

Surface initiated ring-opening metathesis polymerization of norbornene onto Wang and Merrifield resins

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Abstract

Merrifield and Wang resins were successfully converted to supported vinyl-functionalized solid supports with excellent yields by reacting the Cl or OH functionality with an α,ω -difunctional spacer bearing a carboxylic acid group and a terminal alkene. The ruthenium initiator ($(PCy_3)_2Cl_2Ru=CHPh$ (Grubbs I catalyst) was then immobilized on the resins *via* cross metathesis (alkylidene exchange) and was used to initiate ROMP of norbornene. Number-average molecular weight and polydispersity index of the grafted polymers were determined after cleavage of the ester link between the resin and the spacer. The results showed a competition between ROMP and intramolecular “ring-closing” metathesis and/or intermolecular “cross” metathesis, which leads to an overestimated ruthenium initiator loading.

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Keywords: Merrifield resin; Wang resin; Supported catalyst; Norbornene; Ring-opening metathesis polymerization; Grubbs catalyst

1. Introduction

Polymer brushes are surface-modified materials with many applications in chemistry and materials science [1,2]. Surface initiated living polymerization gains access to a broad variety of polymeric architectures, including block and random copolymers as well as telechelic polymers [3–6]. Ring-opening metathesis polymerization (ROMP) is a well-established living polymerization technique since the development of stable, well-characterized, and well-understood initiators for metathesis polymerization techniques. In particular, the ruthenium-based systems developed by Grubbs ($(R_3P)_2Cl_2Ru=CHPh$) have attracted interest because of their high tolerance towards an array of polar functional groups [7]. Immobilization of these catalysts on solid supports is expected to facilitate the work-up and make the metathesis reactions more attractive for practical applications. The first Ru-based metathesis catalyst was immobilized on phosphine-functionalized polystyrene-divinylbenzene (PS-DVB) polymers via phosphine exchange reactions as reported by Nguyen and Grubbs [8]. In this case, the activity of the PS-DVB supported ruthenium carbene is retarded in compar-

ison to the homogeneous one. Immobilization of ruthenium catalysts through the *N*-heterocyclic carbene ligand [9,10] or through halogen exchange [11–13] has also been carried out either on porous silica or polymers. Most surface-grafted Ru-initiators are synthesized by attachment to the support through the alkylidene moiety. The resulting polymer-coated particles [14–17] or surfaces [18–22] can be used for chromatographic or microelectronic applications. This approach has been devised by Barrett et al. [23] to obtain ROM polymers as templates for the construction of synthetic libraries, as ROMPgel-supported reagents for solution phase combinatorial chemistry, and also as high-loading scavengers for impurity annihilation [24]. The organic supported reagents used are low cross-linked gel type polystyrene beads derived from Merrifield’s chloromethylated polystyrene. The polystyrene core profits from free-flowing handling, good swelling, and physical/chemical stability. Grafting of polymer on polystyrene beads is usually assessed by elemental analysis, FT-IR spectroscopy and mass increase of the resulting resin but no information is given about the number-average molecular weight and polydispersity index of the grafted polymers.

Herein, we report the synthesis of resins with well-defined supported polynorbornene. In our strategy, we have modified the functionality of the resin by a spacer: (1) to move the functionality away from the core in order to increase the activity of

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the PS-DVB supported ruthenium carbene, (2) to allow cleavage of the supported homopolymer in order to determine its number-average molecular weight and its polydispersity index and (3) to avoid the decomposition of the supported initiator by back-biting [8,24]. This approach has been applied to Merrifield and Wang resins. In this later case, the Wang resin can be regenerated after cleavage. ROMP of norbornene has been carried out and the resulting supported homopolymers have been characterized.

2. Experimental

2.1. Materials

Merrifield (2.0–2.2 mmol g⁻¹, 35–75 μm) and Wang (0.9–1.1 mmol g⁻¹, 35–75 μm) resins, ethyl vinyl ether (99%), α-chloro-*p*-xylene (99+%), diisopropylazodicarboxylate (94%, DIAD), triphenylphosphine (99%, PPh₃), trifluoroacetic acid (99%, TFA), undec-10-enoic acid (99%), *p*-vinylbenzoic acid (96%), *N,N*-dimethylformamide (+99%, DMF), P₂O₅ (+98%), CaCl₂ (96%), Cs₂CO₃ (99.5%), MgSO₄ (97%) were purchased from ACROS and used as received. Chloroform and dichloromethane were dried with CaCl₂ and distilled from P₂O₅ under argon. Methanol, diethyl ether, and tetrahydrofuran (THF, SDS) were dried and distilled according to standard procedures [25]. (PCy₃)₂(Cl)₂Ru=CHPh (Grubbs I catalyst) was purchased from Strem Chemicals. Dicyclopentadiene (BHT stabilizer) was cracked just prior to use. Deuterated solvent was purchased from SDS and used without further purification.

