

# Olefin metathesis on nanostructures

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## Abstract

Alkene metathesis processes on nanostructures can proceed via radial or lateral pathways. Radial metathesis installs new functionalities on the surface of a nanostructure through outward growth from its core. Lateral metathesis involves successive crosslinking of neighboring alkenes on the nanostructure and creates a polymer shell around the particle.

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## 1. Introduction

Nanomaterials exhibit tremendous potential for diverse applications in biological diagnostics, medical therapy, information storage, energy conversion, catalysis, and sensing [1,2]. This potential is driven in part by the unique chemical and physical properties of many materials at the nanoscale. Advances in the preparation and characterization of organic, inorganic, and hybrid nanomaterials with good control over shape and size are also fueling the rapid growth in nanoscience. The olefin metathesis reaction is finding increasing application in the design, stabilization, and functionalization of nanomaterials. The alkene functional group is tolerant of many experimental conditions encountered during nanoparticle synthesis and purification, and the mild reaction conditions for olefin metathesis enables its application to a wide variety of nanostructures.

Alkene metatheses on nanostructures can be classified into two general categories – radial metathesis and lateral metathesis. As shown in Fig. 1, radial metathesis installs new functionalities at the surface of a nanostructure through outward growth from its core. A ring opening metathesis polymerization (ROMP) is frequently used for

radial functionalization, which is essentially a surface initiated grafting process. Both radial ROMP and radial cross metathesis utilize exogenous alkenes, and provide a method of altering nanostructure stability and functionality.

Lateral metathesis involves successive crosslinking of neighboring alkenes to one another, creating a polymer shell around the particle. The shell can provide stability to the overall structure without major alterations to particle shape or size. Typically, only alkenes already present on the nanostructure are involved in lateral metathesis, although exogenous alkenes are sometimes added to facilitate the process. Particle aggregation can be a problem if the solubility of the crosslinked material is poor or if inter-particle metatheses have occurred. Removal of the original nanostructure after lateral metathesis affords an empty cross-linked polymer shell, or nanocapsule.

This review describes the application of olefin metathesis to existing nanostructures. The focus is primarily on olefin metathesis as a synthetic tool at the nanoscale. Nanostructures that are subsequently formed from polymers synthesized using metathesis, and applications of nanoparticles for olefin metathesis are not discussed [3–10].

## 2. Radial metathesis

Olefin metathesis has frequently been used to functionalize surfaces at the micro- or macroscale through surface

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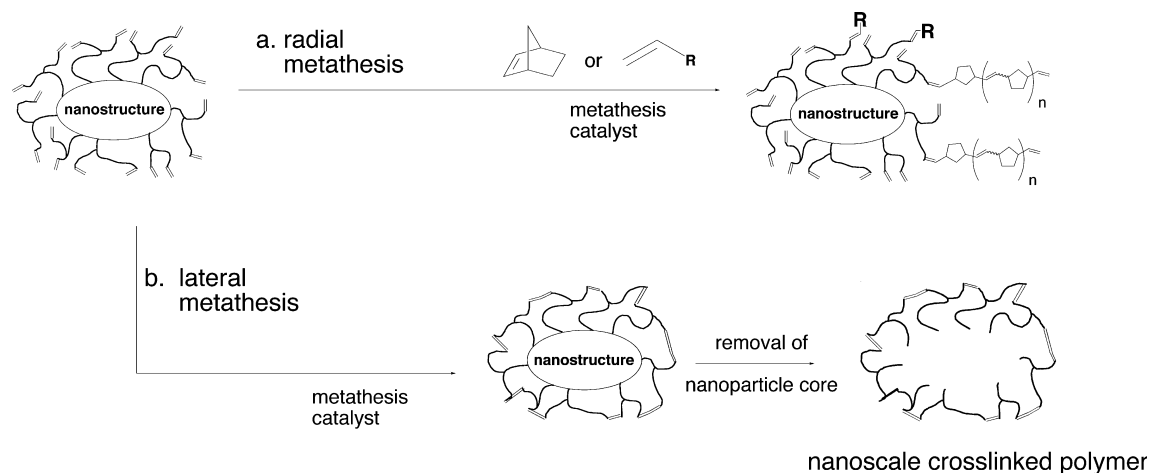


Fig. 1. Radial and lateral olefin metathesis on nanostructures.

initiated polymerizations as well as cross metatheses [11–15], and a similar strategy is also effective on the nanoscale. Structures of several metathesis initiators and monomers used in nanoscale polymerizations are shown in Fig. 2. The majority of radial metathesis involves polymerizations, and only one example of a radial cross metathesis has been reported (vide infra).

