Surface Initiated Polymerization (SIP) From Nanoparticles:

Core-Shell Nanoparticles and Nanocomposites
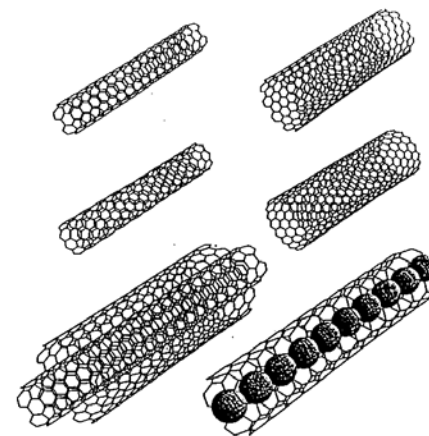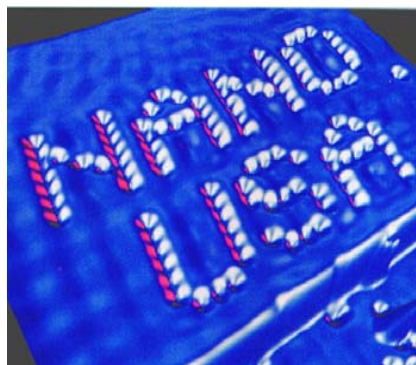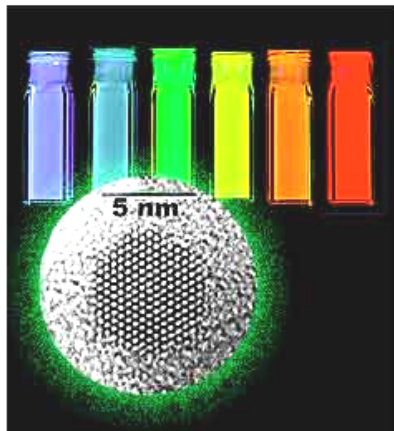
Rigoberto C. Advincula

University of Houston

Department of Chemistry, *www.chem.uh.edu*

rcadvincula@uh.edu

Nanoscience or Nanotechnology ?

Nanostructured Material
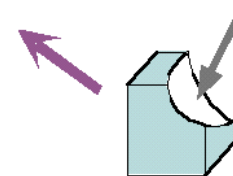

- self-assembly
- quantum effects
- molecular building blocks
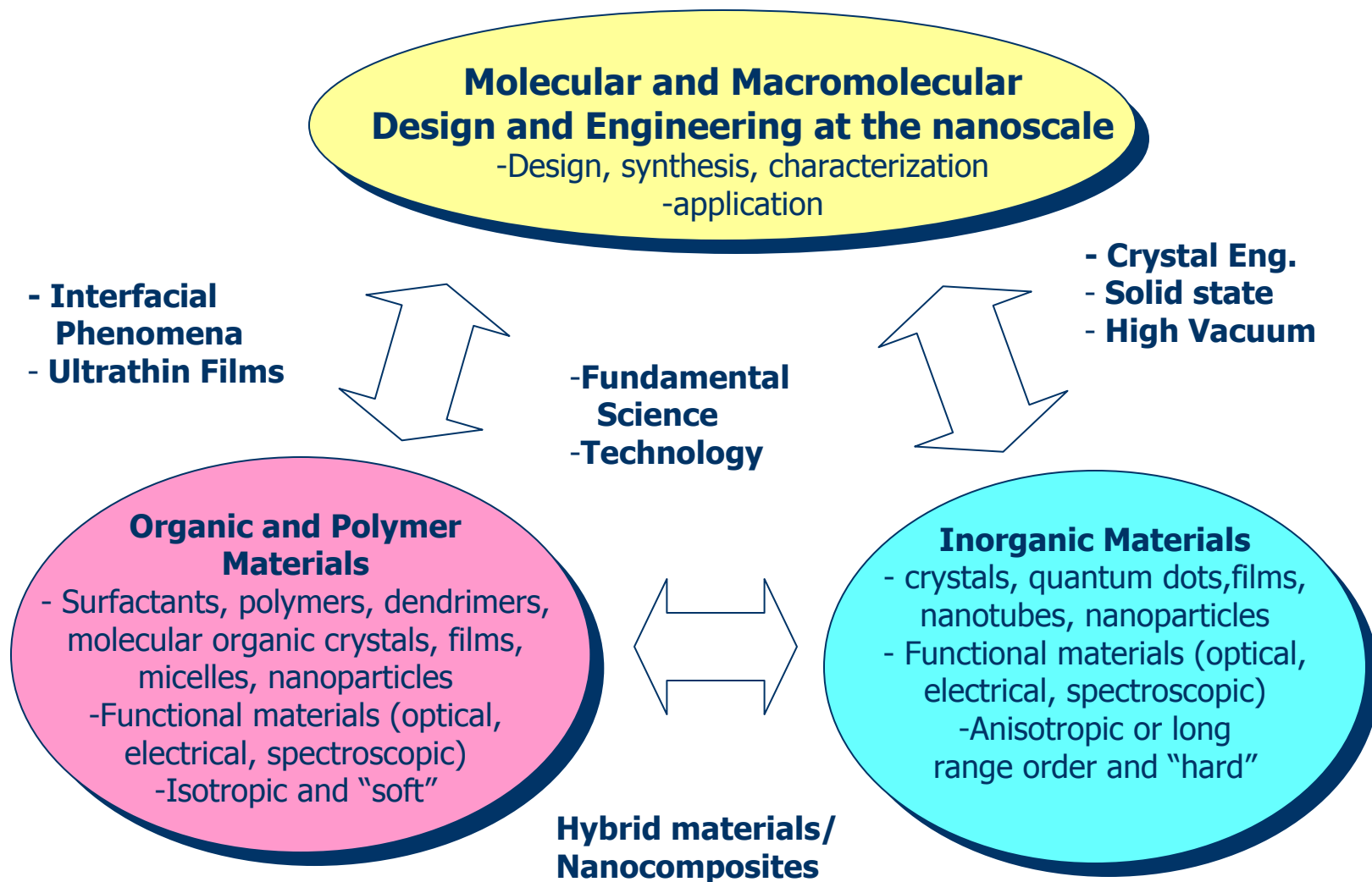- surface science
- Self-assembly or directed assembly
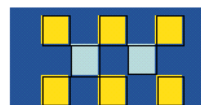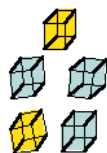
Assemble from
Nano- building Blocks

• powder/aerosol compaction
• chemical synthesis

'Sculpt' from Bulk

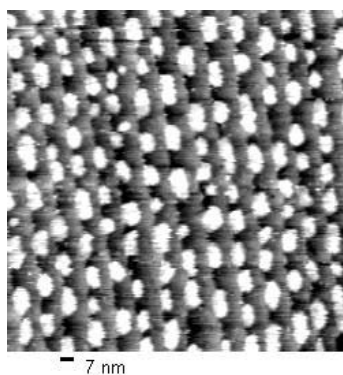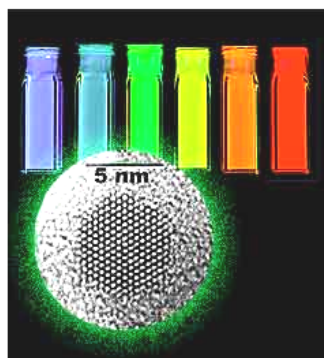• mechanical attrition (ball milling)
• lithography/etching...

Nanostructured Materials

**Molecular and Macromolecular
Design and Engineering at the nanoscale**
-Design, synthesis, characterization
-application

- **Interfacial
  Phenomena**
- **Ultrathin Films**

- **Crystal Eng.**
- **Solid state**
- **High Vacuum**

-**Fundamental
Science**
-**Technology**

**Organic and Polymer
Materials**
- Surfactants, polymers, dendrimers,
molecular organic crystals, films,
micelles, nanoparticles
-Functional materials (optical,
electrical, spectroscopic)
-Isotropic and "soft"

Inorganic Materials
- crystals, quantum dots,films,
nanotubes, nanoparticles
- Functional materials (optical,
electrical, spectroscopic)
-Anisotropic or long
range order and "hard"

**Hybrid materials/
Nanocomposites**

Nanostructured Materials : Inorganic/Metals
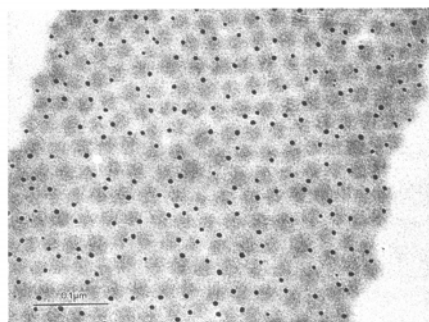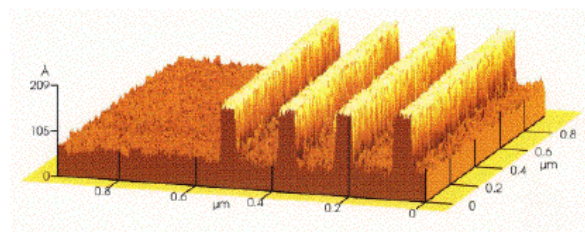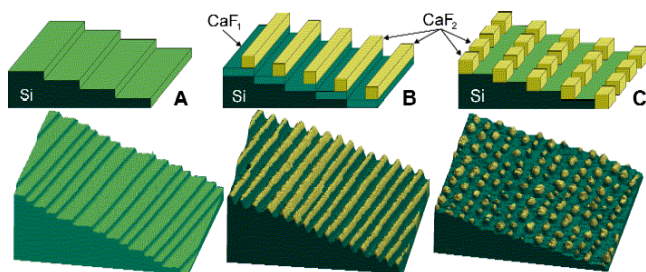
Inorganic

- **Nanoparticles :** quantum dots, nanocrystals, shape anisotropic nanoparticles

- Glasses and Ceramic particles

- **Ultrathin Films:** solid state, high vacuum, STM, doping, vacuum deposited.

