# Tailor-Made Polymer Supports *via* Metathesis Polymerization: Concepts and Applications

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SUMMARY: Ring opening metathesis polymerization (ROMP) and alkyne polymerization have been applied to the preparation of surface-functionalized inorganic and organic supports using various coating, grafting, precipitation and bulk-polymerization techniques. Well-defined carrier materials in terms of particle diameter, specific surface, pore volume and functionalization have been prepared. The resulting materials have been used for applications in heterogeneous catalysis (e. g. Heck couplings) as well as in bioanalytical (e. g. protein) separations.

## Introduction

The synthesis of supports that possess a well-defined and stable surface chemistry is still an intensively investigated area. Such high definitions are basic requirements for various applications e. g. in heterogeneous catalysis, chromatography, drug delivery, etc. Standard functionalization procedures of organic supports require the use of divergent synthetic approaches that entail a step by step transformation of surface-bound functional groups. In order to avoid such ill-defined syntheses, we elaborated a conceptually new approach based on metathesis polymerization[1] that allows the synthesis of such supports by a convergent synthetic route, starting from functional monomers. In the following, a few recent examples shall be outlined and their general usefulness shall be underlined by a few examples of application.

**Ring-opening metathesis precipitation polymerization**

Ring-opening metathesis precipitation polymerization may be used to generate beaded, highly cross-linked polymers with a high density of functional groups at the surface. The reaction sequence entails the use of functional monomer. The polymerization system itself must fulfill a class VI living system[2]. Subsequent cross-linking of the "living" linear polymer chains by a suitable norbornene-based cross-linker in course of the precipitation polymerization leads to the formation of irregularly shaped polymer beads (Scheme 1)[3]. Even complex functionalities may be introduced with high reproducibility and without any change in the chemical nature, geometry and even absolute configuration of the corresponding functional group.
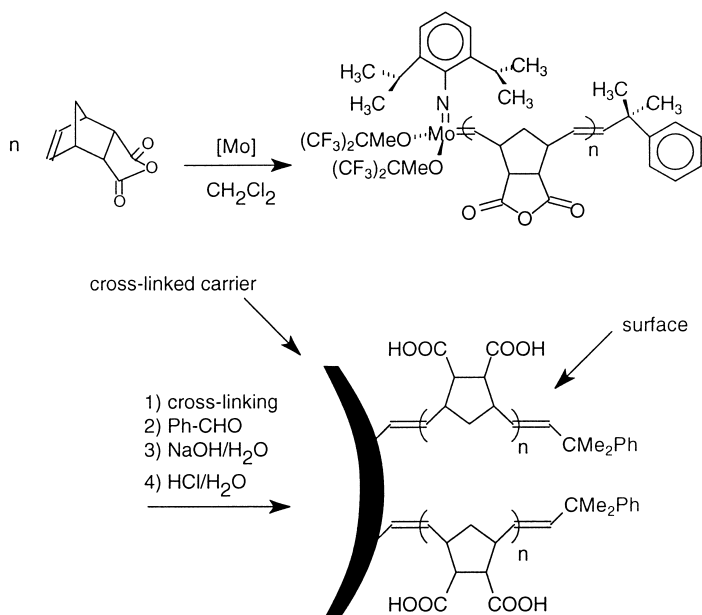


**Scheme 1:** Synthesis of succinic acid derivatized polymer beads by ring-opening metathesis precipitation polymerization[3]. $[Mo]$ = $Mo(N-2,6-i-Pr_2-C_6H_3)(CHCMe_2Ph(OCMe(CF_3)_2)_2$. = cross-linker = $1,4,4a,5,8,8a$-hexahydro-$1,4,5,8$-*exo-endo*-dimethanonaphthalene.

The amount of functional monomer immobilized by this approach may be varied within a range of 0 – 8 mmol/g. Table 1 gives an overview over the functional monomers and beaded materials as well as their physico-chemical properties.

Table 1. Poly(norbornene-5,6-dicarboxylic acid)- and poly(norbornene-5-dipyridyl carbamide) $(C(O)Npy_2)$-functionalized resins[3, 4].

| # | functional group | capacity [mmol/g] | swelling[a] [%] | $\sigma$ [m$^2$/g] | yield [%] |
|---|---|---|---|---|---|
| 1 | succinic acid | 7.30 | 44 | 30 | 100 |
| 2 | succinic acid | 3.75 | 36 | 14 | 98 |
| 3 | succinic acid | 3.13 | 64 | 24 | 100 |
| 4 | $C(O)Npy_2$ | 1.0 | 39 | 6[b] /4[c] | 97.1 |
| 5 | $C(O)Npy_2$ | 0.6 | 35 | 4 | 95.0 |

A-B-block-copolymers (A = functional monomer, B = cross-linker = 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo-endo*-dimethanonaphthalene), $\sigma$ = specific surface, [a] in water, [b] from BET measurements, [c] calculated from GPC data, average particle size = 40±10 μm.