### 2.1. Radial polymerization

Gold plays a central role in nanoscience. Gold nanoparticles and surfaces can be readily prepared and functionalized with thiol-containing molecules [16,17]. Their stability and ease of modification provides a robust platform for evaluating nanoscale synthetic methods. Mirkin and Ngu-

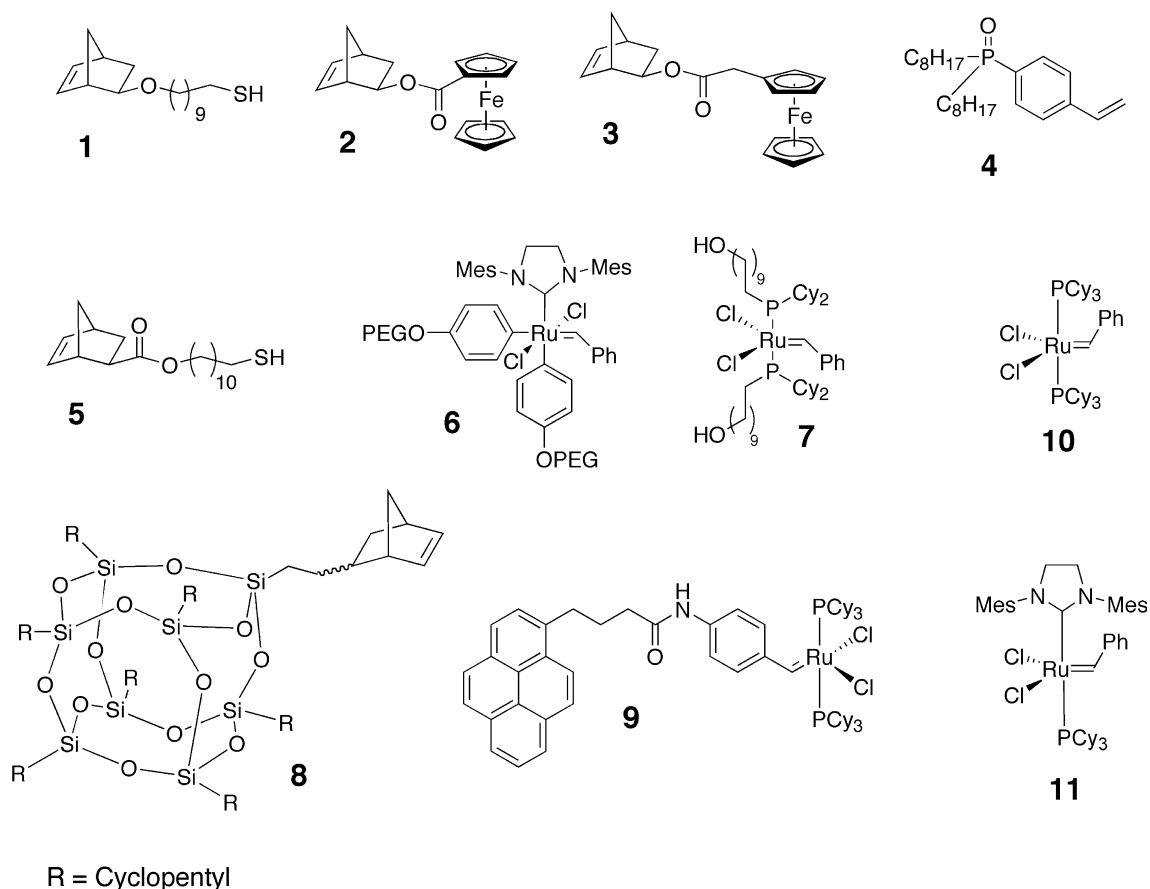


Fig. 2. Compounds that participate in radial metathesis.