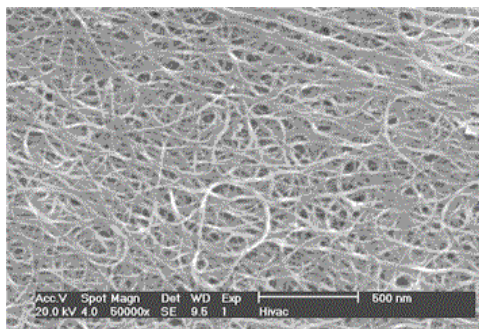- **Superlattice structures:** multilayer films, supramolecular structures, patterning

Nanostructured Materials : Carbon

Carbon

- **Carbon-Based Nanomaterials** nanotubes (SWNT and MWNT), fullerenes, polyacene structures
- Electrical and magnetic effects
- Nanomechanical properties
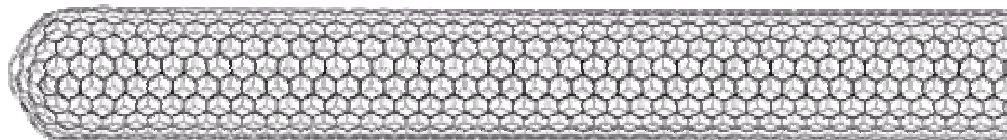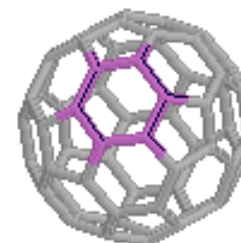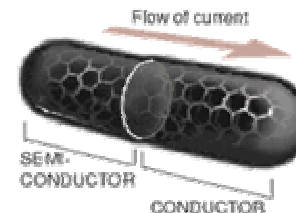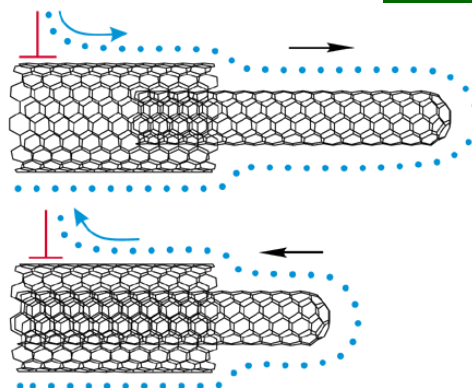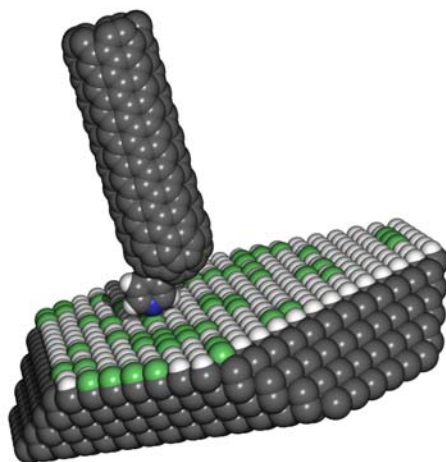
Nanostructured Materials: Organic

Organic

- ***Organic Polymers :*** homopolymers, block-copolymers, polyelectrolytes

- ***Dendrimers and hyperbranched molecules –*** functional macromolecules with controlled shape and dimension

- ***Small Molecules:*** organic crystals, dyes, oligomers, amphiphiles

- ***Supramolecular Assemblies:*** mesophases, supramolecular structures

- ***Ultrathin Films:*** Langmuir-Blodgett films, Self-assembled Monolayers (SAM), Layer-by-layer, epitaxy
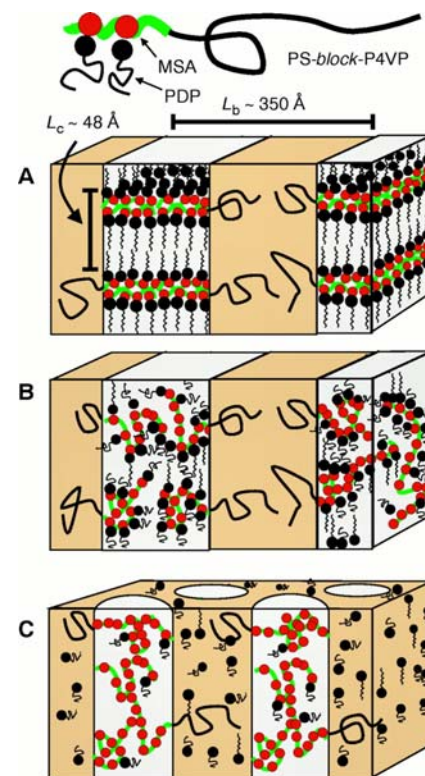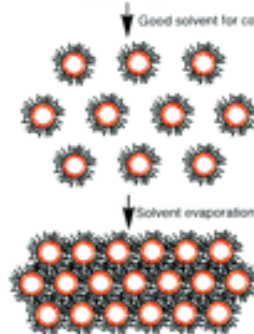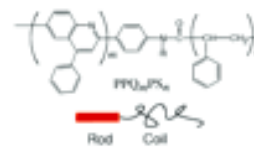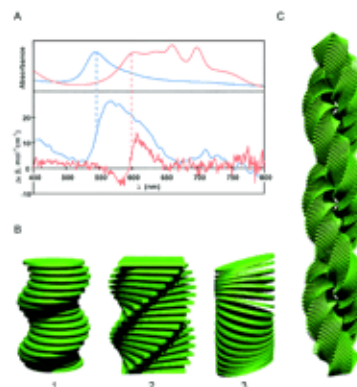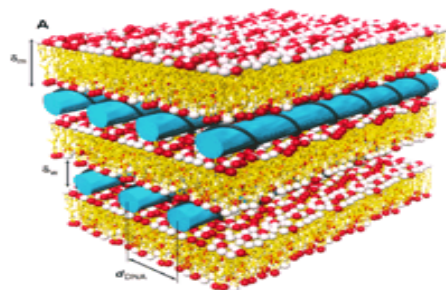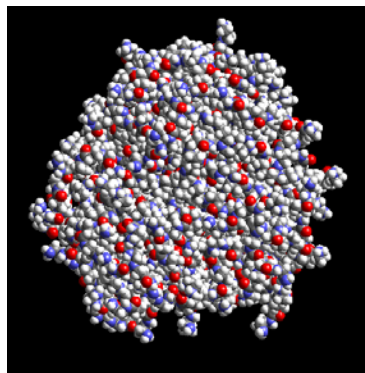
Convergence of Materials in Interfacial and Colloidal Phenomena
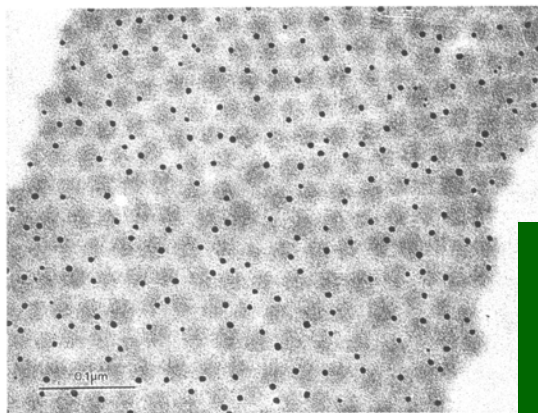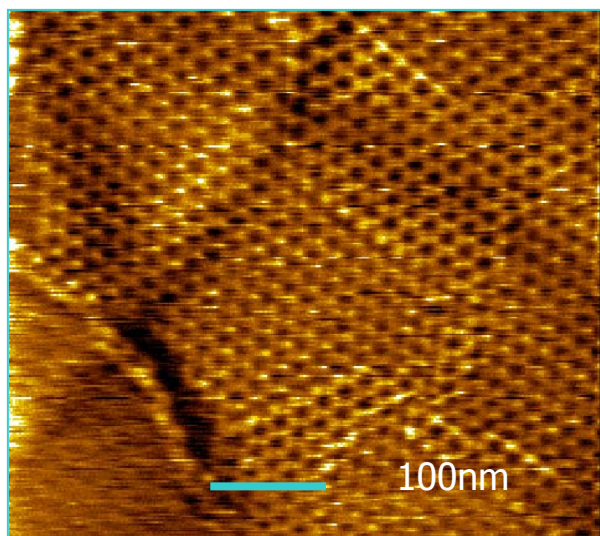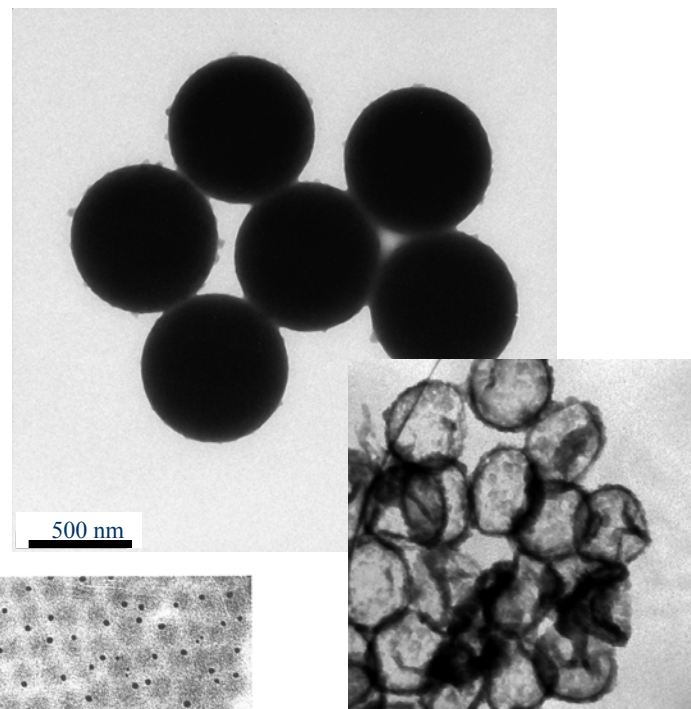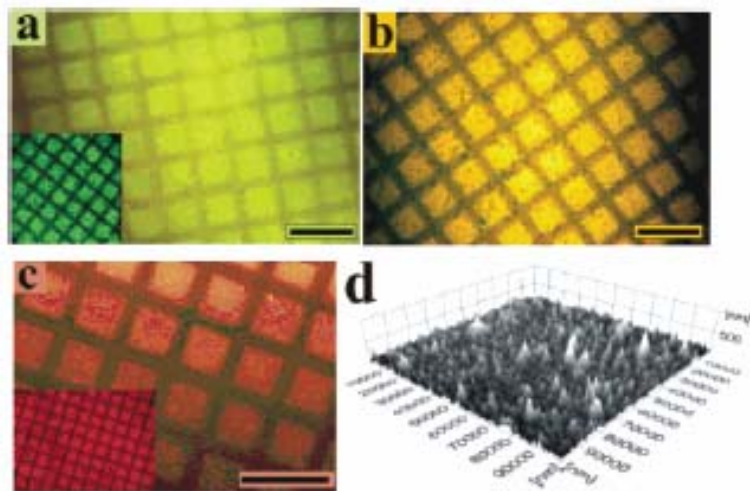
- Quantum dot nanoparticles
- Colloidal particles
- Organic nanoparticles
- Polyelectrolytes, surfactants
- Hybrid organic-inorganic
- nanocomposites

