Tetrahedron Letters 51 (2010) 5827–5829

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Removal of an olefin metathesis catalyst using 4-nitrophenyl acrylate based polymer supports

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ARTICLE INFO

Article history:
Received 20 June 2010
Revised 11 August 2010
Accepted 31 August 2010
Available online 7 September 2010

ABSTRACT

A polymer-supported 1,4-butanediolvinyl ether derivative was used for removal of an olefin metathesis catalyst $(PCy_3)_2(Cl)_2Ru$(3-phenyl-indenylid-1-ene) (**M1**, PCy_3 = tricyclohexylphosphine) from the reaction solution. Poly(styrene-*co*-4-nitrophenyl acrylate), cross-linked with either ethylene glycol dimethacrylate or divinylbenzene was prepared via suspension polymerisation and modified chemically to yield a supported acid chloride and subsequently a 1,4-butanediolvinyl ether derivative. A batch reaction of supported vinyl ether with **M1** resulted in binding of the catalyst onto the polymer. A high accessibility of up to 43% of reactive sites in the polymer matrix could be achieved.

Olefin metathesis is a carbon–carbon bond-forming reaction widely used in organic and polymer chemistry and has also become a versatile tool in materials science.[1] In particular, ruthenium-based complexes have been employed extensively for the synthesis of organic compounds, natural products and polymers. The most prominent representatives of Ru-based metathesis catalysts are the 'Grubbs type' including $[(PCy_3)_2Cl_2Ru$(benzylidene)] (**G1**; PCy_3 = tricyclohexylphosphine),[2] $[(H_2IMes)(PCy_3)Cl_2Ru$(benzylidene)] (**G2**; H_2IMes = *N*,*N*-bis(mesityl) 4,5-dihydroimidazol-2-yl)[3] and $[(H_2IMes)(py)_2Cl_2Ru$(benzylidene)] (**G3**; py = pyridine or 3-bromopyridine).[4] These complexes are considerably active and exhibit outstanding functional group tolerance.[5] Similar commercially available complexes featuring the indenylidene instead of the benzylidene ligand are termed NEOLYST **M1** and **M2**.[6] Several reports on applications of **M1** and **M2** in organic synthesis are available.[7] Moreover, Burtscher et al.[8] recently demonstrated the preparation of a new complex $[(H_2IMes)(py)Cl_2Ru$(3-phenyl-indenylid-1-ene)] (**M3**; py = pyridine) which enables ring-opening metathesis polymerisation (ROMP) of norbornene and 7-oxanorbornene derivatives and is thus a promising alternative to **G3**.

One important issue associated with the use of olefin metathesis catalysts is removal of the ruthenium complexes from the reaction products. Residual ruthenium might cause problems such as olefin isomerisation, decomposition and increased toxicity of the products. In general, two main strategies for catalyst removal have been used so far. The first requires the use of an initiator grafted to a solid support.[9] Thus, the initiator can be easily removed by filtration. A second concept involves heterogenisation of the homogeneous catalysts or precursors through formation of 'self-supporting' metal organic polymeric (or oligomeric) networks.[10]

Numerous examples of utilising insoluble polymers for the removal of various species following the reaction are known.[11] This principle simplifies greatly the synthetic methods and facilitates the purification of the product. The preparation of suitable polymer materials as scavengers includes the design of chemical and morphological features of the polymer. This is very important since the scavenging reaction takes place at the interface of the solid and liquid phase. 4-Vinylbenzyl chloride is still the most frequently used monomer for the preparation of supports, although it can be disadvantageous in terms of solvent compatibility. Aryl acrylates, such as 4-nitrophenyl acrylate and 2,4,6-trichlorophenyl acrylate can be used as reactive monomers for functionisable polymer supports.[12] The relatively low pK_a values of 4-nitrophenol and 2,4,6-trichlorophenol make such polymers susceptible to nucleophilic attack. Various derivatives were made from cross-linked 4-nitrophenyl acrylate based polymers, such as amides, hydrazides, amino acids or esters.[13] Due to the possibility of derivatisation of cross-linked 4-nitrophenyl acrylate to the immobilised acid chloride[13b,14] and therefore modifications with alcohols, this was our polymer of choice for the preparation of a scavenging material for removal of ruthenium-based olefin metathesis catalysts.

In this report, we describe the preparation of a 1,4-butanediolvinyl ether (BDVE) derivative of cross-linked poly(styrene-*co*-4-nitrophenyl acrylate) and its efficient use for the removal of metathesis catalyst **M1**.