yen showed that gold nanoparticles coated with an norbornene functionalized alkane thiol **1** could be used to initiate polymer growth outward from the particle surface [18]. The norbornene particles were treated with catalyst **10** to immobilize an active ruthenium alkylidene on the particle, followed by addition of a ferrocene linked norbornene **2** and subsequent termination with ethyl vinyl ether. Block copolymers were prepared by the sequential addition of two different norbornenes, **2** and **3**. Purification of the polymer nanoparticle hybrids was facilitated by the differential solubility of the monolayer coated nanoparticle and the polymer functionalized particle. The progress of the reaction could be monitored by following changes in the alkene resonances by  $^1\text{H}$  NMR. Formation of the block copolymer was confirmed both by NMR and cyclic voltammetry.

A similar strategy was reported by Coughlin and Emrick, using cadmium selenide nanoparticles (quantum dots) coated with a styrene modified trialkyl phosphine oxide **4** to initiate radial polymerization [19,20]. Treatment of the styrene coated particles with catalyst **10** or **11** followed by cyclooctene generates a polymer coated quantum dot composite. Loading of the catalyst on the nanoparticle surface was monitored by NMR, which clearly resolved the alkylidene protons of the free catalyst and the various particle bound species. Dicyclopentadiene and oxanorbornene derivatives were also successfully polymerized. The absorption and emission spectra of the quantum dots were not affected when the particles were embedded in the polymer

matrix. However, care must be taken to completely remove the ruthenium from the composite, as residual metal can quench particle-derived fluorescence. The particles remain well dispersed within the polymer, and aggregation was not observed.

CdSe quantum dots which have been passivated with the norbornene terminated alkanethiol **5** aggregate at the organic–aqueous interface in water-in-toluene emulsions, forming vesicles with 10–100  $\mu\text{m}$  diameters which can be visualized by fluorescence microscopy [21]. Addition of the polyethylene glycol modified catalyst **6** to the vesicles results in intra and interparticle crosslinking of the nanoparticles, creating a polymer/nanoparticle shell around the water droplet. TEM analysis of the cross-linked capsules indicates that they remain intact after dehydration with methanol.

Stober silica nanoparticles have been functionalized with polymers using two different strategies. Seery has reported an approach involving particles terminated with a norbornene on the surface. In a manner similar to that used with metal and semiconductor nanoparticles, exposure of the silica particles to a solution of **10** followed by norbornene resulted in the formation of silica polymer composites [22,23]. The resulting polymers were cleaved off the particles by HF treatment. Subsequent analysis by gel permeation chromatography (GPC) was used to determine molecular weight, polydispersities, and the number of polymer chains per particle. Increases in the number of

