

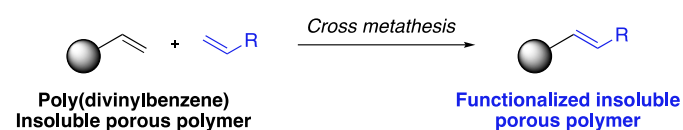
Olefin cross metathesis as a versatile method for the facile functionalization of porous polymers

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Supporting Information Placeholder



ABSTRACT: Olefin cross metathesis has been employed for the first time for the post-polymerization chemical modification of porous polymers. High quality microspheres of poly(divinylbenzene) were synthesized by the precipitation polymerization of divinylbenzene-55 in porogenic solvents, and the olefin cross metathesis reactions of the pendent (polymer-bound) vinyl groups not consumed by polymerization were performed with diverse coupling partners in dichloromethane using the Grubbs 2 catalyst, leading to microspheres decorated with a wide range of functional groups.

Porous resins are used in an extraordinarily wide range of advanced and everyday applications, from combinatorial chemistry,¹⁻³ solid-phase organic synthesis^{4,5} and polymer-supported reagents,^{6,7} through to environmental analyses^{8,9} and the purification of drinking water.¹⁰ The installation of chemical functional handles on the resins is often a prerequisite for their successful exploitation, and this is normally achieved by either the post-polymerization chemical modification of resins or the copolymerization of monomers bearing functional groups. Neither approach is generic, and substantial optimization of the reaction conditions is often required. Thus, there is a demand for generic chemical functionalization methods for such materials.

In tackling the chemical functionalization requirements described above, we have focused upon the development of olefin cross metathesis-based methods¹¹ for the functionalization of porous organic polymer networks, with a special focus upon porous polymer microspheres with low mean particle diameters and narrow particle size distributions since such materials are very appealing from an applications perspective. In 1996, Blechert and co-workers¹² reported the first example of olefin cross metathesis (CM) reactions on resin-bound substrates. However, the chemical functionalization of porous particulates using olefin CM, where the crosslinker serves simultaneously as a crosslinking agent and reactive handle for CM, has not been described previously.¹³ Here we report upon the functionalization of a porous poly(divinylbenzene) under very mild conditions, where the poly(divinylbenzene) was prepared by precipitation polymerization (PP).^{14,15} One of the goals was to demonstrate the ease with which a broad range of diverse functionality can be installed into beaded resins by an appropriate choice of

coupling partner for the polymer-bound vinyl groups. The method exploits residual unsaturation arising from incomplete consumption of crosslinker-derived vinyl groups during polymerization, so it is generic; however, the approach can be extended with ease to include the CM of unsaturated functional groups installed into the polymers using a functional monomer approach.

Poly(DVB-55) particles were prepared in good yield (62%) by the precipitation polymerization of DVB-55 under dilute conditions (4% w/v) in a porogen comprising of acetonitrile and THF (60/40 v/v). SEM analysis of the product showed that spherical particles were obtained (mean particle diameter = 4.8 μm , with a standard deviation of 1.5 μm and a coefficient of variation (CV) of 32%). Nitrogen sorption analysis of the particles showed that they were porous in the dry state (BET specific surface area = 245 m^2/g , with a mean pore diameter of 21 \AA and specific pore volume of 0.13 cm^3/g). The porous microspheres could then be used directly in olefin CM reactions, since it has been established that normally not all of the vinyl groups in the divinylbenzene monomer are consumed by free radical polymerization. In 1998, Law *et al.* reported a quantitative study of the level of residual (unreacted) vinyl groups in poly(divinylbenzenes), by integration of the diagnostic signals in the ¹³C solid-state NMR spectra of the products. They found that for polymer resins prepared with the 55% grade of commercial divinylbenzene (*i.e.*, DVB-55, which is a mixture of the *meta*- and *para*- isomers of divinylbenzene and ethylvinylbenzene), 32% of the vinyl groups remained intact (unreacted) and pendent once the polymerization was complete.¹⁶ For the poly(DVB-55) described above, the pendent vinyl groups that

survive the polymerization, and which are therefore available as chemical handles for functionalization, give rise to diagnostic signals in the FT-IR and ^{13}C solid-state NMR spectra (Figure 1). Figure 1a shows the FT-IR spectrum of the poly(DVB-55); the polymer-bound vinyl groups give rise to a diagnostic band at 910 cm^{-1} . Figure 1b shows the ^{13}C solid-state NMR spectrum of the poly(DVB-55); here, the vinyl groups give rise to resonances at 135 and 110 ppm, arising from the two distinct carbon environments. Later on in the current study, these vinyl signals proved to be useful for the monitoring of the subsequent CM reactions.

