circumvents the problems commonly encountered in attempted homo or copolymerization of norbornene with some functionalized monomers. The new haloalkyl polynorbornenes reported here open a way to cover a broad composition range, both in the nature of the pendant functionality and in its concentration in the final polymer.

Experimental Section

Materials and General Considerations. NMR spectra were recorded at 298 K using Bruker AC-300, ARX-300 and AV-400 instruments. Chemical shifts (δ) are reported in ppm and referenced to $SiMe_4$ (^1H and ^{13}C) and $CFCl_3$ (^{19}F). The solid state NMR spectra were recorded at room temperature under magic angle spinning (MAS) in a Bruker AV-400 spectrometer using a Bruker BL-4 probe with 4 mm diameter zirconia rotors spinning at 10 kHz. The halogen content in the polymers was determined by oxygen-flask combustion of a sample and analysis of the residue by mercurimetric titration of the chloride.[17] Size exclusion chromatography (SEC) was carried out using a Waters SEC system on a three-column bed (Styragel 7.8 × 300 mm columns: 50−100 000, 5000−500 000 and 2000−4 000 000 Da) and a Waters 410 differential refractometer. SEC samples were run in $CHCl_3$ at 313 K and calibrated to polystyrene standards. Solvents were dried using a Solvent Purification System (SPS). Norbornene, dicyclopentadiene, benzoic acid, DBU, tetrabutylammonium cyanide, sodium azide, dimethylacetylenedicarboxylate, thiophenol, and the organic halides were purchased from Aldrich, Acros, Merck, or Lancaster. The compound $[Ni(C_6F_5)_2(SbPh_3)_2]$ was prepared according to the literature.[8,18]

Synthesis of Haloalkyl Norbornenes. *Synthesis of **4***. A mixture of 6-bromo-1-hexene (1.56 mL, 11.66 mmol) and dicyclopentadiene (0.78 mL, 5.83 mmol) is heated at 200 °C for 72 h. The resulting mixture is distilled under reduced pressure (180 °C, 0.6 mmHg) to obtain a colorless liquid, **4**, which is a 83:17 *endo*:*exo* mixture of isomers (0.710 g, 27% yield). MS (EI, *m*/*z* (%)): 230 (1) $[M^+]$, 228 (1) $[M^+]$, 149 (1) $[M^+ - Br]$, 93 (2) $[M^+ - (CH_2)_4Br]$, 79 (5) $[M^+ - NB(CH_2)_4]$, 66 (100) $[M^+ - CH_2CH(CH_2)_4Br]$.

1,[19] **2**,[20] and **3**[21] were synthesized in the same way, starting from the corresponding bromo- or chloroalkene.



endo-**4**. ^1H NMR (300.13 MHz, δ, $CDCl_3$): 6.09 (dd, 1H, H^5), 5.90 (dd, 1H, H^6), 3.39 (t, 2H, H^{11}), 2.74 (br, 2H, H^1, H^4), 1.96 (m, 1H, H^2), 1.82 (m, 3H, H^3, H^{10}), 1.38 (m, 3H, H^7, H^9), 1.20 (d, 1H, $H^{7'}$), 1.07 (m, 2H, H^8), 0.47 (ddd, 1H, $H^{3'}$). $^{13}C\{^1H\}$ NMR (75.4 MHz, δ, $CDCl_3$): 137.02 (s, 1C, C^5), 132.21 (s, 1C, C^6), 49.55 (s, 1C, C^7), 45.32 and 42,50 (s, 2C, C^1, C^4), 38.56 (s, 1C, C^2), 33.93 and 33.82 (s, 2C, C^8, C^{11}), 32.99 (s, 1C, C^{10}), 31.58 (s,1C, C^3), 27.15 (s,1C, C^9).

exo-**4**. ^1H NMR (300.13 MHz, δ, $CDCl_3$): 6.06 (dd, 1H, H^6), 6.00 (dd, 1H, H^5), 2.50 (br, 1H, H^1). $^{13}C\{^1H\}$ NMR (75.4 MHz, δ, $CDCl_3$): 136.76 (s, 1C, C^6), 136.20 (s, 1C, C^5), 46.27 (s, 1C, C^1) [Most signals are overlapped by the resonances of the *endo* isomer.]