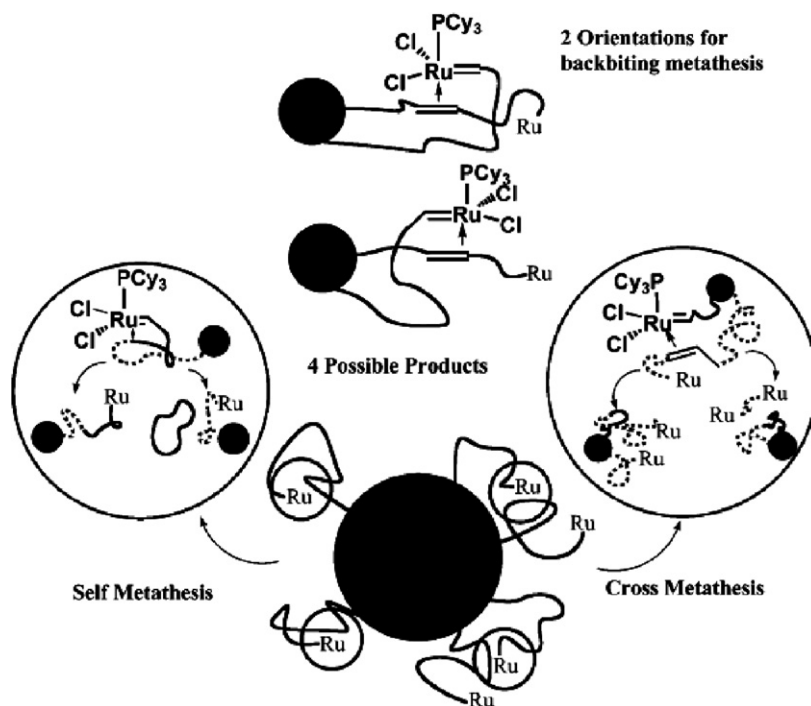


Fig. 3. Schematic of the backbiting and cross metathesis reaction pathways. Backbiting (left) either regenerates the growing chain or produces an inert cyclic fragment and a shorter growing chain. Cross metathesis (right) either “swaps” the terminal chain ends or produces a chain with two growing ends, leaving a loop on the surface. Dashed and solid lines are intended to distinguish chain segments, and organometallic fragments in products are abbreviated with “Ru”, indicating the metal center. Two of the four possibilities produce fragments that will tend to increase polydispersity. Reprinted with permission from [22]. Copyright 2005 American Chemical Society.

grafted chains could be obtained, but often at the cost of greater polydispersity. Only 2% of the immobilized norbornenes serve as initiation sites for polymerization, a result attributed to partial lateral polymerization on the surface that occurs before addition of the norbornene monomer. The surface initiated polymerization can potentially give rise to cyclic polymers or particle bound loops through undesirable back-biting (Fig. 3). A careful study of the reaction conditions revealed that these side reactions could be minimized by using short polymerization times and high monomer concentrations.

An alternative strategy for radial metathesis, reported by Mingotaud and coworkers, involves immobilization of the ruthenium catalyst on silica using a variant of **10** in which the phosphine is tethered to a terminal alcohol **7** [24]. The tether covalently linked the ruthenium carbene complex to the surface of a carboxylic acid-terminated Stober particle. At high concentrations of norbornene, the polymerization rapidly generated a gel-like material, while lower concentrations resulted in particle solutions of varying viscosities. TEM analysis of these composites revealed the expected core-shell architecture. Quenching of the immobilized ruthenium carbene with ethyl vinyl ether released the polymers from the particles for subsequent analysis by size exclusion chromatography (SEC). The norbornene functionalized polyhedral cubic silsesquioxane (POSS, **8**) has been used to initiate cyclooctene polymerization [25]. The POSS moieties can crystallize in two dimensions to form lamellar sheets of POSS sandwiched between polynorbornene cushions. The sheets of POSS can in turn undergo further self assembly into micron length fibers.

Two examples of nanotube functionalization using ROMP have been published. Based upon a report by Dai and coworkers that polyaromatic hydrocarbons can be used to non-covalently anchor materials to single walled carbon nanotubes, a ruthenium alkylidene complex **9** tethered to a pyrene moiety was prepared [26]. The pyrene alkylidene was adsorbed onto a nanotube and used to initiate ROMP off the tube surface. When the coated tubes were exposed to a solution of norbornene, they were uniformly coated with poly-norbornenes with thicknesses as high as 20 nm, as determined by AFM and TEM. Prolonged reaction times led to desorption of the polymer from the nanotube. In a complementary approach, Liu and Adronov have reported covalent modification of carbon nanotubes using ROMP [27]. Single walled carbon nanotubes with carboxylic acid functionalized ends were covalently modified with norbornene monomers. These monomers were used for the surface initiated polymerization of a norbornene solution using **10**. The polymerization enhanced the solubility of the tubes in THF. Examination of the tubes by AFM revealed coatings ranging in thickness from 8 to 15 nm, with thicker coatings found closer to the initiation sites on the tips of the nanotubes.

Nanoscale patterning of gold and silicon substrates with polymers has been carried out using the dip-pen nanolithography (DPN) developed by Mirkin [28]. An AFM tip

which has been immersed in a solution of norbornene thiol **1** is brought into contact with a gold coated substrate. Capillary action drives liquid from the tip to the surface, whereupon **1** orients itself into a monolayer after formation of a Au–S linkage. The AFM tip can be moved around the surface to ‘write’ a pattern of molecules only in locations where the tip is directed. After the norbornene was patterned onto the substrate, the remaining unfunctionalized gold on the surface was passivated with decanethiol. The entire substrate was then immersed in a solution of **10**, opening the norbornene and consequently immobilizing the ruthenium. Excess unbound catalyst was rinsed off and the substrate was immersed in a solution of *exo*-5-norbornen-2-ol to initiate polymer growth off the surface. Polymer brushes ranging in height from 1–10 nm could be fabricated by adjusting the polymerization times. No further growth was observed after a 4 h period, suggesting that the catalyst may have become deactivated and/or inaccessible. Block copolymers with ferrocene modified norbornene monomers were prepared, and the resulting surfaces were characterized by differential pulse voltammetry, confirming the modification of the surface by the electroactive functionalities.