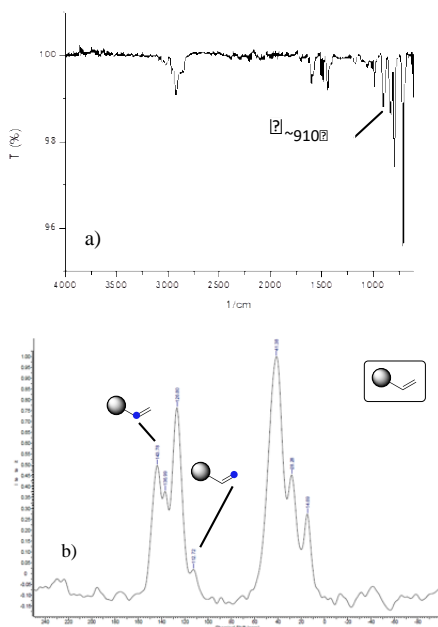
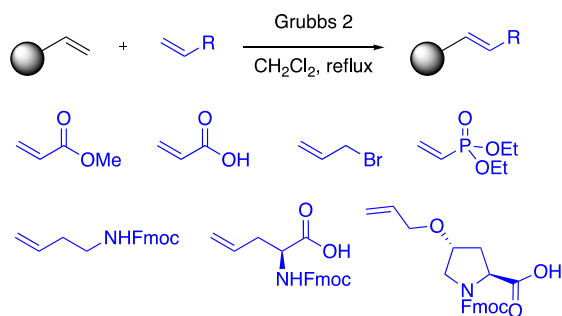


Figure 1. a) FT-IR spectrum of poly(DVB-55); b) ^{13}C Solid-state NMR spectrum of poly(DVB-55).

To the best of our knowledge, olefin CM has never before been employed for the functionalization of porous polymer microspheres. The objective was to perform the functionalizations under mild reaction conditions and with a wide range of coupling partners, as illustrated in Scheme 1, whilst retaining the integrity of the polymer beads.

Scheme 1. Olefin CM reactions between porous poly(DVB-55) microspheres bearing pendent vinyl groups and a range of chemically distinct coupling partners



A noteworthy advantage of the CM method over other methods that can be used to target vinyl groups, is the retention of olefinic character in the functionalized polymers. This olefinic

character provides a potential site for yet further chemical elaboration/diversity.

CM reactions on the poly(DVB-55) were evaluated using methyl acrylate as the coupling partner in the first instance, since methyl acrylate is known to be a good CM partner for styrene in solution.¹¹ Following the CM reaction with methyl acrylate, the appearance of new bands in the FT-IR spectrum of the functionalized product, at 1740 cm^{-1} (C=O str.) and 830 cm^{-1} (C-H out-of-plane def.), were consistent with a successful CM (Figure 2a). Furthermore, a new signal appeared at 65 ppm in the ^{13}C solid-state NMR spectrum, which can be assigned unambiguously to the methoxy group of the immobilized ester (Figure 2b).

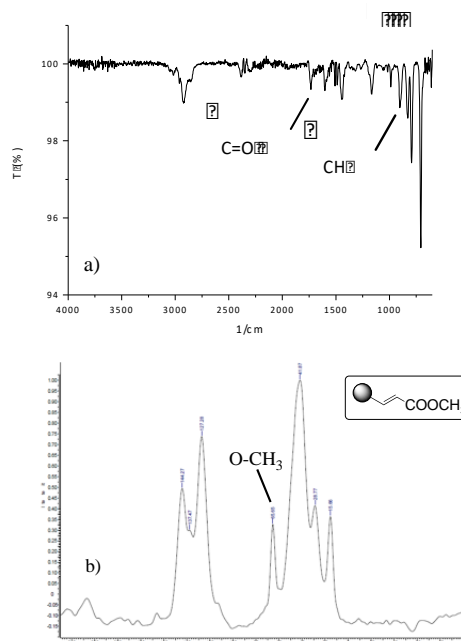


Figure 2. a) FT-IR spectrum, and b) ^{13}C solid-state NMR spectrum, of poly(DVB-55) following a CM reaction with methyl acrylate.