2.2. Measurements

Liquid-state NMR spectra were recorded on a Bruker AC-400 spectrometer for ¹H NMR (400 MHz) and ¹³C NMR (100 MHz). Chemical shifts were reported in ppm relative to the deuterated solvent resonances. ¹³C NMR spectra of commercial and modified resins were carried out in CDCl₃ by gel-phase NMR on a Bruker 300 MHz. Solid-state ¹³C NMR spectra were recorded on a Bruker MSL 300 equipped with CP-MAS (cross polarization magic-angle-spinning) accessories. Dipolar decoupling was systematically used during the acquisition sequence. The samples were spun at a rate from 5 to 10 kHz at room temperature in a 4 mm ZrO₂ rotor, the accumulation of 3072 scans was used to obtain a satisfactory signal to noise ratio. Beads morphology was characterized by scanning electron microscopy (SEM) using an Hitachi 2300 apparatus combined with Link Isis software. The samples were added on an electron microscope stub with double-sided adhesive tape and coated with carbon. Molecular weights and molecular weight distributions were measured using size exclusion chromatography (SEC) at 35 °C on a system equipped with a SpectraSYSTEM AS 1000 autosampler, a guard column (Polymer Laboratories, PL gel 5 μm Guard column, 50 mm × 7.5 mm), two analytical columns (Polymer Laboratories, 2 PL gel 5 μm MIXED-D columns, 2 mm × 300 mm × 7.5 mm), and a SpectraSYSTEM RI-150 detector. The eluent used was THF at a flow rate of 1.0 mL min⁻¹. Polystyrene standards

((580–483) × 10³ g mol⁻¹) were used to calibrate the SEC. FT-IR spectra were recorded on a Bruker IFS 66 spectrometer in the range 4000–400 cm⁻¹ with a resolution of 2 cm⁻¹. Elemental analyses were performed by the Service Central d'Analyses du Centre National de Recherche Scientifique, Vernaison (France).

2.3. Synthesis of *p*-xylylundec-10-enoate 4

In a 250 mL round-bottom flask, an aqueous solution of cesium carbonate (10%) was added dropwise to a solution of undec-10-enoic acid **1** (2.91 g, 15.8 mmol) in methanol (80 mL) and water (8 mL) until pH 7. DMF (40 mL) was added to the mixture and the organic phase was separated. The solvent was then evaporated and the cesium undec-10-enoate was obtained in quantitative yield. α-Chloro-*p*-xylene **3** (1.40 g, 10 mmol) was dissolved in DMF (25 mL) in a 100 mL round-bottom flask equipped with a condenser and a magnetic stirrer. The cesium undec-10-enoate (3.16 g, 10 mmol) was added and the reaction mixture was stirred for 24 h at 50 °C. DMF was evaporated. Diethyl ether (50 mL) was added to the mixture and the solution was filtered to eliminate CsCl. The crude mixture was evaporated and dried overnight in vacuo. *p*-Xylylundec-10-enoate **4** was obtained as a pale yellow liquid (4.46 g, 98%).

¹H NMR (CDCl₃), δ (ppm): 7.23 and 7.17 (d, 4H, *J* = 4.5 Hz, H_{aro}), 5.81 (m, 1H, RCH=), 5.06 (s, 2H, O–CH₂-cycle), 4.90 (m, 2H, =CH₂), 2.32 (s, 3H, CH₃), 1.27 (m, 16H, CH₂). ¹³C NMR (CDCl₃), δ (ppm): 173.3 (s, C=O), 137.5 and 132.6 (s, C_{aro}), 128.8 and 127.9 (d, C_{aro}), 118.7 (d, RCH=), 113.7 (t, =CH₂), 65.6 (t, CH₂-O), 33.9–24.5 (t, CH₂), 20.4 (q, CH₃). FT-IR (KBr) (cm⁻¹): 3022 and 2926 (vs, C–H), 1736 (vs, C=O), 1625 (vs, C=C).