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Synthesis of New Materials: inorganic and organic
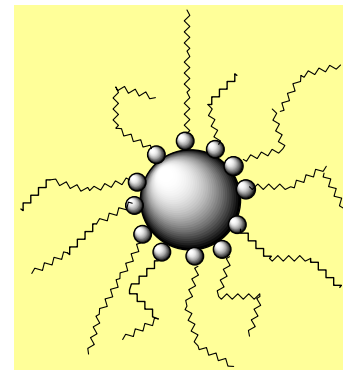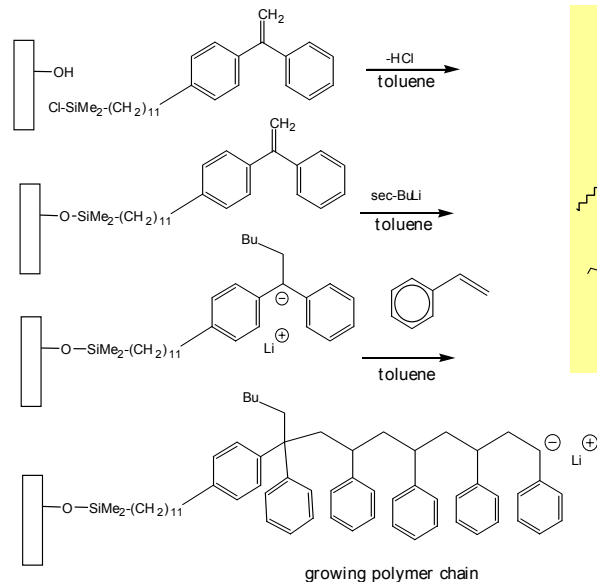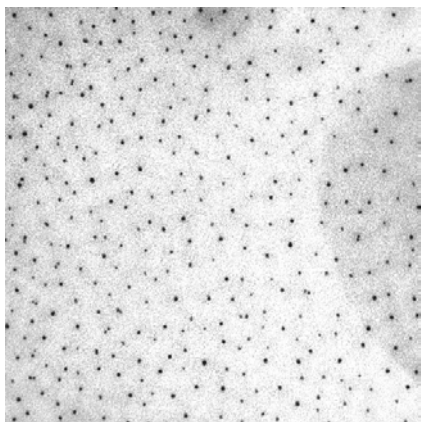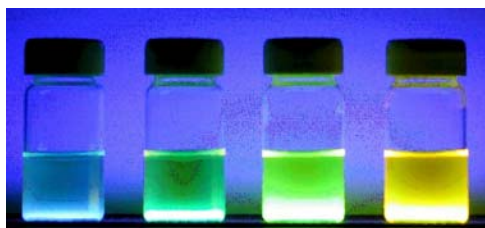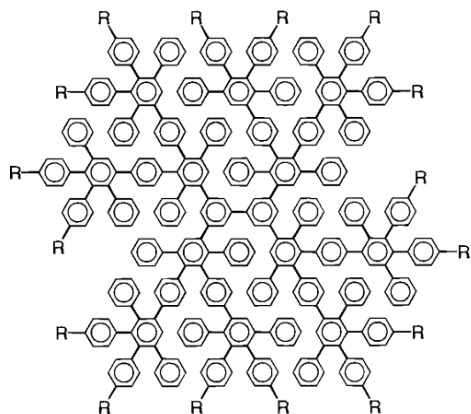
1. Polyionic block
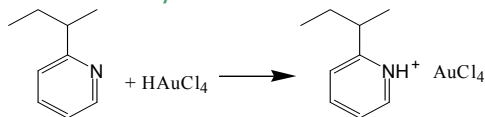
2. Reduction with Hydrazine

$$4HAuCl_4 + 3N_2H_4 \longrightarrow 4Au + 3N_2 + 16\ HCl$$
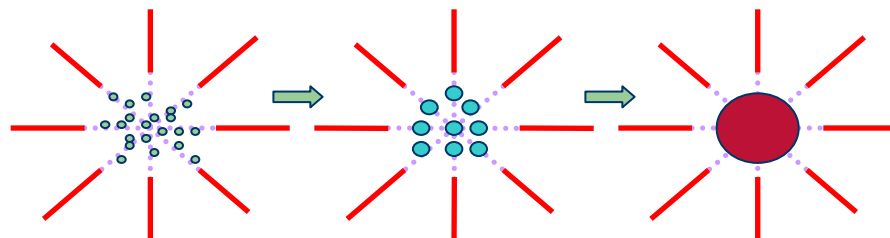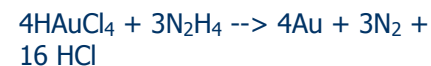
Polyionic star block copolymer

Reduction, Nucleation and Growth

R.C. Advincula/ University of Houston

Contents

- Introduction

- Why Surface Initiated Polymerization of Nanoparticles

- Basic Approach: Grafting to and Grafting from

- Different Polymerization Mechanism

- Different Characterization Methods

- Different methods of surface initiated Polymerization

- A focus on Living Anionic Surface Initiated Polymerization (LASIP)

- Conclusions

Importance of Polymer Coatings

bulk material

polymer layer
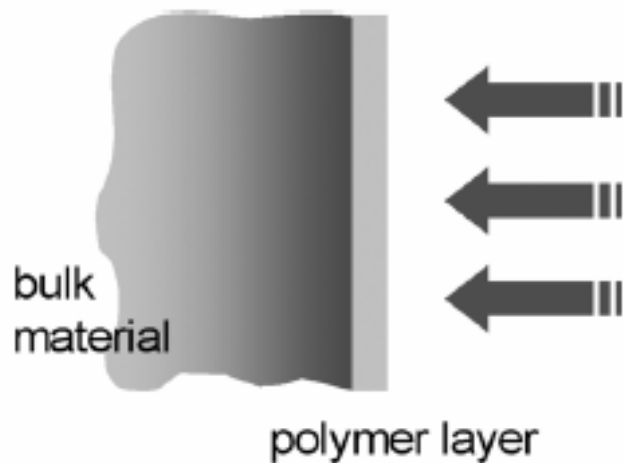
- Bulk properties and the surface determines the performance of a material
- Control of the interaction between the material and its environment
- Coatings serve as a barrier with the hostile environment and allows for protection against corrosion or other chemical or photochemical degradation
- Thin film organic coatings are very common