Homopolymerization Reactions. *Homopolymerization of **2***. A solution of $[Ni(C_6F_5)_2(SbPh_3)_2]$ (0.0391 g, 0.035 mmol) in dry CH_2Cl_2 (5.9 mL) is added dropwise to bromomethylnorbornene (0.5000 g, 2.670 mmol). The starting yellow solution gets darker and the viscosity increases gradually. The mixture is stirred for 24 h at room temperature and then poured onto MeOH (30 mL). A solid precipitated which was stirred for 30 min, filtered, washed with MeOH (2 × 5 mL) and air-dried. The homopolymer is obtained as a white solid (0.2520 g, 50% yield).

7 (a/b = 0). ^1H NMR (300.13 MHz, δ, $CDCl_3$): 3.4 (br, 2H, H^8) 2.8−0.4 (br, H^1−H^7). $^{13}C\{^1H\}$ NMR (75.4 MHz, δ, $CDCl_3$): 52−39 (br, 4C, C^1, C^4, C^5, C^6), 39−31 (br, 4C, C^2, C^3, C^7, C^8). ^{19}F NMR (282 MHz, δ, $CDCl_3$): −162.7 (F_{meta}), −157.0 (F_{para}), −139.7, −135.9 (F_{ortho}). IR (KBr, cm^{-1}), υ(C−Br): 634(m). The polymer contains 399.48 mg of Br/g of Cop.

The homopolymerization reactions of **1**, **3**, and **4** were carried out in the same way.

6 (a/b = 0). ^1H NMR (300.13 MHz, δ, $CDCl_3$): 3.4 (br, 2H, H^8) 2.9−0.4 (br, H^1−H^7). $^{13}C\{^1H\}$ NMR (75.4 MHz, δ, $CDCl_3$): 51−45 (br, 2C, C^5, C^6), 47 (br, 1C, C^8), 45−40 (br, 2C, C^1, C^4), 40−35 (br, 1C, C^7), 35−30 (br, 2C, C^2, C^3). ^{19}F NMR (282 MHz, δ, $CDCl_3$): −162.3 (F_{meta}), −156.7 (F_{para}), −139.4, −135.5 (F_{ortho}). IR (KBr, cm^{-1}), υ(C−Cl): 722 (m). The polymer contains 212.61 mg of Cl/g of Cop.

8 (a/b = 0). ^1H NMR (300.13 MHz, δ, $CDCl_3$): 3.4 (br, 2H, H^9), 2.7−0.4 (br, H^1−H^8). $^{13}C\{^1H\}$ NMR (75.4 MHz, δ, $CDCl_3$): 50−41 (br, 2C, C^5, C^6), 41−38 (br, 3C, C^1, C^4, C^8), 38−34 (br, 1C, C^7), 32 (br, 1C, C^9), 32−29 (br, 2C, C^2, C^3). ^{19}F NMR (282 MHz, δ, $CDCl_3$): −162.9 (F_{meta}), −157.1 (F_{para}), −139.6, −135.2 (F_{ortho}). IR (KBr, cm^{-1}), υ(C−Br): 566 (m). The polymer contains 327.01 mg of Br/g of Cop.

9 (a/b = 0). ^1H NMR (300.13 MHz, δ, $CDCl_3$): 3.4 (br, 2H, H^{11}) 2.9−0.4 (br, H^1−H^{10}). $^{13}C\{^1H\}$ NMR (75.4 MHz, δ, $CDCl_3$): 52−35 (br, 4C, C^1, C^4, C^5, C^6), 34 (br, 2C, C^8, C^{11}), 34−32 (br, 1C, C^7),33 (br, 1C, C^{10}) 32−28 (br, 2C, C^2, C^3), 27 (br, 1C, C^9). ^{19}F NMR (282 MHz, δ, $CDCl_3$): −163.4 (F_{meta}), −158.3 (F_{para}), −139.2, −135.2 (F_{ortho}). IR (KBr, cm^{-1}), υ(C−Br): 562 (m). The polymer contains 306.10 mg of Br/g of Cop.