2.4. Synthesis of vinyl-functionalized Merrifield and Wang resins

2.4.1. Reaction with undec-10-enoic acid **1** (**M1** and **W1**, respectively; **M** = Merrifield resin, **I** = undec-10-enoic acid, and **W** = Wang resin)

Vinyl-functionalized Merrifield resin **M1**: In a 100 mL round-bottom flask equipped with a condenser, commercial Merrifield resin **M** (0.57 g, 3.3 mmol), DMF (4 mL), and cesium undec-10-enoate (0.60 g, 3.3 mmol) were introduced. The reaction was carried out with mechanical stirring (100 rpm) at 50 °C for 24 h. The beads were filtered and subsequently washed with DMF, DMF/water (1/1), methanol/water (1/1), and methanol. The product was filtered and dried overnight in vacuo.

Solid-state ¹³C NMR, δ (ppm): 146.0 (s, C_a and C_{a'}), 139.4 (t, C_f), 128.6 (d, C_b and C_{b'}), 115.0 (t, C_f), 66.2 (t, C_{c'}), 34.6–20.2 (t, C_e). FT-IR (cm⁻¹): 3068, 3033, 2927 and 2854 (vs, C–H), 1738 (vs, C=O), 1654 (vs, C=C).

Vinyl-functionalized Wang resin **W1**: Commercial Wang resin **W** (1.02 g, 1.24 mmol), undec-10-enoic acid **1** (1.13 g, 6.2 mmol), triphenylphosphine (3.24 g, 12.4 mmol), and THF (50 mL) were introduced in a 250 mL round-bottom flask set under nitrogen atmosphere and the mixture was cooled at 5 °C. A solution of DIAD (2.49 g, 12.4 mmol) in THF (6.2 mL) was

added dropwise and the mixture was stirred with mechanical stirring (100 rpm) at room temperature for 15 h. The beads were filtered and subsequently washed with THF, methanol, diethyl ether and THF. The product was filtered and dried overnight in vacuo.

Gel-phase ^{13}C NMR (CDCl_3), δ (ppm): 138.7 (d, C_f), 131.7 and 128.0 (d, C_b and $\text{C}_{b'}$), 113.8 (t, C_f'), 65.4 (t, $\text{C}_{c'}$), 33.9–24.5 (t, C_e). FT-IR (cm^{-1}): 3057, 3023, 2917 and 2850 (vs, C–H), 1729 (vs, C=O ester), 1635 (vs, C=C), 1221 (vs, C–O–C).

2.4.2. Reaction with *p*-vinylbenzoic acid **2** (**W2**, *W* = Wang resin, and **2** = *p*-vinylbenzoic acid)

Vinyl-functionalized Wang resin **W2**: **W2** beads were synthesized using the *p*-vinylbenzoic acid spacer **2** according to the same procedure as for **W1**.

Gel-phase ^{13}C NMR (CDCl_3), δ (ppm): 166.2 (s, C_3), 145.3 (s, C_a and $\text{C}_{a'}$), 141.9 (s, C_{aro}), 136.0 and 116.4 (s and d, C_f and C_f'), 129.9 and 126.0 (d, C_{aro}), 127.9 (d, C_b and $\text{C}_{b'}$), 66.4 (t, $\text{C}_{c'}$). FT-IR (cm^{-1}): 3024 and 2912 (vs, C–H), 1711 (vs, C=O ester), 1267 (vs, C–O–C).

2.5. Typical ROMP procedure (**M1-PNBE**, **W1-PNBE** and **W2-PNBE**) (**M1**, **W1** and **W2**; **M** = Merrifield resin and **W** = Wang resin, **1** = undec-10-enoic acid, **2** = *p*-vinylbenzoic acid, **PNBE** = polynorbornene)

In an inert-atmosphere glovebox, a solution of initiator was prepared in a vial by dissolving the catalyst (61.9 mg, 0.07 mmol) in anhydrous CHCl_3 (1.9 mL). The resulting purple solution was stored until further use.