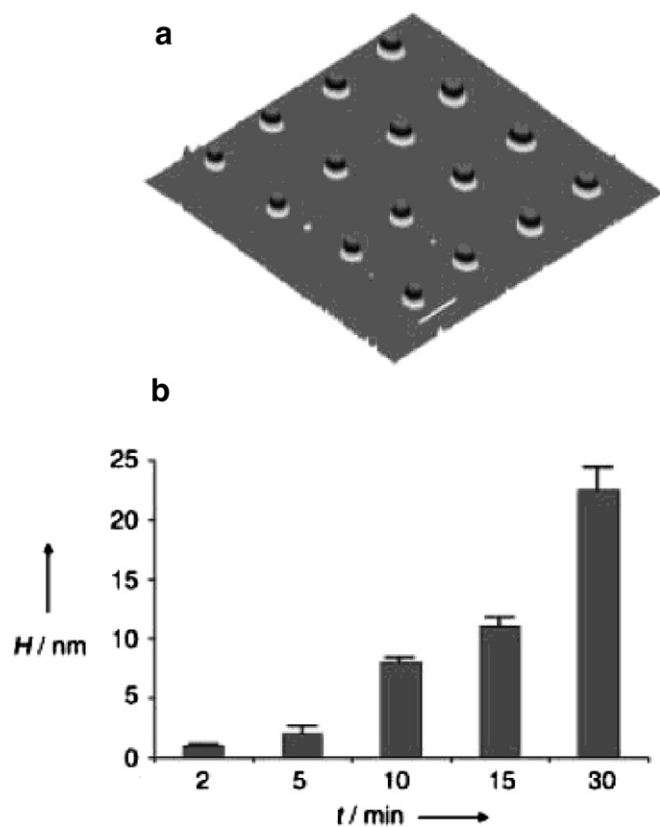


Fig. 4. (a) Three-dimensional topographic AFM image of an array of polymer brush dots generated by DPN (the scale bar is 2 nm); (b) a plot of nanostructure height (poly-*exo*-5-norbornen-2-ol) as a function of tip-induced polymerization reaction time (as measured by tip–substrate contact time). The data points are the averaged measurements, and the vertical bars correspond to the standard deviation. Reprinted with permission from [28]. Copyright 2005 Wiley-VCH.

An alternative approach for nanoscale patterning involves modifying the approach above so that the monomers themselves are delivered to the substrate in a spatially resolved manner using DPN. This was demonstrated by coating a silicon surface with norbornene, followed by uniform activation of the surface with ruthenium. Instead of immersing the entire solution in a solution of monomer, the norbornene was delivered only to specific locations via DPN. This created polymer islands on the surface, and the height of these islands could be varied by adjusting the contact time of the tip to the surface (Fig. 4).

## 2.2. Radial cross metathesis

Sarkar and coworkers have carried out a radial cross metathesis using gold nanoparticles covered with mixed monolayers of octanethiol and an alkene terminated thiol [29]. Treatment of these particles with a variety of allyl ethers/amine and acrylate derivatives in the presence of the catalyst **10** afforded functionalized particles. The presence of the cross metathesis product on the particles was confirmed by IR, NMR or electrochemical measurements, as appropriate. The degree of particle functionalization was not determined.

## 3. Lateral metathesis

Lateral metathesis provides a means both for modifying existing nanostructures as well as creating new nanoscale

organic materials when the original nanostructure is used as a sacrificial template. In its latter manifestation, lateral metathesis is a promising new addition to the toolkit of the nanoscale synthetic chemist. The polymers generated by lateral metathesis are usually novel materials which do not have an analogous solution counterpart, in contrast to the products of a radial metathesis.