Copolymerization Reactions. *Copolymerization of Norbornene and **2***. Bromomethylnorbornene (0.5000 g, 2.670 mmol) and 0.67 mL of a solution of NB in CH_2Cl_2 (4 M, 2.670 mmol) are mixed under a nitrogen atmosphere.[22] A solution of $[Ni(C_6F_5)_2(SbPh_3)_2]$ (0.0391 g, 0.035 mmol) in dry CH_2Cl_2 (5.0 mL) was added dropwise to the former mixture. The starting yellow solution gets darker and the viscosity increases gradually. The mixture is stirred for 24 h at room temperature and then poured onto MeOH (30 mL). A solid precipitates which was stirred for 30 min, filtered, washed with MeOH (2 × 5 mL) and air-dried. The copolymer is obtained as a white solid (0.5522 g, 74% yield).

7 (a/b = 1.7). ^1H NMR (300.13 MHz, δ, $CDCl_3$): 3.4 (br, 2H, H^8), 2.7−0.4 (br, H^1−H^7). ^{13}C NMR (75.4 MHz, δ, $CDCl_3$): 52−48 and 48−45 (br, 2C, C^5, C^6), 45−38 (br, 2C, C^1, C^4), 37 (br, 1C, C^8), 38−34 (br, 1C, C^7), 31−28 (br, 2C, C^2, C^3). ^{19}F NMR (282 MHz, δ, $CDCl_3$): −163.4 (F_{meta}), −158.6, −157.8 (F_{para}), −140.5, −140.1, −135.5, −133.9 (F_{ortho}). IR (KBr, cm^{-1}), υ(C−Br): 639 (m). The copolymer contains 230.97 mgBr/gCop, which corresponds to a NB:**2** = 1.7:1 ratio.

The copolymerization reactions using a different monomer feed ratio or different haloalkylnorbornenes (Table 1) were carried out in the same way.

6 (a/b = 1.6). ^1H NMR (300.13 MHz, δ, $CDCl_3$): 3.4 (br, 2H, H^8), 2.9−0.2 (br, H^1−H^7). ^{13}C NMR (75.4 MHz, δ, $CDCl_3$): 55−45 (br, 2C, C^5, C^6), 48 (br, 1C, C^8), 44−38 (br, 2C, C^1, C^4), 36−34 (br, 1C, C^7), 31−29 (br, 2C, C^2, C^3). ^{19}F NMR (282 MHz, δ, $CDCl_3$): −163.1 (F_{meta}), −157.6 (F_{para}), −139.6, −134.8 (F_{ortho}). IR (KBr, cm^{-1}), υ(C−Cl): 718 (m). The copolymer contains 121.81 mg of Cl/g of Cop, which corresponds to a NB:**1** = 1.6:1 ratio.

8 (a/b = 1.3). ^1H NMR (300.13 MHz, δ, $CDCl_3$): 3.4 (br, 2H, H^9), 2.7−0.3 (br, H^1−H^8). ^{13}C NMR (75.4 MHz, δ, $CDCl_3$): 55−49 and 49−45 (br, 2C, C^5, C^6), 45−39 (br, 2C, C^1, C^4), 41−39 (br, 1C, C^8), 39−34 (br, 1C, C^7), 34−31 (br, 1C, C^9), 31−29 (br, 2C, C^2, C^3). ^{19}F NMR (282 MHz, δ, $CDCl_3$): −162.9 (F_{meta}), −157.5 (F_{para}), −139.3, −134.1 (F_{ortho}). IR (KBr, cm^{-1}), υ(C−Br): 569 (m). The copolymer contains 243.36 mg of Br/g of Cop, which corresponds to a NB:**3** = 1.3:1 ratio.