ROMP onto supported Grubbs catalyst: In a vial, the vinyl-functionalized resin (92 mg, 1 equiv) was stirred in CHCl_3 for 12 h. A solution of catalyst (61.9 mg, 0.07 mmol in 1.9 mL CHCl_3) was added and the mixture was stirred at room temperature for 2 h. The beads were filtered and washed with CHCl_3 until the filtrate remains colorless. In an inert-atmosphere glovebox, the supported Grubbs catalyst and CHCl_3 were subsequently introduced in a vial and the mixture was stirred for 12 h. A solution of **NBE** (707 mg, 100 equiv) in CHCl_3 (7 mL) was then added. The reaction mixture was stirred inside the glovebox until the color of the solution turned from purple to brown. The reaction mixture was brought out of the glovebox and quenched by addition of a small amount of ethyl vinyl ether (200 μL). The beads were filtered and subsequently washed with THF, methanol and THF. The grafted resin was filtered and dried overnight in vacuo.

2.6. Cleavage procedure

The grafted beads **W1-PNBE** (0.20 g) were introduced into a vial with 2 mL of dichloromethane, and trifluoroacetic acid (2 mL) was added dropwise. The mixture was kept under magnetic stirring at room temperature for 5 h. Filtration was ensured to isolate cleaved polymer. α,ω -**PNBE** was precipitated in methanol, recovered by evaporation, and dried overnight in vacuo.

^1H NMR (CDCl_3), δ (ppm): 7.90 and 7.55 (m, 4H, H_{aro}), 5.34 (s, $\text{H}_{1\text{ trans}}$ and $\text{H}_{7\text{ trans}}$), 5.15 (d, $\text{H}_{1\text{ cis}}$ and $\text{H}_{7\text{ cis}}$), 2.77 (m, $\text{H}_{2\text{ cis}}$ and $\text{H}_{5\text{ cis}}$), 2.43 (m, $\text{H}_{2\text{ trans}}$ and $\text{H}_{5\text{ trans}}$), 1.83 (m, $\text{H}_{3\text{ trans}}$ and $\text{H}_{4\text{ trans}}$), 1.35 (m, H_6), 1.05 (m, $\text{H}_{3\text{ cis}}$ and $\text{H}_{4\text{ cis}}$). ^{13}C NMR (CDCl_3), δ (ppm): 180.42 (s, C_9), 132.90, 132.00 and 131.84 (s and d, C_{aro}), 128.20 and 127.32, 125.42 and 111.15 (d, C_8 , C_7 , C_1 and $\text{C}_{1'}$), 42.40 and 42.10 (t, C_6), 41.06 and 40.34 (d, $\text{C}_{2\text{ cis}}$ and $\text{C}_{5\text{ cis}}$), 37.63 and 37.38 (d, $\text{C}_{2\text{ trans}}$ and $\text{C}_{5\text{ trans}}$), 31.89, 31.33 and 31.18 (t, C_3 and C_4). FT-IR (cm^{-1}): 3354 (s, O–H), 2955 and 2854 (vs, C–H), 1723 (vs, C=O ester), 1666 (vs, C=C).

2.7. Swelling capacity of the beads

Swelling capacity of the beads was determined using various solvents. Experiments were conducted as follows: Dry beads (150 mg) were carefully weighted before being placed in a 10 mL vial containing 3 mL of the solvent. Beads were taken out from the solvent, wiped using a filter paper and weighted. The swelling capacity was the ratio between the weights of wet and dry beads.