### 3.1. Lateral ring closing metathesis

In an early example of lateral metathesis, Wu et al. treated gold nanoparticles functionalized with the triene thiol ligand **12** with catalyst **10** to effect lateral crosslinking [30]. Since each ligand has three pendant terminal alkenes, metathesis can occur between two alkenes within the same tripod or between alkenes on adjacent tripods. Both processes can be formally considered to be macrocyclic ring closing metatheses. The metathesis reaction forms a cross-linked polymer shell around the nanoparticle. The formation of internal alkenes was confirmed by NMR and IR analysis of the particles. Subsequent oxidative removal of the gold core generated an organic polymer, presumed to be a hollow capsule. The gold core was more resistant to oxidation after crosslinking, and harsh conditions had to be employed for core removal. The capsules were characterized by AFM, and the observed dimensions (~10 nm) were consistent with the value predicted based on the size of the gold template and the length of the thiol ligand. These results suggested that the structural integrity of the

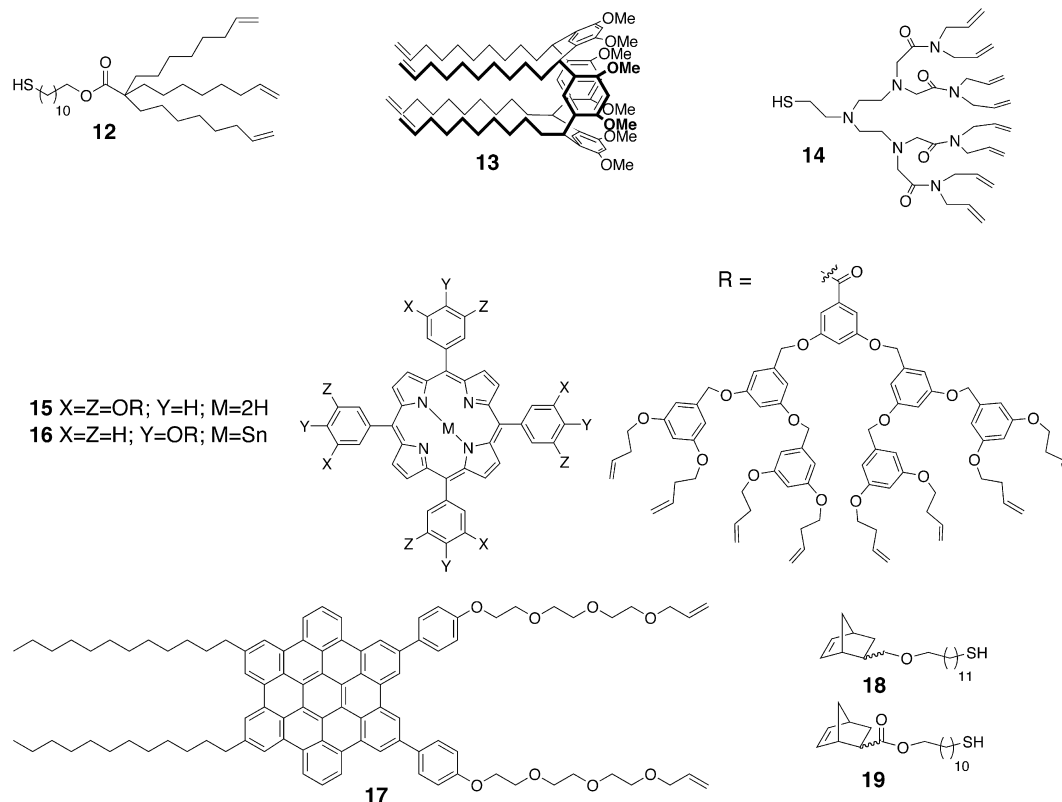


Fig. 5. Compounds used for lateral metathesis.

polymer capsules was maintained after the etching of the gold template. An analogous crosslinking has been carried out by Wei using gold nanoparticles coated with the tetra-alkene functionalized resorcinarene **13**. These particles were encapsulated in crosslinked shells by olefin metathesis using **10** [31]. Although the particles were less soluble after crosslinking, they withstood passage through a GPC column (Fig. 5).