Organic Ultrathin Film Multilayer Assemblies

**Langmuir-Blodgett
(LB) Film**

**Organic
and Polymeric
Ultrathin
Multilayer films**

Chemisorption

**Layer-by-Layer
(LbL) Film**

Substrate

Deposition of thin film

Vaporized material

Source material

Evaporator

Heater

Vacuum Chamber
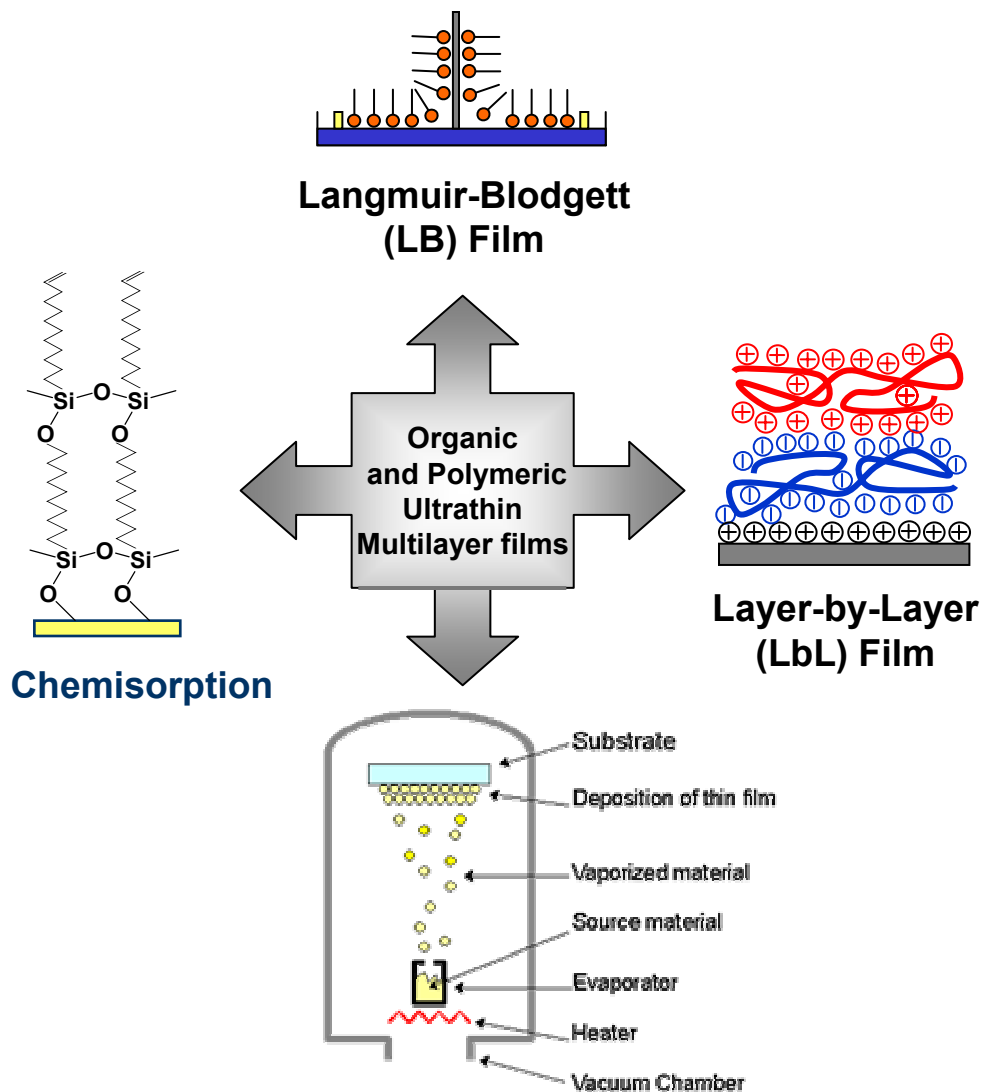
- How different is this from spin-coating?

- Nanostructured multilayer architecture

- control molecular orientation and organization on the nanoscale

- precisely tunes the macroscopic properties of the organic and polymer thin films

- Applications in microelectronics, electro-optics, sensors, and biotechnology

- To be explored? Organic and polymer multilayers by vapor deposition and thermal evaporation methods

- Polymer Brushes?

The study of Polymer brushes

DEFINITION: An assembly of polymer chains tethered by one end to a surface or an interface with sufficient density such that the polymer chains are crowded and forced to stretch away from the surface to avoid crowding. *it is possible to prepare grafted polymers were the average distance between grafting points is much smaller than the radius of gyration (Rg).*

- *Tethering of Polymers on surfaces*
- *Physical Adsorption :* homopolymers, block-copolymers, polyelectrolytes
- *Chemical adsorption –* end-functional macromolecules, amphiphiles
- *"Grafting to"* - all adsorption methods including self-assembled monolayers
- *"Grafting from" -* surface initiated polymerization
- *Ultrathin Films:* comparable to Langmuir-Blodgett films, Self-assembled Monolayers (SAM), Layer-by-layer, epitaxy.
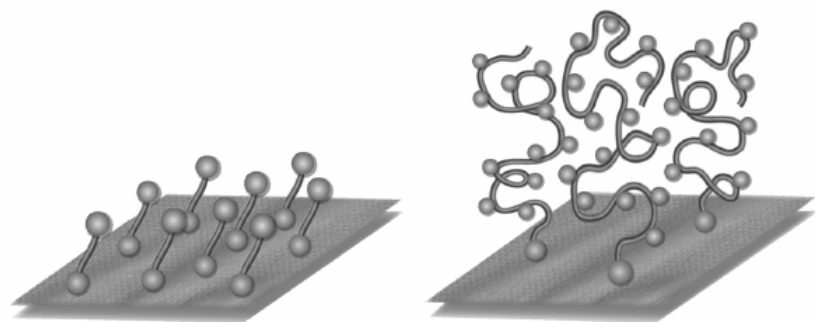
Physical adsorption

- Different interfaces and tethering points
- Solid or fluidic interfaces
- Thermally and solvolytically unstable
- Not very high grafting density

Adsorbed Block Copolymers
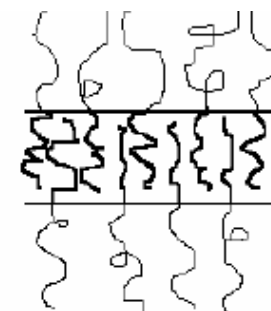
Ordered Diblock Copolymer Phases
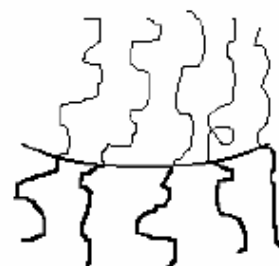
Block Copolymers at Fluid-Fluid Interfaces

Micelles

Chemical adsorption

- End-functional amphiphiles and polymers
- Solid or fluidic interfaces
- Thermally and solvolytically stable
- Not very high grafting density
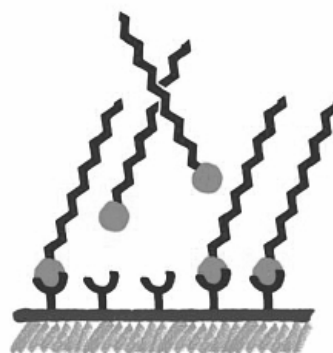
Thiols / Disulfides

SH   S-S

Silanes

$SiCl_3$ $Si(OMe)_3$

Phosphoric or Phosphonic acids

$O=P-OH$ $O=P-OH$

Grafting Methods for Polymer Brushes
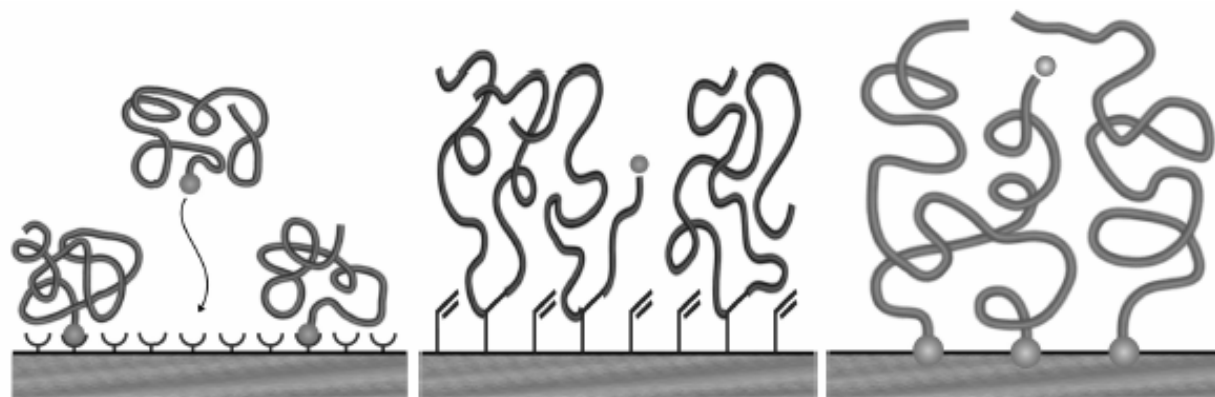
"grafting to"   **surface bound monomer**   **"grafting from" or SIP**

Why Surface Initiated Polymerization (SIP)?