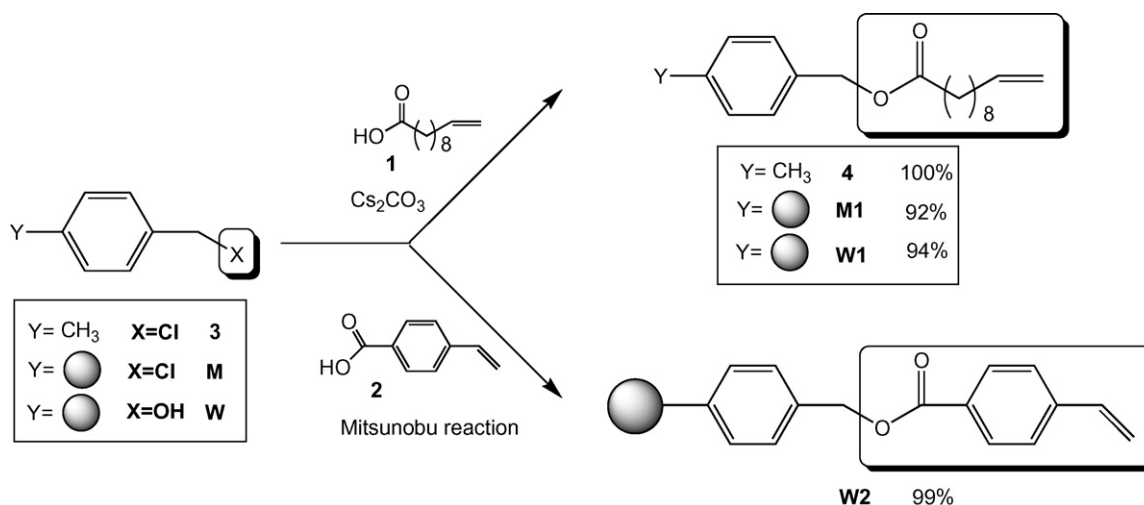
3. Results and discussion

3.1. Synthesis of vinyl-functionalized resins

Two vinyl-functionalized polymer supports were synthesized starting from Merrifield (**M**) and Wang (**W**) resins (Scheme 1). Immobilization of the vinyl functionality on the resin was carried out by reaction between the Cl (Merrifield resin) or the OH (Wang resin) functionality of the initial resin and an α,ω -spacer bearing a carboxylic acid group and a terminal alkene.

The reaction of Merrifield resin **M** with undec-10-enoic acid (**1**) was performed in the presence of an excess of cesium carbonate in DMF at 50 °C to get a vinyl-functionalized Merrifield resin (**M1**). Immobilization of undec-10-enoic acid (**1**) and *p*-vinylbenzoic acid (**2**) spacers on Wang resin **W** was carried out according to the Mitsunobu conditions (DIAD, PPh_3) [26] to give (**W1**) and (**W2**) resins, respectively. The FT-IR spectra of the modified Merrifield **M1** and Wang **W1** resins showed the disappearance of the C–Cl band at 696 cm^{-1} and of the O–H band at 3500–3400 cm^{-1} and the appearance of the C=O (ester) band at 1740 and 1736 cm^{-1} , respectively. Samples **M** and **M1** were also analyzed by solid-state ^{13}C NMR (Fig. 1).

The spectrum of **M** is shown in Fig. 1A. The peak at 45.9 ppm corresponds to the methylene carbon atom $\text{CH}_2\text{–Cl}$. The other peaks originate from the carbons in the poly(styrene-*co*-divinylbenzene) core between 120 and 150 ppm. The spectrum of **M1** shows new peaks (Fig. 1B). These peaks were attributed using ^{13}C chemical shifts of a model molecule, *p*-xylylundec-10-enoate (**4**), which was prepared by reaction between α -chloro-*p*-xylene (**3**) and **1** (Table 1). In Fig. 1B, the peak at 66.2 ppm was attributed to the new methylene carbon atom $\text{CH}_2\text{–O–}$ (65.6 ppm for **4**; Table 1). The modification of **M** does not proceed in a quantitative yield as shown by the remaining peak at 46.5 ppm (methylene carbon atom $\text{CH}_2\text{–Cl}$). **W1** and **W2** were characterized by gel-phase ^{13}C NMR in CDCl_3 (Table 1)



Scheme 1. Synthesis of vinyl-functionalized resins.

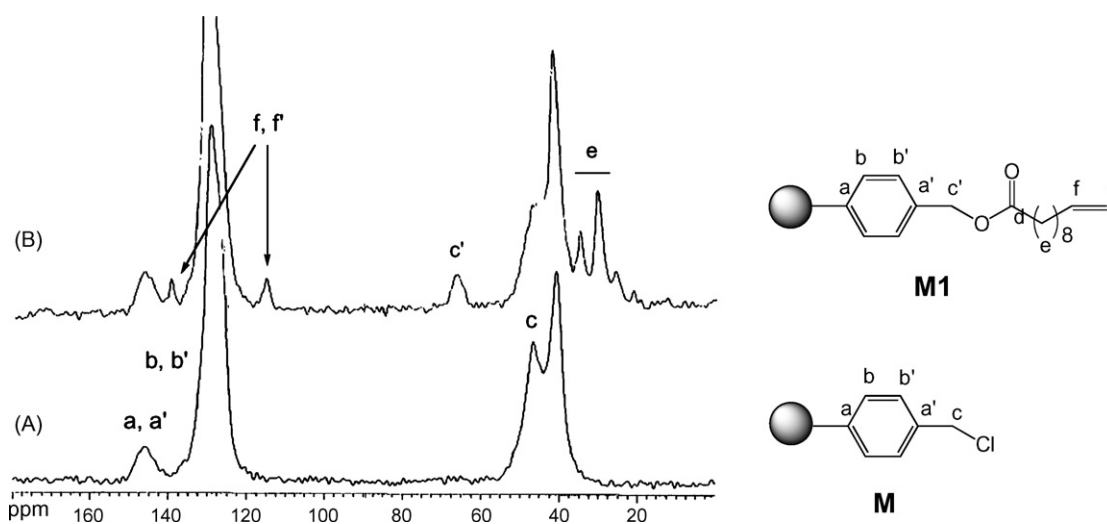
Fig. 1. Solid-state ¹³C NMR spectra of: (A) commercial **M** and (B) modified Merrifield supports **M1**.