As can be deduced from Table 1, polymer beads prepared by this method only possess a certain microporosity and mainly macropores (> 1000 Å). The particles have a mean diameter of 20 - 40 μm, and are characterized by a low specific surface area (4 <$\sigma$ < 30 m$^2$/g). Values for $\sigma$ as determined by BET are in good agreement with those obtained from inverse GPC[5]. Swelling is acceptable (< 40 %) for resins with $\sigma$ < 10 m$^2$/g. As a consequence of the polymerization order, the linear polymer chains bearing the functional groups form tentacles that are attached to the surface of the cross-linked carrier. This ensures a fast mass transfer with any kind of mobile phase or liquid and lets these materials appear as highly attractive for extraction and immobilization purposes. Thus, poly(norbornene-5,6-dicarboxylic acid)-functionalized resins prepared by ring-opening metathesis precipitation polymerization have been successfully used for the analysis of organic compounds from water[6, 7] and air[8] as well as for the selective enrichment of lanthanides[9]. Addionally, dipyridyl carbamide-based materials may be used as supports for

heterogeneous catalysis as it represents a typical small particle catalyst[15]. Thus, the palladium-loaded chelating groups are located exclusively at the surface of the particle[52,60], they are easily accessible, diffusion plays a minor role and coupling reactions proceed within the interphase[65,66]. As a consequence of the high selectivity of the ligand for palladium, no substitution by other metal ions that might be present in technical grade chemicals occurs. The high affinity of the ligand for palladium also leads to a high temperature stability of up to 150°C and to an extraordinary pH-stability (0 < pH < 10) of the resulting complex.

**Table 2:** Summary of Heck-couplings and polymerizations[10]. TBAB = tetrabutylammonium bromide. [1] tri-$n$-butylamine; [2] $K_2CO_3$/$Na_2CO_3$ [3] 0.21 mmol/g immobilized $Pd^{2+}$ (+ 0.4 mmol free ligand), [4] isolated yields. [5] 0.35 mmol/g immobilized Pd (0) (+ 0.65 mmol free ligand). [6] DMAC [7] DMF. Unless stated otherwise, Heck-couplings were carried out at T = 140 °C, t = 90 h.

| Ar-X | $H_2C=CHR$ | product | resin[3] [mg] | yield[4] [%] | TON x $10^3$ |
|---|---|---|---|---|---|
| iodobenzene | styrene | *trans*-stilbene | 1.2[2,6] | 99.0 | 111.0 |
| iodobenzene | styrene/TBAB | *trans*-stilbene | 1[1,7] | 98 | 93.2 |
| iodobenzene | ethylacrylate | ethyl cinnamate | 2[1,7] | 75.0 | 175.1 |
| iodobenzene | vinylferrocene | α-ferrocenylstyrene | 1[1,7] | 81.1 | 17.4 |
| bromobenzene | styrene | *trans*-stilbene | 3[2,6] | 90.0 | 40.0 |
| 4-bromobenzonitrile | styrene | 4-cyano-*trans*-stilbene | 1[1,5,7] | 83.0 | 157.7 |
| 4-bromo-1-fluorobenzene | styrene | 4-fluoro-*trans*-stilbene | 2[2,6] | 58.5 | 34.4 |
| 4-methoxybromobenzene | styrene | 4-methoxy-*trans*-stilbene | 105[2,6] | 70.0 | 0.9 |
| chlorobenzene | styrene/TBAB | *trans*-stilbene | 10[2,5,6] | 89.0 | 23.6 |
| 4-chloroacetophenone | styrene/TBAB | 4-acetyl-*trans*-stilbene | 20[2,6] | 95.0 | 6.1 |
| dibromobenzene | divinylbenzene | PPV | 2[2,6] | >99 | 18 |

Consequently, this heterogeneous catalyst turned out to be highly active (94 - 99 % yields) in the vinylation of aryl iodides and aryl bromides (Heck couplings) with turn-over numbers (TONs) of up to 210 000[10]. High yields ($\leq$ 95 %) and TONs ($\leq$ 24 000) may additionally be achieved in the tetrabutylammonium bromide (TBAB) assisted vinylation of aryl chlorides (Table 2).