- High brush density: ave. distance b/w grafting points < radius of gyration (Rg).
- Functionalized surfaces, controlled surface energies, controlled surface chemistry
- different methods of initiation: free-radical, ATRP, cationic, anionic,etc.
- Model polymerization studies in confined environments
- Novel and advanced materials, colloidal particle stabilizers, polymeric surfactants, nanotechnology

General strategy for SIP
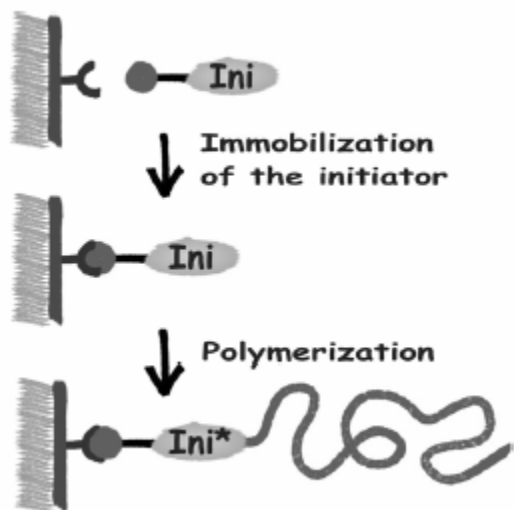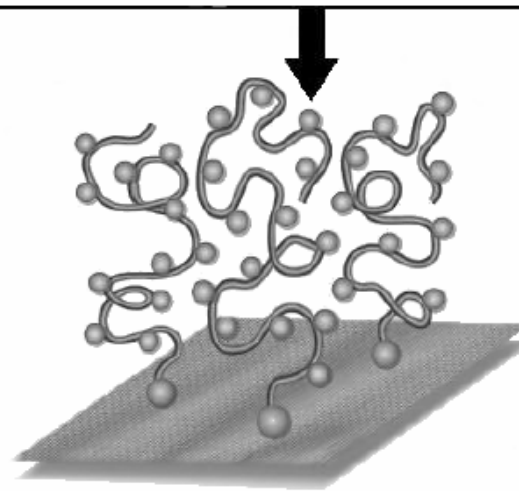
- Common synthetic strategy for the generation of polymer brushes via surface-initiated polymerization. An initiator molecule is deposited on a surface by means of a self-assembly process via the reaction of an anchor group to suitable surface sites, and subsequently, chains are grown on the surface from the initiating site.
- Examples of functional groups incorporated in polymer brushes.

Why surface initiated polymerization instead of "grafting to"?

Differences between "grafting to" and "grafting from"

- *physisorption* and *chemisorption* are "grafting to" and *surface initiated polymerization*, a "grafting from"
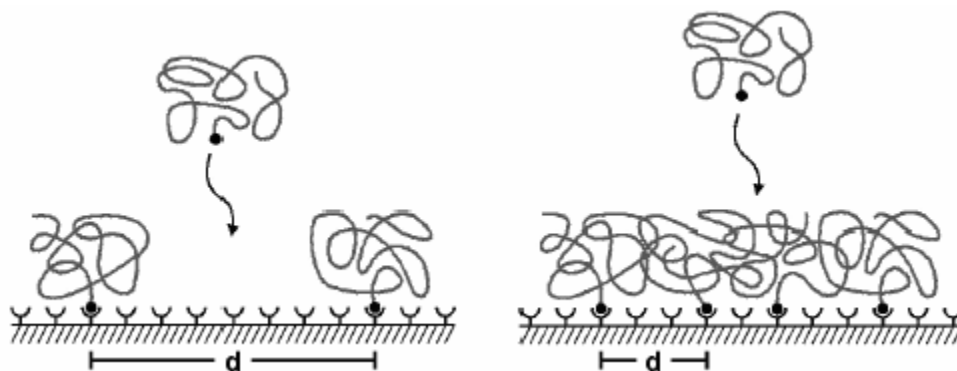
In a "grafting to " process the chains that are to be attached to the surface can easily reach the surface at low graft densities, (b) the attachment process comes to a virtual halt as soon as the surface is covered with polymers, as the already attached chains form a kinetic barrier against which incoming chains have to diffuse to reach the surface.

Particles: situation can be different depending on substrate geometry

Polymer Brush Regimes: limiting cases
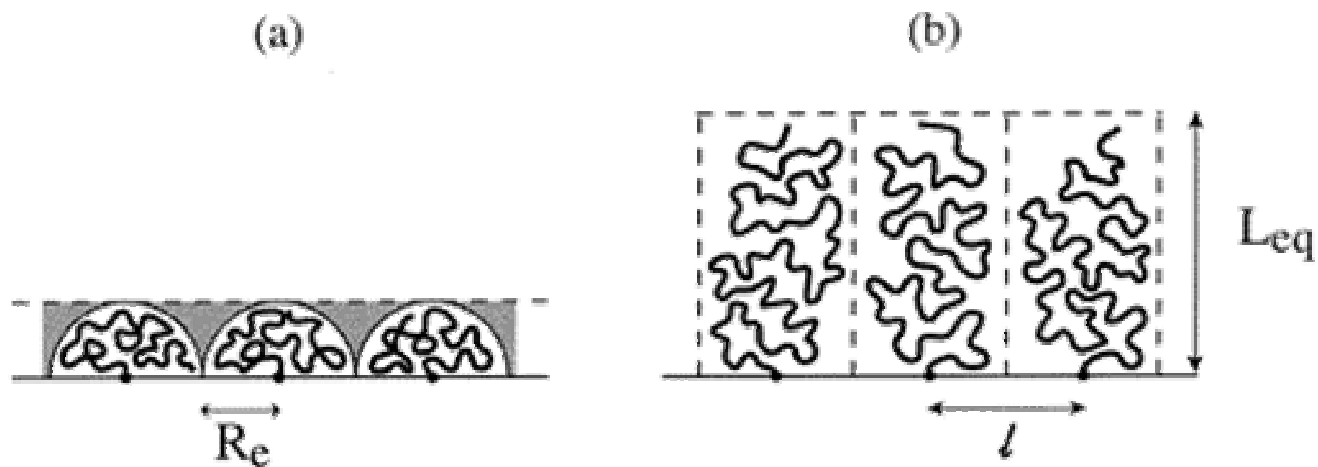
The two limiting cases of a polymer brush regime, showing: (a) tethered chains having the

critical grafting density $\sigma^* = 1/\pi R_e^2$ and (b) chains having $\sigma > \sigma^*$ and forming the stretched brush. Other types of brush regime terminologies have been reported in literature. In this case, a characteristic length in the uncompressed brush (part b) is given by $l = \sigma^{-1/2}$.

(source: Watanabe, H.; Kilbey, S. M., II; Tirrell, M.; *Macromolecules,* **2000***, 33,* 9146 or ref. 49).

Different Polymer Brush Regimes
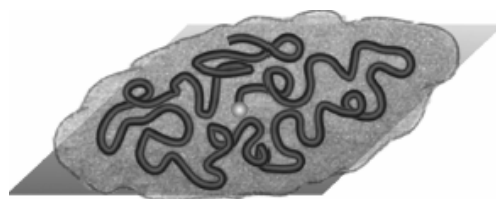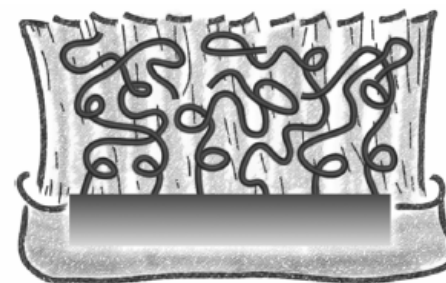
Mushroom   pancake   brush

- "mushroom", "pancake" and "brush" regimes as coined by de Gennes for the different possible conformations of surface-attached polymers

- Segment density profiles for surface attached polymers in different regimes
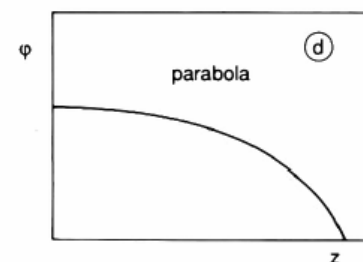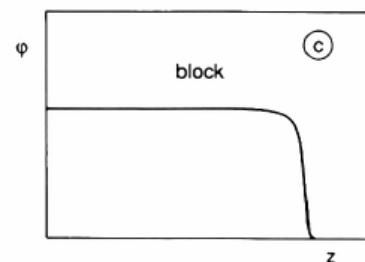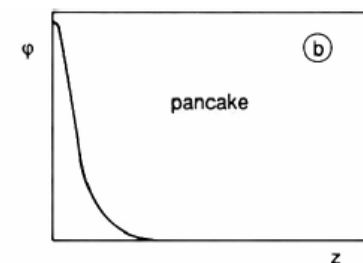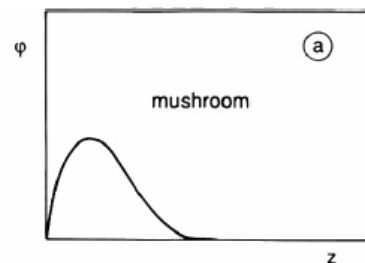
Nanoparticles