SEM analysis of the poly(DVB-55) (Figure 3a) and poly(DVB-55) post-CM (Figure 3b) showed that the particle integrity and quality was retained, thus validating CM as a mild technique for polymer functionalization. There was no evidence for bead aggregation either, which implies that self-metathesis involving vinyl groups on separate beads did not occur.

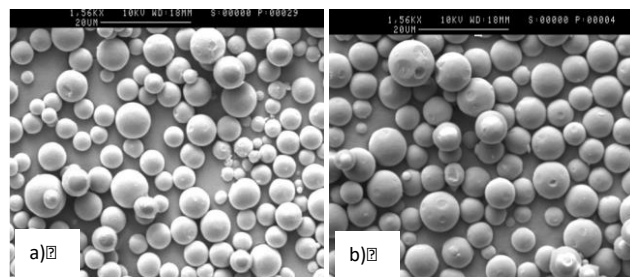


Figure 3. SEM micrograph of a) poly(DVB-55), and b) poly(DVB-55) functionalized using CM with methyl acrylate as the coupling partner.

After having validated the feasibility of the CM reaction with methyl acrylate, a range of CM coupling partners was tested to probe the versatility of the functionalization method. In this regard, the next coupling partner used was allyl bromide, since measurement of the bromine content of the functionalized product, using elemental microanalysis, enables the functional group loading level (expressed in mmol g⁻¹) to be established. CM with allyl bromide as coupling partner was successful; this CM yielded a beaded product with a bromine content of 0.8 wt%, which corresponds to a functional group loading level of 0.10 mmol g⁻¹.

The next CM partner used was diethyl vinylphosphonate. Similarly to the allyl bromide example, elemental microanalysis of the product (quantification of P, rather than Br), enables the functional group loading level to be established. Following a successful CM with diethyl vinylphosphonate, which was confirmed by the appearance of a signal at 18 ppm (phosphonate) in the ³¹P solid-state NMR spectrum of the product, the level of phosphorous in the functionalized polymer was determined; the phosphorous content was found to be 1.0 wt%, which corresponds to a functional group loading level of 0.32 mmol g⁻¹. This functional group loading level is higher than that for the polymer functionalized with allyl bromide, and this is probably reflective of a difference in reactivity between the metathesis coupling partners. Allyl bromide, a Type 1 olefin, tends to homodimerize rapidly and it is the dimer that reacts with the polymer. Due to the increased size of the dimer relative to allyl bromide, only the most reactive, sterically unencumbered vinyl groups on the polymer's surface can be functionalized. However, diethyl vinylphosphonate is a Type 3 olefin, thus does not homodimerize and reacts directly with the polymer-bound vinyl groups leading to higher functional group loadings.¹¹

Carboxylic acid residues were installed *via* a CM reaction between poly(DVB-55) and acrylic acid, to yield a product which could potentially be exploited as a weak cation-exchange resin, for example in solid-phase extraction (SPE) work. As before, FT-IR spectroscopic analysis of the CM product was used to verify the success of the polymer-analogous reaction; new bands were observed at 3600 cm⁻¹ (OH str.) and 1705 cm⁻¹ (C=O str.), and assigned to the carboxylic acid.