## Ring-opening metathesis graft-copolymerization

Due to the considerable swelling that was observed in ring-opening metathesis precipitation polymerization-based polymer supports with $\sigma$ > 10 m$^2$/g, we sought to synthesize entirely pressure-stable ROMP-based supports. For these purposes, a ROMP-based grafting approach for the preparation of surface-functionalized HPLC supports has been elaborated[11]. Bromomethylated, beaded polymer supports based on poly(styrene-divinylbenzene) (PS-DVB) were prepared either *via* direct bromomethylation or *via* transhalogenation of chloromethyl-PS-DVB and subsequently surface-derivatized with norborn-2-ene groups by reaction with sodium norborn-2-ene-5-ylmethanolate. Norborn-2-ene-derivatized silica-based supports were prepared by silanization employing norborn-2-ene-5-yltrichlorosilane. Surface grafting of the norbornene-modified supports with a series of norbornene-based, L-valine and L-phenylalanine-containing chiral monomers was accomplished using ROMP.
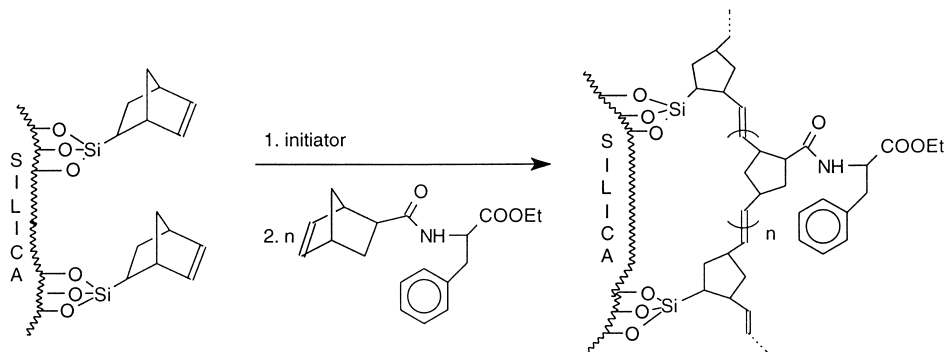


**Figure 2:** Ring-opening metathesis graft copolymerization[11]. Initiator = Mo(N-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_2$Ph(OCMe(CF$_3$)$_2$)$_2$, Cl$_2$(PR$_3$)$_2$Ru(=CHPh) (R = cyclohexyl).
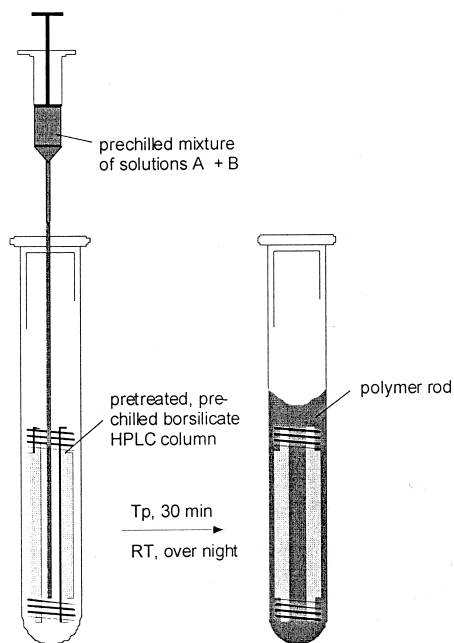
Both Schrock-type and Grubbs-type initiators were found suitable for that purpose. Scheme 2 gives an overview over the entire reaction sequence. Poly-(N-(norbornene-5-carboxyl)-ß-cyclodextrin ester) as well as poly-(N-(norbornene-5-carboxyl)-phenylalanine ethylester)-surface-grafted, porous 5 µm silica were found suitable for chiral HPLC-separations. In analogy, poly(ethynylferricinium)- and poly(ethynyl-1-(octamethylferrocenylethenyl)benzene)-based anion exchangers have been prepared following the grafting concept described above[12]. Thus, metathesis polymerization of the corresponding terminal alkynes using a Schrock-type catalyst and subsequent grafting of the living polymer onto a NBE-derivatized silica support yielded the desired metallocene-grafted stationary phase. Oxidation of the parent Fe (II) systems to the corresponding ferricinium cations was easily performed in acetonitrile, resulting in a metallocene-based anion-exchanger that has been used successfully for the separation of oligonucleotides.

**Monolithic separation media prepared by ROMP**

Continuous separation media represent highly attractive supports both for separation sciences and heterogeneous catalysis. Since their introduction into separation sciences by Hjertén et al.[13], these materials have been further developed[14]. Organic continuous beds are either based on acrylates or poly(styrene-divinylbenzene) and are almost exclusively prepared by radical polymerization. While the resulting materials have been reported to be well defined in terms of microstructure, specific surface area and pore volume, the preparation of functionalized monoliths is still somehow limited[15]. Due to the high versatility of ring-opening metathesis polymerization (ROMP) for the preparation of functionalized polymer supports we investigated as to which extent transition-metal catalyzed reactions may be used for the synthesis of continuous polymeric supports[47].