Table 1

Chemical shifts of **3**, **4** and resins **M** and **W** before and after chemical modification by solid-state, gel-phase and solution ¹³C NMR

Compound	Chemical shift δ_c (ppm)								
	a	a'	b	b'	c ^f /c' ^g	d	e	f'/f	
3 ^a	134.2	138.0	129.1	128.2	45.9 ^f	–	–	–	
M ^b		145.9		128.6	46.5 ^f	–	–	–	
4 ^a	137.5	132.6	128.8	127.9	65.6 ^g	173.3	33.9–24.5	113.7/138.7	
M1 ^b		146.0		128.6	66.2 ^g	–	34.6–20.2	115.0/139.4	
W1 ^c		– ^d	131.7	128.0	65.4 ^g	–	33.9–24.5	113.8/138.7	
W2 ^c		145.3		127.9	66.4 ^g	166.2	141.9 ^e , 129.9 ^e –126.0 ^e	116.4/136.0	

^a ¹³C NMR in CDCl₃.^b Solid-state ¹³C NMR.^c Gel-phase ¹³C NMR in CDCl₃.^d Not visible.^e Aromatic carbons of spacer **2**.^f Signal assignment to carbon c.^g Signal assignment to carbon c'.

Table 2
Conversion and vinyl loading of resins **M1**, **W1** and **W2**

Resin	[Spacer]/[X ^d]	τ (%)		Loading ^c (mmol C=C/g resin)
		τ_w increase in weight	τ_{EA} elemental analysis	
M1	0.2 ^a	25	23	0.54
M1	1 ^a	91	90	2.05
M1	5 ^a	92	91	2.07
W1	5 ^b	94	–	1.14
W2	5 ^b	99	–	1.20

^a Merrifield resin: 35–75 μm , loading: 2.25 mmol Cl/g resin, 2% cross-linked.

^b Wang resin: 35–75 μm , loading: 1.21 mmol OH/g resin, 1% cross-linked.

^c Loading = loading₍₀₎ \times ($\tau_w + \tau_{EA}$)/2; loading₍₀₎ = loading of the commercial resin.

^d X = Cl or OH.

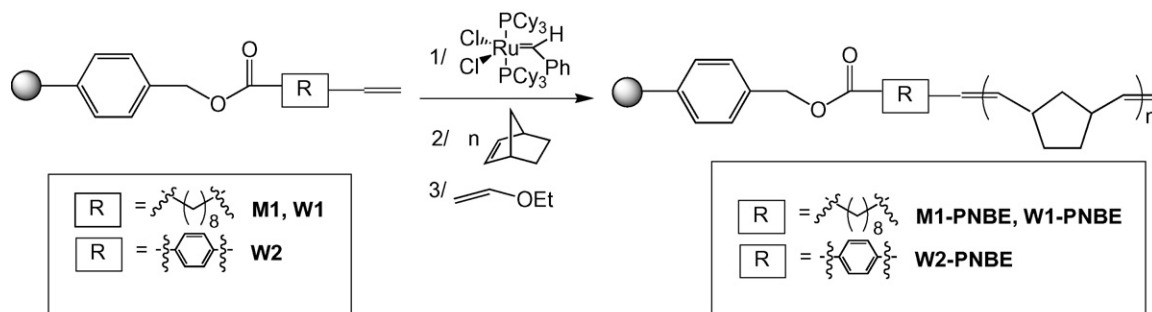
and a good agreement was observed between **4** (solution), **M1** (solid-state) and **W1** (gel-phase).

The modified Merrifield resins were subjected to chlorine elemental analysis, the results of which were related to the increase in weight of the resin. These results and the vinyl loading are given in Table 2.

