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**NANOPARTICLE MODIFICATIONS WITH SURFACE INITIATED  
POLYMERIZATION VIA ORGANOMETALLIC CATALYSTS**

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# Nanoparticle Modifications with Surface Initiated Polymerization via Organometallic Catalysts

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Well-defined organometallic catalysts are used for synthesizing organic-inorganic hybrid materials utilizing a "from the ground up" approach to modify nanometer scale inorganic cores. The transition metal catalyst is ligated to the nanometer-size fumed silica, the inorganic core, after "seeding" the silica surface with a coupling agent, and, consequently, a polymeric coating is formed through the surface bound catalyst. Due to the nature of the polymerization reaction, the monomer inserts between the surface to be modified and the active site of the organometallic catalyst which in turn directs the polymerization to take place only at the surface and not in the bulk.

Living poly(hexyl isocyanate) semiflexible polymer brushes are covalently attached to the silica surface through synthesis that uses a Ti(IV) catalyst. The living chains are end-capped by acetyl chloride to seal off the chain ends. Bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride (Grubbs's catalyst) is used as a Ring Opening Metathesis Polymerization (ROMP) catalyst to prepare covalently attached surface layers from strained cyclic olefins. The living chain ends are end-capped by reaction with vinyl acetate.

The modified surfaces are characterized using FT-IR, NMR, TGA, GC-MS, SEM. Polymers grown on the surface are cleaved off using tetrabutyl ammonium fluoride as a "soft" mediator without disturbing the polymer structure. Brushes separated in this way are dissolved in THF, and GPC analysis is done to determine the molecular weight distribution and polydispersity.

## **I-1 Introduction to Surface Initiated Polymerization**

### **I-1.1. Abstract**

The nature of polymer monolayers bound to a hard surface is discussed. Formation of a polymer brush with adsorption, "grafting to", and "grafting from" techniques are also discussed. Particular attention is paid to surface initiated polymerization as a method for "growing" polymer brushes directly from the substrate surface and the elements of surface initiated polymerization.

### **I-1.2. What is a polymer brush**

An assembly of polymer chains tethered by their ends in mutual proximity to a substrate is referred to as a polymer brush<sup>1</sup>. At high surface coverage and moderate to strong excluded volume interactions, polymer chains tethered at one end to the surface are strongly stretched. This is the origin of their interesting behavior. The distinctive properties of densely tethered chains were first noted by Alexander<sup>2</sup> regarding tethering to a flat surface. Tethering introduces into physics a new length scale, namely, the distance,  $d$ , between tethering points. In a flat layer, according to Alexander, each tethered polymer chain is confined to a cylindrical region of radius  $d$  and height  $L$ . The size of the cylinder defines the size of the blobs and so each chain appears equivalent to a linear stack of blobs of constant size. In other words, the layer is made up of a stratified, multilayer array of blobs such that each chain contributes a single blob on average to each of the monolayers. Figure I-1.2.1 schematically represents polymer brushes tethered to a flat surface.

Daoud and Cotton (1982)<sup>3</sup> took Alexander's approach to spherical geometries and made the connection between tethered chains and branch polymers. In spherical and cylindrical geometries, the volume accessible to each chain grows with the distance from the grafting site. As can be seen from Figure I-1.2.2, the chains are confined to a conical region, which expands with distance from the center of the structure.

Depending on the tethering density, high density and low-density regimes can be defined<sup>4-7, 11</sup>. The densest regime is called a polymer brush, and, as discussed earlier, the polymer chains stretch away from the tethering point; the chain's dimensions normal to the interface scale directly with the degree of polymerization<sup>5</sup>. In a low-density regime, also called a mushroom regime, molecules behave as isolated chains. Since these polymer chains do not experience crowding effects, the chains can form entanglements with the polymer matrix. As a result, mushroom regime structures can provide better adhesion, while brush regime structures provide high performance anti-adhesion and lubricating layers<sup>5</sup>. Between those two extremes lies a broad region called the mushroom-brush transition region.

Polymer length, grafting density, backbone flexibility, and excluded volume of the polymer chains are major factors effecting the brush properties. In the case of polyelectrolyte and block copolymer brushes, charge spacing and block architecture should also be considered<sup>8-10</sup>.