Since acid chlorides are very reactive towards nucleophiles, polymers bearing acid chloride moieties can represent an excellent

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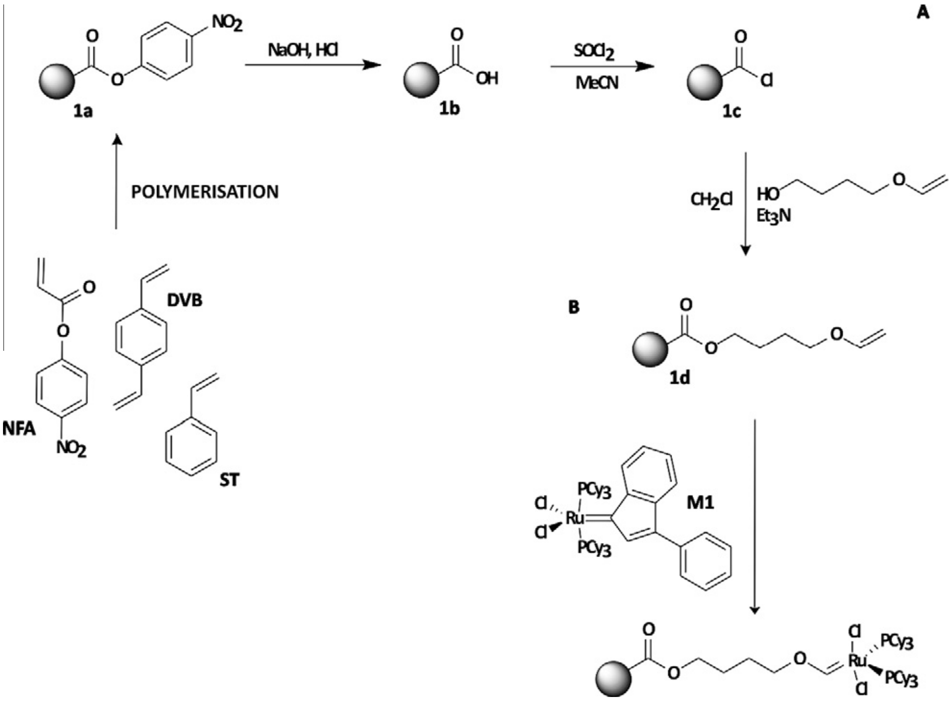
doi:10.1016/j.tetlet.2010.08.114

starting point for tailor-made polymers for polymer-assisted solution phase chemistry and solid phase extraction techniques. The standard termination reagent of olefin metathesis reactions with ruthenium carbenes is ethylvinyl ether. The vinyl group undergoes a metathesis reaction with the propagating carbene species resulting in transfer of a CH$_2$-group to the substrate and the corresponding Fischer-type carbene complex.[15] Therefore, immobilisation of 1,4-butanediolvinyl ether onto a polymer matrix could yield a material for catalyst removal from a solution via covalent bonding to the polymer and simple filtration. Recently, Liu et al. reported di(ethylene glycol) vinyl ether for the removal of olefin metathesis catalysts, however, when the scavenger was supported on a polymer, it was not active.[16] In our case, a suspension was used as the medium for the preparation of the insoluble polymer for scavenger immobilisation. Poly(styrene-*co*-4-nitrophenyl acrylate) cross-linked with either divinylbenzene or ethylene glycol dimethacrylate (EGDMA) were prepared. The two different cross-linkers were chosen due to their different polarities and therefore, possible influence on the solvent compatibility. The accessibility of reactive sites on the polymer matrix is known to be influenced by the type of cross-linker.[17] This is due to different solvent compatibility and also due to different packing of polymer chains. Using a previously established suspension technique, polymer beads of diameters between 50 and 200 microns (Scheme 1) were obtained. Infrared spectroscopy and elemental analysis were used to characterise the materials. From the IR spectrum copolymerisation of the acrylate was evident from the presence of a carbonyl absorption band at 1760 cm^{-1} and an NO$_2$ band at 1340 cm^{-1}. CHN analysis revealed incorporation of 3.7 mmol/g of 4-nitrophenyl acrylate in the case of the DVB cross-linked sample **1a** and 2.7 mmol/g in the case of the EGDMA cross-linked sample **2a**. In both cases, hydrolysis and modification to the immobilised acid chloride proceeded almost quantitatively yielding the acid chloride-bearing materials **1c** and **2c** (Fig. 1, Scheme 1 and Table 1).

The reactivity of the immobilised acid chloride, prepared from poly(styrene-*co*-4-nitrophenyl acrylate), towards oxygen nucleophiles (alcohols), nitrogen nucleophiles (amines), sulfur nucleophiles (thiophenol) and even carbon nucleophiles (malononitrile) has already been demonstrated.[14] Accordingly, 1,4-butanediolvinyl ether was used as a functionalisation reagent. Characterisation revealed a conversion of about 90%; 10% of the acid chloride functions remained unreacted (suggesting that a small proportion of reactive groups were unavailable for the reaction). The remaining acid chloride groups were removed by hydrolysis and methanolysis, releasing the chlorine free materials **1d** and **2d**. Samples **1d** and **2d** contained 2.8 and 2.0 mmol/g of vinyl ether functions, respectively. The FT-IR spectra clearly demonstrated the presence of the electron-rich olefin (1636, 1616 cm^{-1} (C═C), 1320, 964 cm^{-1} (═CH), 1196 cm^{-1} (C–O) and 812 cm^{-1} (═CH$_2$), see Fig. 1).