Vinyl-functionalized Merrifield resins have been obtained with a double bond loading from 0.54 to 2.07 mmol/g corresponding to a remaining Cl functionality of 77 and 9%, respectively. On the other hand, the OH functionality of the Wang resin was totally modified into vinyl group, as proved by the increase in weight, because of the higher reactivity of the terminal OH group compared to Cl group. The swelling capacity of the beads before and after modification has been studied (Fig. 2). Experimental values are consistent with literature data [27]. All beads displayed high levels of swelling in THF, dichloromethane and chloroform.

3.2. ROMP of norbornene (NBE) onto resins

ROMP of norbornene (**NBE**) using supported ruthenium initiator $\text{RuCl}_2 = \text{CHPh}$, generated by metathesis between Grubbs I catalyst and a terminal alkene (**M1**, **W1** and **W2**) according to the Maarseveen strategy [28], was carried out in chloroform at room temperature with monomer to catalyst ratio $[M]_0/[I]_0 = 100$ (Scheme 2). The reaction was quenched by addition of a small amount of ethyl vinyl ether.



Scheme 2. ROMP of **NBE** onto polymeric supports.

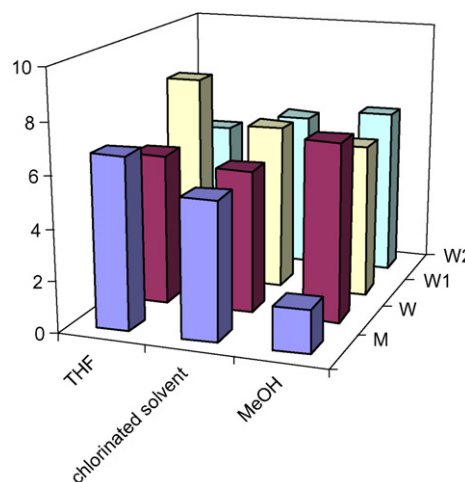


Fig. 2. Swelling properties of Merrifield and Wang supports before and after modification.

Whatever the resin used (**M1** or **W1**), the global yield was about 85% (Table 3) and polynorbornene (**PNBE**) was produced at the same time onto support (**M1-PNBE**) and (**W1-PNBE**), respectively, and in solution. **PNBE** in solution comes from (i) traces of initiator remaining on support even after extensive washing (ii) liberated Grubbs catalyst resulting from the intramolecular “ring-closing” metathesis of the growing polymer chain onto the residual terminal vinyl groups on the resin [18] and (iii) intermolecular cross metathesis between a terminal ruthenium alkylidene of one growing grafted polymer and a double bond into another growing grafted polymer [29]. Conversion of **NBE** onto **W1** was higher than onto **M1** (22 and 39% respectively; Table 3). The beads **W1-PNBE** (see Fig. 3) were visibly larger than beads **W1**, which confirmed that the polymerization took place not only at the surface of the support but also inside the beads.

The **W1** resin was more efficient despite a lower loading in vinyl groups (1.14 instead of 2.07 mmol/g; Table 3), which seems to limit side reactions between the Grubbs catalyst and the double bonds. The efficiency was increased by the use of a more reactive spacer, derived from *p*-vinylbenzoic acid (**2**). The aromatic group is an electron-donating group which promotes the RCM on the neighbouring C=C terminal bond. The results from the resin **W2** show a much higher conversion of **NBE** grafted onto beads (64% instead of 39% with **W1** beads; Table 3).

Table 3
ROMP of NBE on **M1**, **W1** and **W2**-supported Grubbs catalysts

Support	Loading ^a (mmol C=C/g resin)	Product	τ_{global} (%)	$\tau_{\text{P grafted}}^{\text{b}}$ (%)	$\tau_{\text{P in solution}}^{\text{c}}$ (%)	$\bar{M}_{n,\text{theo}}$ (g/mol) ^c	$\bar{M}_{n,\text{exp}}$ (g/mol) ^d	I_{p}^{d}
M1	2.07	M1-PNBE	84	22	62	2200	–	–
W1	1.14	W1-PNBE	89	39	50	3800	–	–
W2	1.20	W2-PNBE	82	64	18	6100	8700	3.8

^a Loading of vinyl-functionalized resin.

^b $\tau_{\text{global}} = \tau_{\text{P grafted}} + \tau_{\text{P in solution}}$.

^c $\bar{M}_{n,\text{theo}} = ([\text{monomer}]_0/[\text{initiator}]_0) \times \tau_{\text{P grafted}} \times M_{\text{monomer}} + 104$.