1. **Silver:** catalysis, photographic processes
2. **CdS:** optoelectronics, photoluminescence
3. **Gold:** optoelectronics, electronics, biosensors
4. **Silica:** insulator, catalyst support, membrane, filling material
5. **Palladium:** catalysis
6. **TiO$_2$:** photoelectrochemistry
7. **Metal oxide:** Mg, Ca, Mn, Fe, Co, Ni, Cu: magnetic properties
8. **Polymer:** conducting composite, drug delivery

I
Synthesis
(Stable and well-defined nanoreactor)

Nanoparticles with
1. Size and shape uniformity
2. Stability

1. Unique properties
2. Ordered deposition
3. Selective decoration
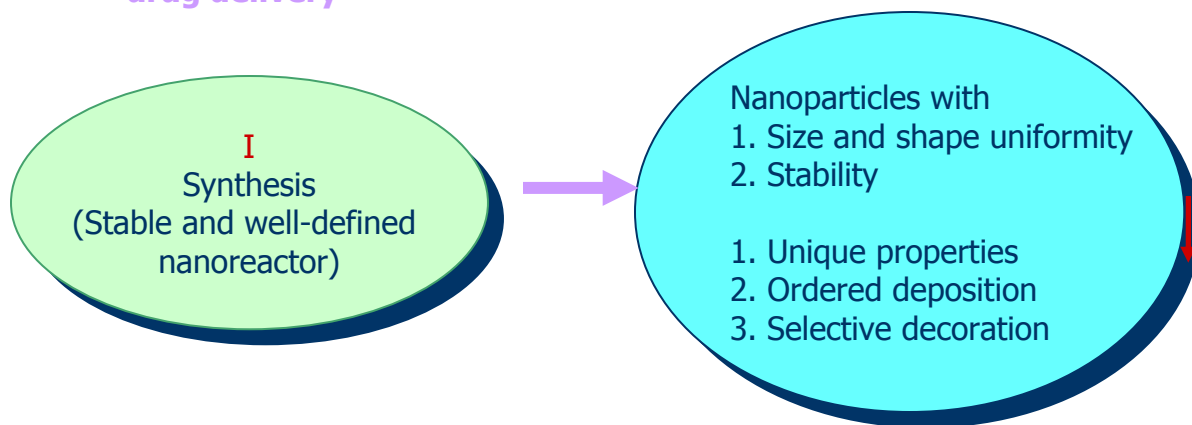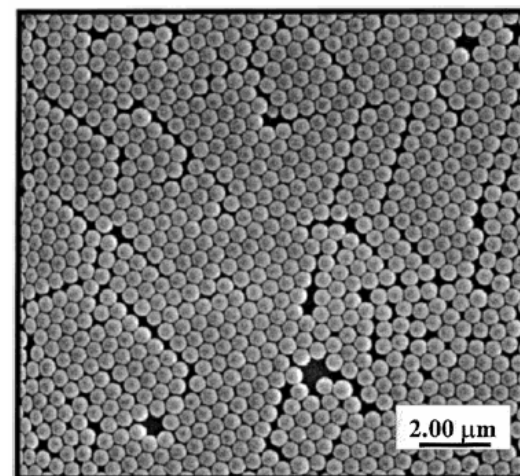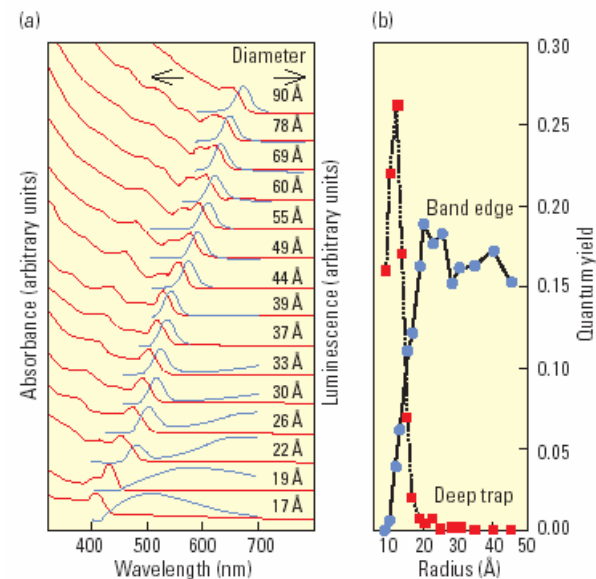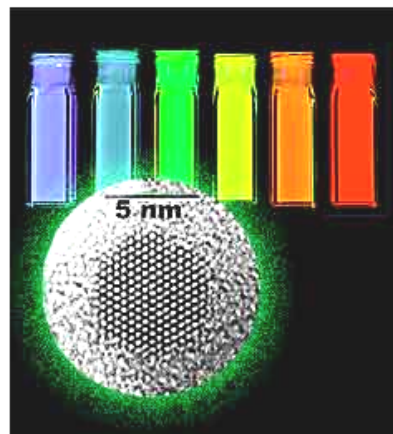
Synthesis of Nanoparticles: the Concept of Nanoreactors
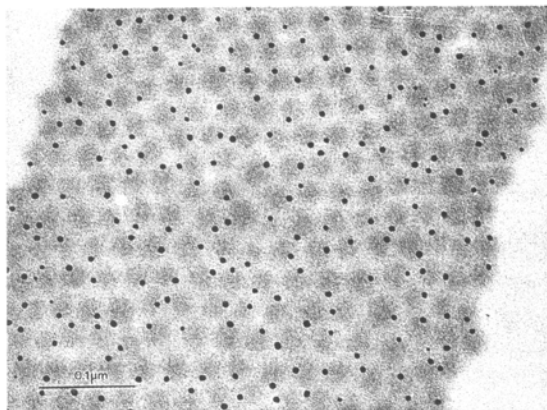
◈ **Nanoparticles** as colloidal systems of a solid-state material - dimensions in between molecules and a bulk solid-state material.

◈ **Strategies for the synthesis of nanoparticles:** surfactant or polymeric amphiphiles (block copolymers) micelles as a "nanoreactor" for nanoparticle synthesis.

◈ **Mechanism** - Metal ions trapped inside the particles exposed to precipitating or reducing agents to start nanoparticle growth: the number of metal ions initially trapped inside the particle determine growth.

◈ **Key step:** Control over the diffusion of reagents into the micelle.

◈ **Design:** The possibility of attaching coordinating ligands to the polymer in order to stabilize both precursors and nanoparticles within.

● **Strategies for the gold nanoparticle preparation**

Cationic polyelectrolytes	Amphiphilic block copolymers (PS-*b*-P2VP)	Dendrimers (PAMAM)	Self-assembled monolayers (*n*-Alkanethiols)
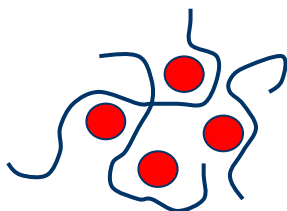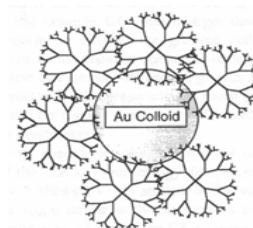
Au Colloid
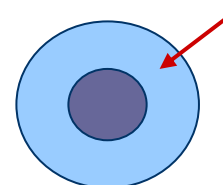
● **"Stable Nanoreactor"** for the control of size and shape of nanoparticles

Nanoparticles and nanostructured Films; Fendler, J. H., Ed.; Wiley-VCH; Weinheim, 1998.

Synthesis of Nanoparticles in General

a   b   c

Star block copolymer (PS-*b*-P2VP) N:Au=10:1
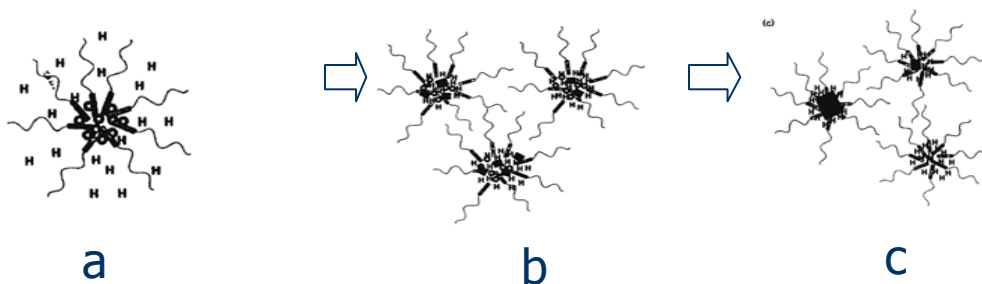
◈Schematic representation of the concurrent process during reduction reaction inside block copolymer micelles.

a) Reduction is initiated by the entry of the reducing agent into the core of the micelles loaded by precursor salt.

b) Destabilized micelles exchange block copolymer and may coagulate.