9 (a/b = 1.4): ^1H NMR (300.13 MHz, δ, $CDCl_3$): 3.4 (br, 2H, H^{11}), 2.8−0.4 (br, H^1−H^{10}). ^{13}C NMR (75.4 MHz, δ, $CDCl_3$): 55−50 and 50−46 (br, 2C, C^5, C^6), 46−38 (br, 2C, C^1, C^4), 38−35 (br, 1C, C^7), 35−33 (br, 2C, C^8, C^{11}), 33−32 (br, 1C, C^{10}), 33−28 (br, 2C, C^2, C^3), 28−27 (br, 1C, C^9). ^{19}F NMR (282 MHz, δ, $CDCl_3$): −162.9 (F_{meta}), −158.1 (F_{para}), −140.0 (F_{ortho}). IR (KBr, cm^{-1}), υ(C−Br): 562 (m). The copolymer contains 219.06 mg of Br/g of Cop, which corresponds to a NB:**4** = 1.4:1 ratio.

Functionalization of Polynorbornenes. *Synthesis of Copol−NB−NB(CH$_2$)$_n$OCOPh (**11**)*. Cop−NBNBCH$_2$Br of composition NB:**2** = 1.95:1 (0.2000 g, 0.540 Br equiv), toluene (10 mL), benzoic acid (0.1662 g, 1.350 mmol), and DBU (0.20 mL, 1.350 mmol) were mixed in a flask. The mixture was refluxed for 11 h. The solvent was evaporated to ca. 2 mL and MeOH was added (50 mL). A solid appeared, which was stirred for 30 min, filtered, washed with MeOH (2 × 10 mL), and air-dried. The product is obtained as a white solid (0.1884 g, 84% yield).

11 (*n* = 1). ^1H NMR (300.13 MHz, δ, $CDCl_3$): 8.0 (br, 2H, H_{ortho} *Ph*), 7.5 (br, 1H, H_{para} *Ph*), 7.4 (br, 2H, H_{meta} *Ph*), 4.3 (br, 2H, H^8), 2.9−0.4 (br, H^1−H^7). ^{13}C NMR (75.4 MHz, δ, CDCl$_3$): 167.0 (br, 1C, O*C*OR), 132.8 (br, 1C, C$_{para}$ *Ph*), 130.5 (br, 1C, C$_{ipso}$ *Ph*), 129.5 (br, 2C, C$_{ortho}$ *Ph*), 128.3 (br, 2C, C$_{meta}$ *Ph*), 68−65 (br, 1C, C^8), 50−46 (br, 2C, C^5, C^6), 44−38 (br, 2C, C^1, C^4), 38−35 (br, 1C, C^7), 33−29 (br, 2C, C^2, C^3). IR (KBr, cm^{-1}), *υ*(C=O): 1720 (s); *υ*(C−O): 1270 (s). The copolymer contains 9.7 mg of Br/g of Cop, which indicates 95% of Br substitution.

Copol−NBNB(CH$_2$)$_2$OCOPh, Copol-NBNB(CH$_2$)$_4$OCOPh were synthesized in the same way. Copol−NBNBCH$_2$OCOMe was prepared following the same method but using acetic acid instead of benzoic acid.

11 (*n* = 2). ^{1}H NMR (300.13 MHz, δ, CDCl$_3$): 8.0 (br, 2H, H$_{ortho}$ *Ph*), 7.5 (br, 1H, H$_{para}$ *Ph*), 7.4 (br, 2H, H$_{meta}$ *Ph*), 4.3 (br, 2H, H^9), 2.8−0.4 (br, H^1−H^8). ^{13}C NMR (75.4 MHz, δ, CDCl$_3$):166.6 (br, 1C, O*C*OR), 132.7 (br, 1C, C$_{para}$ *Ph*), 130.5 (br, 1C, C$_{ipso}$ *Ph*), 129.5 (br, 2C, C$_{ortho}$ *Ph*), 128.3 (br, 2C, C$_{meta}$ *Ph*), 66−63 (br, 1C, C^9), 55−51 and 51−45 (br, 2C, C^5, C^6), 45−38 (br, 2C, C^1, C^4), 40−38 (br, 1C, C^8), 38−34 (br, 1C, C^7), 34−28 (br, 2C, C^2, C^3). IR (KBr, cm^{-1}), *υ*(C=O): 1719 (s); *υ*(C−O): 1273 (s). The copolymer contains 5.8 mg of Br/g of Cop, which indicates 97% of Br substitution.