Due to the high volatility and low polarity of the formed Fisher carbenes, unsupported ethyl vinyl ether is not suitable for use as a scavenger. Liu et al.[16] overcame this drawback by utilising di(ethylene glycol) vinyl ether as the quenching reagent. However, a resin-based vinyl ether scavenger was not effective. Our main goal was therefore to prepare an immobilised ethyl vinyl ether-based scavenger. By analysing the ruthenium content in the quenched polymer via ICP it was found that 43% of the available vinyl sites reacted with **M1** when divinylbenzene was used as the cross-linking agent. A lower amount of catalyst was removed from the solution in the case of the ethylene glycol dimethacrylate cross-linked support; 24% of appropriate sites reacted. It can be assumed that this is due to a better compatibility of the reaction medium with the polymer matrix and a higher flexibility of the polymer backbone in the case of beads cross-linked with DVB compared to beads cross-linked with EGDMA, and suggests a high influence of polymer chain solvation on the performance of the scavenger. Another reason for the difference in performance of scavenging material may also be in the amount of cross-linking, being higher in the case of EGDMA cross-linked polymer. The cross-linking amount is known to influence the site accessibility of polymeric scavengers.

In summary, it was shown that a polymer-supported 1,4-butanediolvinyl ether derivate can be used for the effective removal of ruthenium-based olefin metathesis catalysts from the reaction mixture. The dependence of the polymer-supported scavenger on the type of precursor polymer cross-linker suggests that further improvements could be made by optimising the



Scheme 1. Polymer-supported vinyl benzyl ether preparation (A) and removal of a catalyst from solution (B).

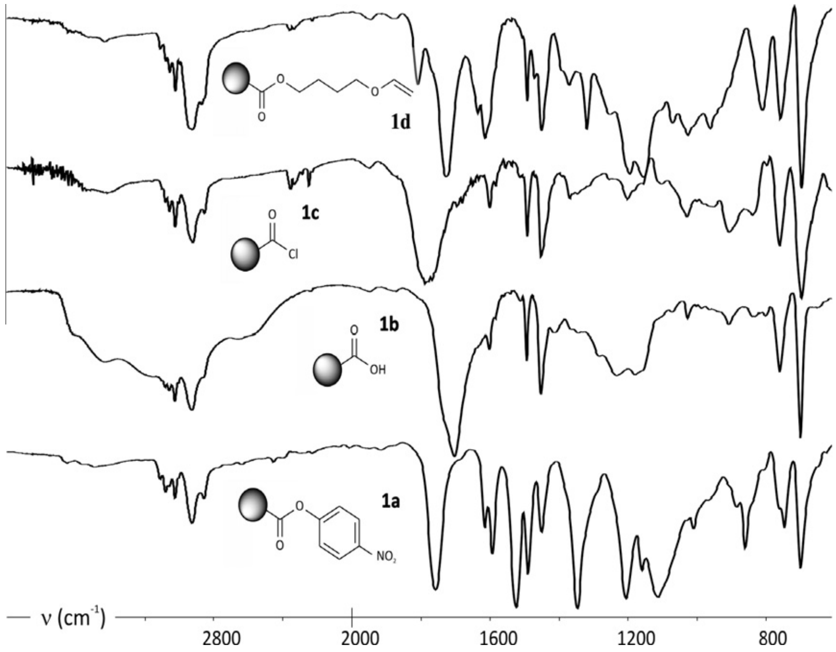


Figure 1. FT-IR spectra of polymer supports cross-linked with DVB (1a—poly(styrene-*co*-4-nitrophenyl acrylate), **1b**—poly(styrene-*co*-acrylic acid), **1c**—poly(styrene-*co*-acryloyl chloride, **1d**—poly(styrene-*co*-BDVE).

Table 1
Composition of polymer resins

Polymer	Monomer				Elemental analysis		
	NFA	ST	DVB	EGDMA	C	H	N
1a	48	47	5	—	69.99[a] 70.25[b]	5.20[a] 5.42[b]	4.45[a] 5.20[b]
2a	40	40	—	20	66.68[a] 66.67[b]	5.56[a] 5.74[b]	3.53[a] 3.75[b]

[a] Calculated.
[b] Found.

morphology of the material. Our investigations are ongoing with the aim of preparing monolithic porous columns for use under flow conditions.

Acknowledgements

Financial support from Österreichischer Austauschdienst and the Slovenian Research Agency is gratefully acknowledged (ÖAD, Project SI 27/2007 and 21/2009). We thank Professor B. Stanovnik from Ljubljana University for elemental analyses.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.08.114.

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