ROMP-based monolithic materials have been prepared by ring-opening metathesis copolymerization of norborn-2-ene (NBE) and 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo, endo*-dimethanonaphthalene (DMN-H6) within borosilicate columns in the presence of porogenic solvents such as toluene, methylene chloride, methanol and 2-propanol[16] (Figure 3). Grubbs-type initiators of the general formula $Cl_2(PR_3)_2Ru(=CHPh)$ (R = cyclohexyl) were used

throughout. The resulting separation media possess microstructures consisting of microporous, spherical microglobules with a narrow size distribution.  By variation of the polymerization conditions in terms of stoichiometry of the monomers, porogenic solvents and temperature, microglobule diameters may be varied within a range of $2 \pm 1$ µm up to $8 \pm 2$ µm.  Specific surface areas ($\sigma$) and inter-microglobule void volumes ($\varepsilon_z$) may be altered within $60 - 190$ m$^2$/g and $5 - 50\%$, respectively.



prechilled mixture
of solutions A + B

pretreated, pre-
chilled borsilicate
HPLC column

polymer rod

Tp, 30 min

RT, over night

**Figure 3.**  Polymerization arrangement for the preparation of molded continuous rods using ROMP.

Table 3 gives an overview over these monoliths.  Functionalized continuous rods were synthesized by one additional synthetic step that takes advantage of the living character of the ROMP-based copolymerization.  This "in situ" derivatization was achieved after the formation of the continuous rod by reacting the active, surface-bound initiator with functional norborn-2-ene- and 7-oxanorborn-2-ene-based monomers including *endo/exo*-7-oxanorborn-2-ene-5-yl-ß-

cyclodextrin, by passing solutions thereof in dichloromethane and DMF, respectively, over the rigid rod (Table 4).

**Table 3.** NBE = norborn-2-ene, DMN-H6= 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo, endo*-dimethanonaphthalene, **1** = $Cl_2(PR_3)_2Ru(=CHPh)$ (R = cyclohexyl), $T_p$ = polymerization temperature, σ = specific surface, $V_p$ = pore volume[5], $d_p$ = microglobule diameter[5], [1] by weight.

| # | NBE [%[1]] | DMN-H6 [%[1]] | toluene [%[1]] | 2-PrOH [%[1]] | 1 [%[1]] | $T_p$ [°C] | σ [$m^2$/g] | $\varepsilon_z$ [%] | $V_p$ [mL] | $d_p$ [μm] |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 20 | 20 | 10 | 50 | 0.4 | 0 | 62 | 33 | 0.31 | 4±1 |
| 2 | 20 | 20 | 20 | 40 | 0.4 | 0 | 74 | 21 | 0.31 | 4±1 |
| 3 | 15 | 15 | 10 | 60 | 0.4 | 0 | 76 | 37 | 0.31 | 2±1 |
| 4 | 25 | 25 | 10 | 40 | 0.4 | 0 | 85 | 15 | 0.34 | 2±1 |
| 5 | 25 | 25 | 10 | 40 | 1 | 0 | 86 | 14 | 0.34 | 4±1 |
| 6 | 25 | 25 | 20 | 30 | 0.4 | 0 | 91 | 15 | 0.33 | 4±1 |
| 7 | 25 | 25 | 10 | 40 | 0.4 | -20 | 98 | 17 | 0.32 | 6±2 |
| 8 | 15 | 15 | 20 | 50 | 0.4 | 0 | 110 | 49 | 0.28 | 3±1 |
| 9 | 30 | 30 | 10 | 30 | 0.4 | 0 | 191 | 5 | 0.35 | 8±2 |

**Table 4.** Capacities of functionalized ROMP monoliths. [a] determined by titration, [b] determined by elemental analysis (percent of nitrogen). [1] by weight.

| # | monomer | capacity [mmol/g] |
|---|---|---|
| 1 | norbornene-2-carboxylic acid | 0.2[a] (3.3 %)[1] |
| 2 | norbornene-2,3-dicarboxylic acid | 0.14[a] (2.0 %)[1] |
| 3 | N,N-(norbornene-5,6-dicarboxyyl)valine-N'-(3-nitrophenyl)amide | 0.03[b] (1.1 %)[1] |
| 4 | N-phenyl-7-oxanorbornene-2,3-dicarbimide | 0.22[b] (5.3 %)[1] |
| 5 | N-(4-hydroxyphenyl)-7-oxanorbornene-2,3-dicarbimide | 0.06[b] (1.5 %)[1] |
| 6 | N-(4-dimethylaminophenyl)-7-oxanorbornene-2,3-dicarbimide | 0.26[b] (7.4 %)[1] |

# Conclusion

It has been shown that ROMP represents a highly versatile tool in the preparation and modification of functional polymer supports. In contrast to standard binary and ternary systems, the use of well-defined initiators allows the highly reproducible preparation of tailor-made materials with regards to particle size, diameter, pore volume and functionalization. Most polymerization techniques such as precipitation- graft- and even bulk polymerization may be used for these purposes.

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