^d From SEC data in THF relative to polystyrene standards.

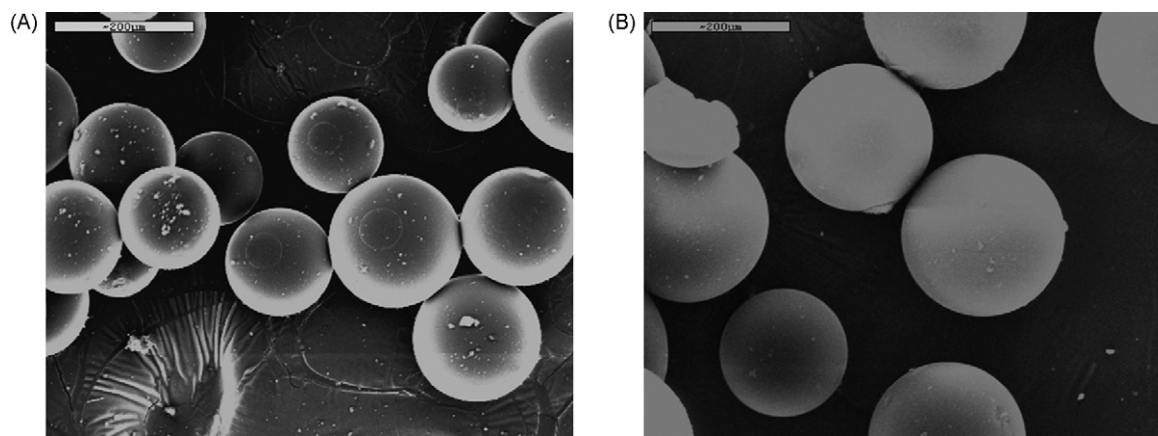
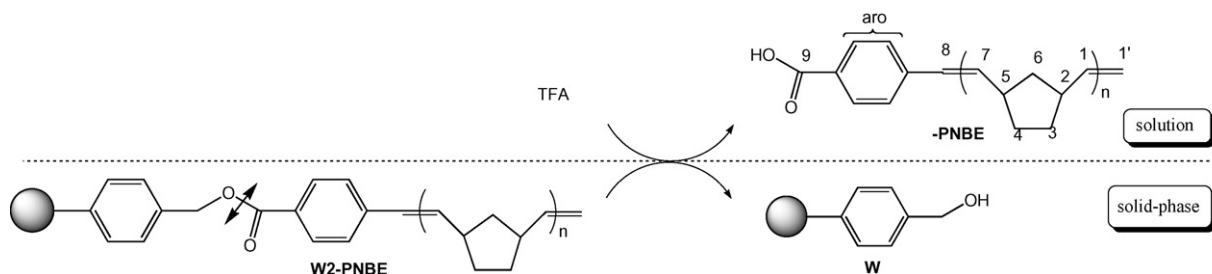


Fig. 3. SEM photographs of (A) beads **W1** and (B) beads **W1-PNBE** after polymerization of NBE.



Scheme 3. Cleavage of grafted **PNBE** from resin using trifluoroacetic acid treatment.

Number-average molecular weight and polydispersity index of the grafted **PNBE** onto the more efficient **W2** resin were determined by size exclusion chromatography (SEC) after cleavage of the polymer from the resin by trifluoroacetic acid treatment for 6 h at room temperature (Scheme 3).

The $\bar{M}_{n,\text{exp}}$ value of the resulting **PNBE**, higher than the expected one: 8700 g/mol (PS equivalent) instead of 6100 g/mol (Table 3), and the polydispersity index value ($I_{\text{p}} = 3.8$) suggest a lack of control over the supported-ROMP. However, the resulting (**PNBE**) with a carboxylic acid and a vinyl end-groups was recovered with 98% yield.

4. Conclusions

Vinyl-functionalized Merrifield (**M1**) and Wang (**W1** and **W2**) resins were synthesized with excellent yields using a spacer bearing a carboxylic acid group and a terminal alkene. Anchor-

ing of the spacer has been checked by solid-state and gel-phase NMR experiments. Supported Grubbs I catalysts were then prepared via an alkylidene exchange reaction and were used to graft polynorbornene. Best results have been obtained with the Wang resin initially totally modified with an aromatic spacer, which seems to improve the activity of the supported catalyst.

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