C) "Empty" micelles are formed besides block copolymer stabilized gold particles.

H: reduction agent; **O**: precursor salt; crystal.

Legend:
- P4VP (NaBH$_4$)
- PAMAM Dendrimer (UV)
- PS-b-P2VP (Hydrazine)

Absorbance vs Wavelength (nm)

200 nm

R.C. Advincula/ University of Houston

General Stages of SIP on particles

initiation   **polymerization**

- reactive functional surface
- coating with stable surfaces
- size / geometry

- controlled SAM initiator formation / coverage
- controlled activation and initiation

- polymerizability
- end-group reactivity
- aggregation / stability
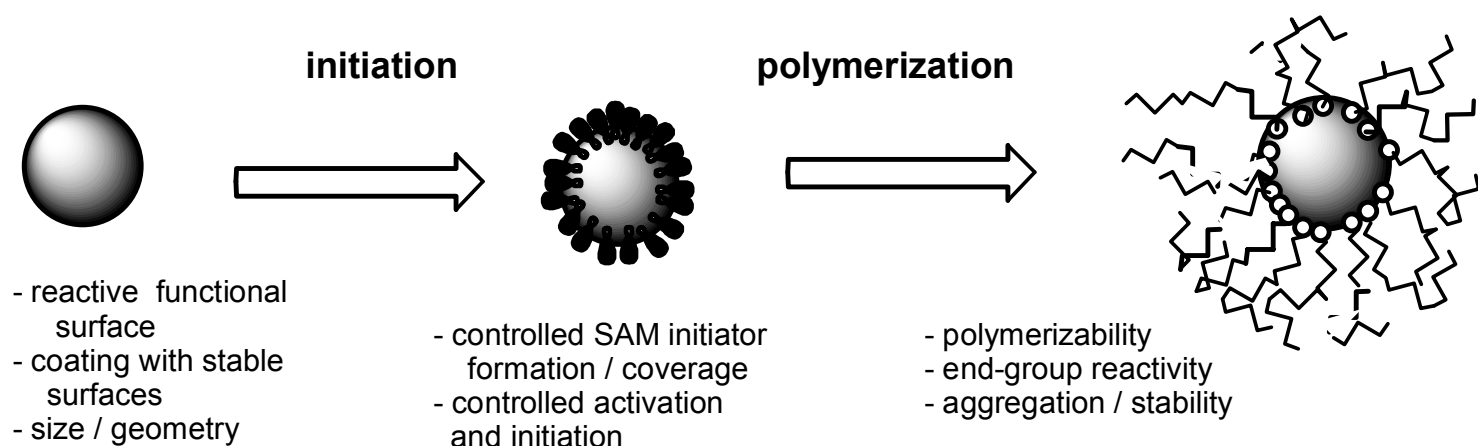
- Particles: size, shape, polydispersity, surface reactivity: Comparison between microparticles and nanoparticles
- Surface preparation: attachment of surface initiator
- Initiator preparation and activation
- Dispersion in solution: colloids or suspension
- Introduction of monomer
- Polymerization: control of kinetics and mechanism
- Different polymerization mechanisms: addition and step polymerization
- Addition: free-radical, ATRP, RAFT, TEMPO, cationic, anionic, metathesis
- Removal of unattached polymers: free-initiators in solution
- In-situ and ex-situ analysis of polymers or particle and polymer

Methods of Analysis of Particles -I

Gravimetric methods: changes in weight before and after each grafting procedure. Key aspects of this procedure include removal of "unattached" material and accurate and precise weighing procedures. The calculations of weight gain and "yield" are straightforward.

Thermal analysis: It is possible to monitor the changes in thermal stability, enthalpy, heat capacity, e.g simply by performing various thermal analysis methods such as DSC and TGA, composition of the hybrid material as well as the decomposition kinetics and mechanism. viscoelastic properties of a material by methods like dynamic mechanical analysis, coupled with other rheological measurements.

Light scattering: *Dynamic Light Scattering (DLS)* or static light scattering (SLS) light scattering measurements can be utilized to probe the change in size with the addition of the polymer "shell" brush and probe the hydrodynamic volume properties.

NMR: For monitoring the appearance and disappearance of specific resonance peaks, e.g. average polymer microstructure.

Methods of Analysis of Particles-II

Zeta potential: These measurements are primarily for determining changes in surface charges, surface charge density, changes in the dispersion properties, surface energy, stability, etc.

Rheology: This is especially important for monitoring changes in melt or solution viscoelastic behavior. The presence of a polymer brush on the particle surface not only stabilizes their dispersion but also dramatically changes the viscoelastic behavior.

Microscopy: Nanoscale vs. mesoscale dispersion properties is especially observed. In particular, TEM imaging has been very effective. It is important to have very good contrast between particle and polymer component. AFM studies have also been utilized to show changes in particle dimension and morphology. It will be interesting to see in the future how SNOM techniques can be used to probe specific particle-polymer interactions.

J. I Amalvy, M.J. Percy, S.P. Armes, H. Wiese, Langmuir, 2001, 17, 4770.

E. Tadd, A. Zeno, M. Zubris, N. Dan, R. Tannenbaum, *Macromolecules,* **2003***, 36*, 6497.

K.-M. Kim, D.-K. Keum, Y. Chujo, *Macromolecules,* **2003***, 36,* 867.

J. Ren, B. F. Casanueva, C.A. Mitchell, R. Krishnamoorti, *Macromolecules,* **2003***, 36,* 4188.

W.L.Yu, M. Borkovec, *J. Phys. Chem. B.,* **2002***, 106,* 13106.

G. K. Agarwal, J.J. Titman, M.J. Percy, S.P. Armes, *J. Phys. Chem. B.,* **2003***, 107,* 12497.

M.J. Percy, V. Michailidou, S.P. Armes, C. Perruchot, J.F. Watts, S.J. Greaves, *Langmuir,* **2003***, 19,* 2072.

M.R. Gittings, D.A. Saville, *Langmuir,* **2000***, 16*, 6416.

R.C. Dunn, *Chem. Rev.* **1999***, 99*, 2891.

Nanocomposite Properties

Bulk analysis of composite materials: These hybrid inorganic particle-organic polymer composites or nanocomposites can be probed just like any bulk polymer system for their physical and mechanical properties:

- Engineering polymer related testing methods includes (tensile modulus, flexural strength, scratch resistance), viscoelastic behavior, barrier properties, melt processing, dimensional stability with temperature, etc. structure property relationships developed.
- Determine percentage loading in structure-property relationships
- Applications: packaging, barriers and coatings, fuel tanks, electro-optical materials etc.

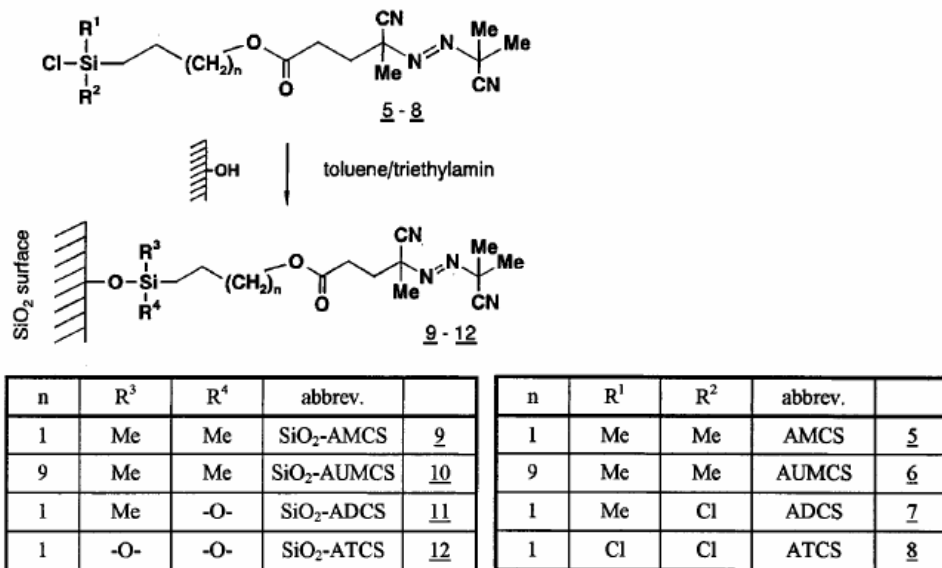| Property	Nylon-6	Nylon-6 / 2.5 wt% clay Nanocomposites
Elastic Modulus (GPa)	1.1	2.1
Tensile Strength (MPa)	69	107
Impact Strength (kJ/m^2)	2.3	2.8

Analysis: Degrafted Polymers from Particles

- Two main methods to detach polymers from surfaces: *1) direct cleavage of the polymer brush from the grafting point, 2) dissolution or destruction of the particle substrate.*

- **Method 1:** requires an initiator such that the polymer once formed can be removed from the surface by a simple and effective "cleavage" reaction and is 100% yield.