11 (*n* = 4). ^{1}H NMR (300.13 MHz, δ, CDCl$_3$): 8.0 (br, 2H, H$_{ortho}$ *Ph*), 7.5 (br, 1H, H$_{para}$ *Ph*), 7.4 (br, 2H, H$_{meta}$ *Ph*), 4.3 (br, 2H, H^{11}), 2.6−0.4 (br, H^1−H^{10}). ^{13}C NMR (75.4 MHz, δ, CDCl$_3$): 166.6 (br, 1C, O*C*OR), 132.7 (br, 1C, C$_{para}$ *Ph*), 130.5 (br, 1C, C$_{ipso}$ *Ph*), 129.5 (br, 2C, C$_{ortho}$ *Ph*), 128.3 (br, 2C, C$_{meta}$ *Ph*), 65.1 (br, 1C, C^{11}), 55−49 and 49−44 (br, 2C, C^5, C^6), 44−38 (br, 2C, C^1, C^4), 38−34 (br, 1C, C^7), 33−28 (br, 3C, C^2, C^3, C^8), 29 (br, 1C, C^{10}), 25 (br, 1C, C^9). IR (KBr, cm^{-1}), *υ*(C=O): 1717 (s); *υ*(C−O): 1272 (s). The copolymer contains 5.2 mg of Br/g of Cop, which indicates 96% of Br substitution.

10 (*n* = 1). ^{1}H NMR (300.13 MHz, δ, CDCl$_3$): 4.0 (br, 2H, H^8), 2.9−0.4 (br, H^1−H^7, C*H*$_3$). ^{13}C NMR (75.4 MHz, δ, CDCl$_3$): 172.0 (br, 1C, O*C*OR), 69−66 (br, 1C, C^8), 54−50 and 50−46 (br, 2C, C^5, C^6), 44−38 (br, 2C, C^1, C^4), 38−35 (br, 1C, C^7), 33−29 (br, 2C, C^2, C^3), 21 (br, 1C, *C*H$_3$). IR (KBr, cm^{-1}), *υ*(C=O): 1744 (s); *υ*(C−O): 1240 (s). The copolymer contains 9.9 mg of Br/g of Cop, which indicates 96% of Br substitution.

Synthesis of Copol−NB−NBCH$_2$SPh (***12***). To a stirred mixture of DBU (0.16 mL, 1.080 mmol) and tiophenol (0.12 mL, 1.080 mmol) in toluene (10 mL) was added a solution of Cop−NBNBCH$_2$Br of composition NB:**2** = 1.95:1 (0.2000 g, 0.540 Br equiv) in toluene (10 mL). The solution was refluxed for 13 h, and then MeOH (50 mL) was added. After the reaction was stirred for 30 min, the white solid was filtered off, washed with MeOH (2 × 10 mL), and air-dried. The polymer was obtained as a white solid (0.1972 g, 91% yield).

^{1}H NMR (300.13 MHz, δ, CD$_2$Cl$_2$): 7.1−7.4 (br, 5H, H Ph) 3.4−2.6 (br, 2H, H^8), 2.6−0.4 (br, H^1−H^7). ^{13}C NMR (75.4 MHz, δ, CDCl$_3$): 137.3 (br, 1C, C$_{ipso}$ *Ph*), 128.5 (br, 4C, C$_{ortho}$ *Ph*, C$_{meta}$ *Ph*), 125.6 (br, 1C, C$_{para}$ *Ph*), 55−46 (br, 2C, C^5, C^6), 46−39 (br, 2C, C^1, C^4), 41−36 (br, 1C, C^8), 36−34 (br, 1C, C^7), 34−28 (br, 2C, C^2, C^3). The copolymer contains 33.5 mg of Br/g of Cop, which indicates 83% of Br substitution.