Peng has used an analogous lateral metathesis strategy to modify alkene dendrimer coated Cd/Se and CdSe/CdS core-shell quantum dots [32]. The octa-alkene derivatized thiol ligand **14** was assembled on nanoparticles, and after cross-metathesis using **11**, the encapsulated nanostructures showed improved stability towards chemical, photochemical, and thermal degradation. Removal of the core after cross-linking and analysis by MALDI-TOF MS identified a polymeric material comprised of 15–20 crosslinked dendrons. The organic material obtained from the crosslinking of **12** and **13** followed by subsequent template etching should consist of nanocapsules with hollow cores. The structure and function of these cores have not yet been fully elaborated. Related shells generated using alternative methods retain their capsular structure and function after etching of the core nanostructures [33–35]. The resulting nanocapsules may find applications in small molecule encapsulation and delivery.

Lateral crosslinking of organic nanoparticles that are based on various dendrimer cores has been carried out by Zimmerman and coworkers [36]. A series of dendrimers were constructed by attaching dendrons to di-, tri-, tetra- and octavalent **15** cores. Each dendron contained eight alkene termini. The dendrimers were subjected to ring closing metatheses using **10** at high dilution. The degree of crosslinking, as determined by NMR and MALDI-TOF MS, was dependent on the reaction time. The radius of gyration, calculated from solution viscosity measurements, decreased as the degree of crosslinking increased, indicating that the dendrimers became more rigid with crosslinking. The rigid crosslinked dendrimers retained their shape when they were deposited on mica for AFM imaging, while non-crosslinked dendrimers tended to deform and flatten out on the surface. Related crosslinked dendrimers which have had their cores removed function as selective receptors for various porphyrins [37].

Lateral metathesis on high aspect ratio nanostructures such as nanotubes has been carried out by Aida. The amphiphilic hexabenzocoronene **17** undergoes self assembly to form organic nanotubes with hydrocarbons chains situated on one side and triethylene glycol chains on the other [38]. The termini of the glycol chains, which are capped as allyl ethers, were laterally crosslinked. After crosslinking, the nanotubes exhibited enhanced stability against thermal degradation. A similar approach to organic nanotubes was reported by Zimmerman using the porphyrin-core dendrimer **16** [39]. Treatment of **16** with succinic acid in the presence of silver oxide generated a series of linear diacid-bridged oligomers ranging

from tetramers to dodecamers. The peripheral alkenes were crosslinked using **10** followed by removal of the porphyrin core using sodium methoxide. The resulting tubular aggregates were characterized by MALDI-MS and SEC.

### 3.2. Lateral ring opening metathesis polymerization

An alternative method for lateral metathesis uses ROMP instead of ring closing metathesis. Huskens and Reinhoudt describe the preparation of gold nanoparticles coated with a mixture of **16** and dodecanethiol [40]. These particles were treated with catalyst **10**, and polymerization was followed by NMR, which indicated rapid consumption of the norbornene. TEM images of the polymerized particles revealed substantial aggregation, perhaps arising from inter-particle crosslinking. The solubility of the particles was considerably worse after polymerization. Polymerization of particles coated with a similar norbornene thiol **17** has been reported by Chechik [41]. The polymerization of **17** was carried out using catalyst **11**, and at much lower particle concentrations than used with **16**. These conditions minimized inter-particle cross-linking, but they were still poorly soluble. However, the solubility was improved by including a small amount of free norbornene during the metathesis. This presumably resulted in the inclusion of norbornene during polymerization in the lateral direction, along with a small amount of radial growth. The cross-linked nanoparticles exhibited an enhanced stability towards thermal treatment and oxidative etching of the core.

In summary, a number of diverse applications of olefin metathesis on nanostructures have been described. Radial polymerization generates nanoscale graft polymers and copolymers. Since radial polymerization is a surface initiated polymerization process, it can exhibit polymerization kinetics and molecular weight distributions that differ from the corresponding solution polymerizations. Cleavage of radial polymerization products from the nanostructure affords polymers which can be characterized using standard solution analytical methods. Lateral polymerization is a process that is more unique to nanomaterials and surfaces, and provides access to novel polymer architectures which are not accessible via traditional solution methods. The capsule products of lateral metathesis may have distinctive chemical and physical properties rendering them useful for applications such as drug delivery. Further studies of both the structure as well as the function of these capsules is needed. Olefin metathesis permits the facile modification of existing nanomaterials as well as creating novel structures, and is poised to make continuing contributions to nanoscience.

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