Three Fmoc-protected amines, Fmoc-homoallylamine,¹⁷⁻¹⁹ Fmoc-allylglycine and Fmoc-4-allyloxyproline,^{17,20,21} were also installed into the poly(DVB-55) precursor polymer by CM (see Table 2 for structures of functionalized polymers). These amine residues, when polymer-bound, can potentially be used and elaborated chemically in a variety of interesting and useful ways, including for the immobilization of metals, amino acids, peptides and proteins, or as heterogeneous organocatalysts. For example, Fmoc deprotection of immobilized Fmoc-homoallylamine yields a porous resin that can potentially function as a weak anion-exchange resin. The CM reactions were tracked by elemental microanalysis, with the nitrogen content of the products being used to establish the functional group loading levels (whilst making allowance for a low level of nitrogen introduced by the polymerization initiator, AIBN). Table 1 shows that respectable loading levels were achieved for all three CM reactions, with loading levels ranging from 0.21-0.39 mmol g⁻¹. The observed variability in the functional group loading levels may be due to the presence of nitrogen centers during the CM reaction, which can coordinate to the ruthenium intermediates in the

CM catalytic cycle.²² Therefore, the allyl groups closer to the nitrogen would react less easily during the CM giving a lower loading level, as is the case for the Fmoc homoallylamine polymer.

Table 1. Elemental microanalysis results and functional group loading of poly(DVB-55) functionalized with Fmoc-homoallylamine, Fmoc-allylglycine and Fmoc-4-allyloxyproline






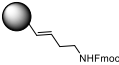
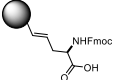
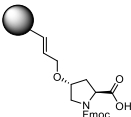
entry	coupling partner	C (%)	H (%)	N (%)	N loading (mmol g ⁻¹)
1	Fmoc-homoallylamine	90.1	7.9	0.6	0.21
2	Fmoc-allylglycine	89.8	8.0	0.7	0.24
3	Fmoc-4-allyloxyproline	87.9	7.8	0.9	0.39

Resins tests are used in solid-phase synthesis methodologies to establish the presence (or absence) of functional groups such as amines, and were used here to verify the immobilization of the Fmoc-protected amines in the first place, and then to establish the presence of polymer-bound amines following Fmoc deprotection. In this regard, the bromophenol blue test was used as a qualitative test for amines (polymer beads turn blue when free amines are present). The polymers decorated with the Fmoc-protected amines gave negative test results when treated with bromophenol blue (no color change). However, following treatment of the polymers with piperidine in CH₂Cl₂ all three polymers turned blue upon treating with bromophenol blue, indicating successful deprotection of the polymer-bound Fmoc-protected amines.²³

With a view to the eventual exploitation of polymers functionalized *via* CM methods, care was taken to establish not only the functional group loading levels but also the porous morphology of the functionalized products. Accordingly, all polymers were subjected to nitrogen sorption analysis to establish their specific surface areas, mean pore diameters and specific pore volumes; this data is summarized in Table 2. The data shows that all of the polymers have well-developed pore structures in the dry state, and have mean pore diameters in a range which indicates that they contain a significant proportion of micropores (pores < 2 nm). This information makes them attractive for use in a range of applications, from analytical chemistry through to organic synthesis.

In conclusion, porous poly(DVB-55) microspheres with a narrow particle size distribution were obtained in good yield by the precipitation polymerization of DVB-55 under dilute conditions. The pendent vinyl groups in the poly(DVB-55) product, derived from the incomplete consumption of the vinyl groups in DVB-55 during polymerization, were subjected to olefin cross metathesis and a range of interesting and useful functional groups were installed into the polymer, under mild reaction conditions, whilst maintaining the unsaturation for potential further functionalization.

Table 2. Elemental microanalysis results and functional group loading of poly(DVB-55) functionalized with Fmoc-homoallylamine, Fmoc-allylglycine and Fmoc-4-allyloxyproline

entry	polymer	BET specific surface area (m ² /g)	C value	Langmuir specific surface area (m ² /g)	mean pore diameter (Å)	Specific pore volume (cm ³ /g)
1		245	260	335	20.9	0.13
2		340	178	465	23.8	0.20
3		40	-52	50	18.2	0.02
4		105	-211	145	21.6	0.06
5		265	288	365	20.8	0.14
6		295	197	405	24.0	0.18
7		245	676	340	21.5	0.14
8		90	-163	120	19.8	0.04

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, characterization data, solid state NMR spectra and FT-IR spectroscopy analysis (PDF).

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Notes

The authors declare no competing financial interests.

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