Synthesis of Copol−NB−NBCH$_2$CN (***13***). To a solution of tetrabutylammonium cyanide (0.2175 g, 0.810 mmol) in THF (10 mL) is added Cop−NBNBCH$_2$Br of composition NB:**2** = 1.95:1 (0.2000 g, 0.540 Br equiv) in THF (10 mL). The solution is refluxed for 9 h. The solvent was evaporated to ca. 2 mL and then MeOH was added (50 mL). The mixture was stirred for 30 min and then the solid copolymer was filtered, washed with MeOH (2 × 10 mL) and air-dried. The product is obtained as a yellow solid (0.2127 g, 82% yield).

^{1}H NMR (300.13 MHz, δ, CDCl$_3$): 2.9−0.4 (br, H^1−H^8). ^{13}C NMR (75.4 MHz, δ, CDCl$_3$): 120 (br, 1C, *C*N), 55−50 and 50−46 (br, 2C, C^5, C^6), 44−38 (br, 2C, C^1, C^4), 38−35 (br, 1C, C^7), 33−29 (br, 2C, C^2, C^3), 20.0 (br, 1C, C^8). IR (KBr, cm^{-1}), *υ*(CN): 2247 (w). The copolymer contains 21.1 mg of Br/g of Cop, which indicates 92% of Br substitution.

Synthesis of Copol−NB−NBCH$_2$N$_3$ (***14***). Cop−NBNBCH$_2$Br of composition NB:**2** = 1.95:1 (0.2000 g, 0.540 Br equivalents) is treated with NaN$_3$ (0.2106 g, 3.240 mmol) in DMF (10 mL) at 120 °C for 24 h. The solid is filtered and washed with DMF (2 × 5 mL), water (2 × 5 mL) and finally with MeOH (2 × 5 mL). The product is obtained as a white solid (0.1547 g, 85% yield), insoluble in common solvents.

IR (KBr, cm^{-1}), *υ*(N$_3$): 2092 (s). ^{13}C CP−MAS NMR (100.61 MHz): 63-21 (br, 8C). The copolymer contains 35.92 mg of Br/g of Cop, which indicates 85% of Br substitution.

Synthesis of Copol−NB−NBCH$_2$triazole (***15***). A mixture of Cop−NBNBCH$_2$N$_3$ (0.1135 g, 0.330 equiv of N$_3$), toluene (5 mL), and dimethyl acetylenedicarboxylate (0.12 mL, 1.000 mmol) was refluxed for 7 h. After this time, MeOH (40 mL) was added and the solid was stirred for 30 min, filtered off, washed with MeOH (2 × 10 mL), and air-dried. The product is obtained as a yellowish solid (0.1171 g, 85% yield) insoluble in common solvents.

IR (KBr, cm^{-1}), *υ*(C=O): 1735 (s); *υ*(C−O): 1225 (s). ^{13}C CP−MAS NMR (100.61 MHz): 160 (br, 2C, O*C*OR), 140 (br, 1C, *C*=C), 130 (br, 1C, *C*=*C*), 63−22 (br, 10 C).

Determination of Reactivity Ratios. Reactivity ratios for the copolymerization of NB/**2** were determined by fitting the data of entries 2−5 in Table 1 to the Finemann-Ross equation.[23] Copolymerization reactions of NB and **3** or **4** were carried out using the same monomer feed ratios and conditions of entries 2−4 in Table 1. Reactivity ratios were estimated using the same procedure followed for **2**.

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Supporting Information Available: Figures showing ^{1}H and ^{13}C NMR spectra of the polymers prepared as well as IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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