- **Method 2:** a core substrate that can be readily decomposed. This means that inorganic reagents should be able to destroy the substrate without harming the polymers.

- In both instances, centrifugation, partition, and filtration methods are used to isolate the desired degrafted polymer from the rest of the unwanted constituents and residues.

- The isolated polymers should be of sufficient purity to apply spectroscopic and macromolecular methods for analyses and should then be readily dissolved in solution.

-Once the polymer readily isolated, one can determine the *MW, MW distribution, polymer microstructure, composition, thermal analysis, etc.* as typically applied to "normal" polymers.

- In this manner the polymer properties are directly determined whereas one has to rely on indirect methods in the case of polymer brushes prepared from flat surfaces. **Size exclusion chromatography (SEC), light scattering, NMR, viscometry, DSC,** etc. can be utilized.

Topic 1: Free-radical chain polymerization on Silica nanoparticles

n	R³	R⁴	abbrev.	
1	Me	Me	SiO₂-AMCS	9
9	Me	Me	SiO₂-AUMCS	10
1	Me	-O-	SiO₂-ADCS	11
1	-O-	-O-	SiO₂-ATCS	12

n	R¹	R²	abbrev.	
1	Me	Me	AMCS	5
9	Me	Me	AUMCS	6
1	Me	Cl	ADCS	7
1	Cl	Cl	ATCS	8

- **Synthesis of Polystyrene Monolayers Attached to high surface area silica gels through SAM of azo initiators**
- **Schematic description of the concept for the preparation of terminally attached polymer monolayers using covalently bonded initiators for radical-chain polymerizations.**
- **Degrafting of surface tethered initiator**
- **Graft density as a function of polymerization time**
- Ruhe et. Al. Macromolecules 1998, 31, 592-601
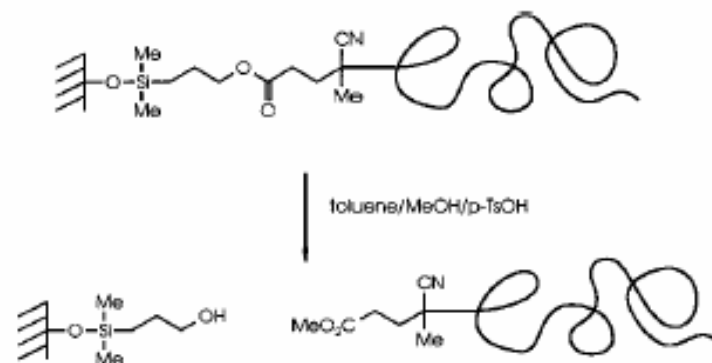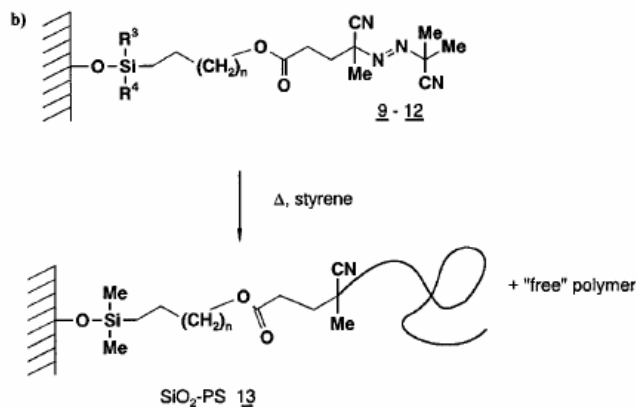
Free-radical polymerization

- Grafting Density of surface attached PS as a function of polymerization time
- XPS spectra of the silica and silica-PS
- Degrafting of surface tethered initiator
- FT-IR spectra
- Ruhe et. Al. Macromolecules 1998, 31, 592-601
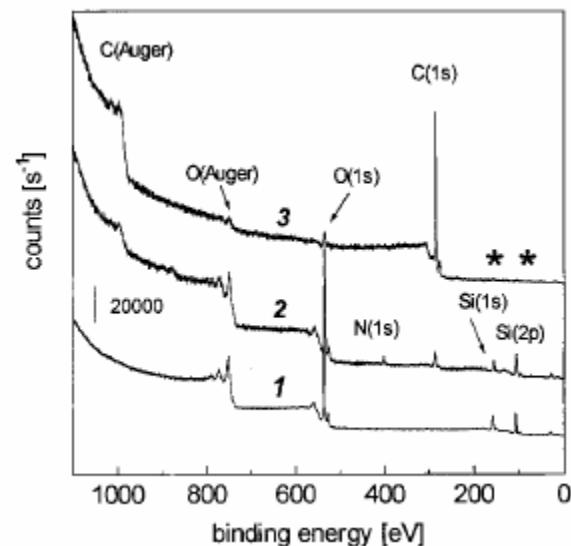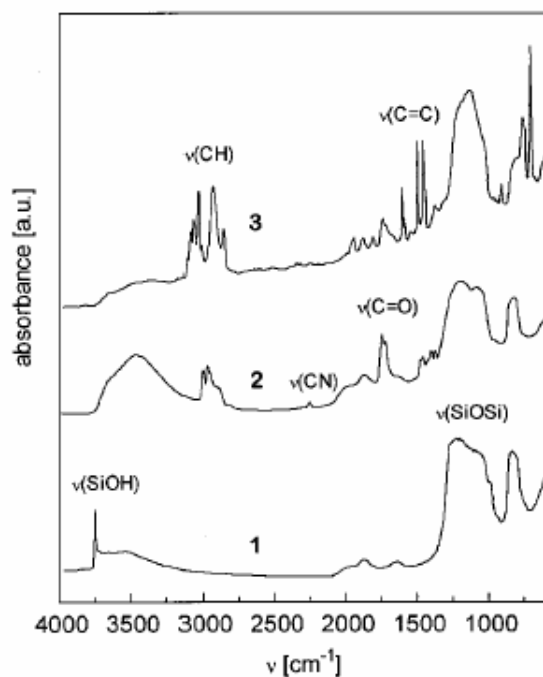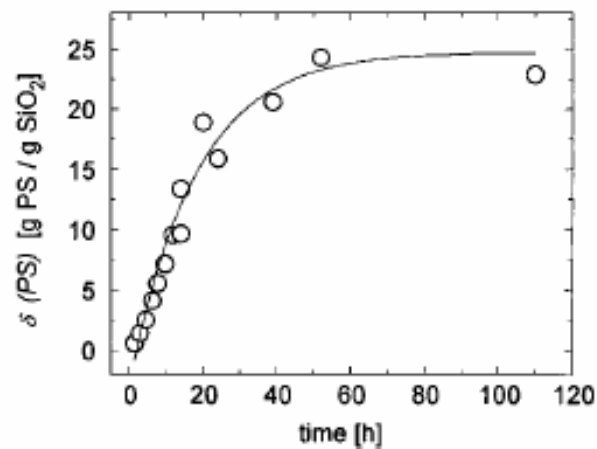
Topic 2: Quantum-Dot Nanoparticles with PMMA shell by ATRP-SIP
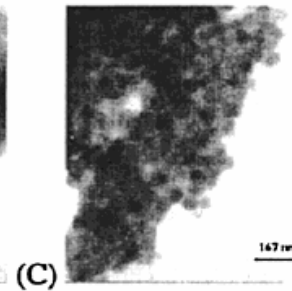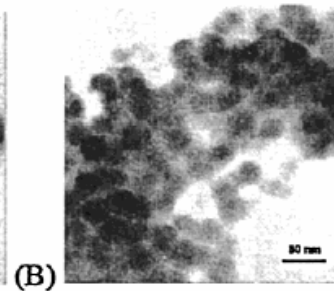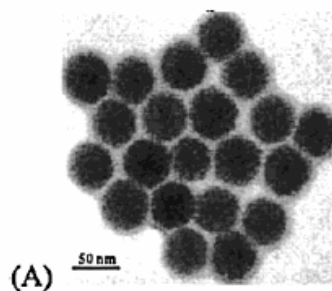

$$Polymer\text{-}x + Mt^n\text{-}X/Ligand \underset{K_{deact}}{\overset{K_{act}}{\rightleftharpoons}} Polymer + Mt^{n-1}\text{-}X_2/Ligand$$

K_{term}

K_p

monomer

Dead Polymer
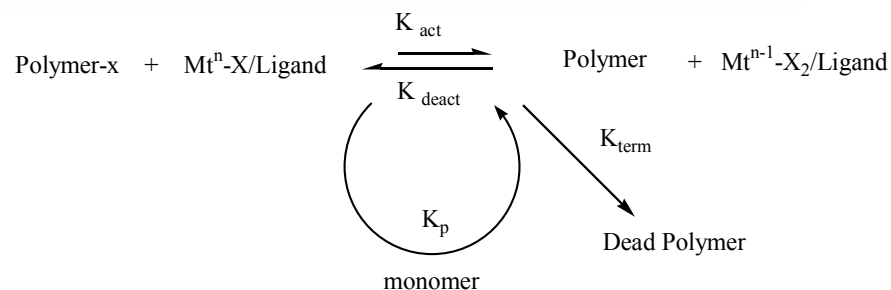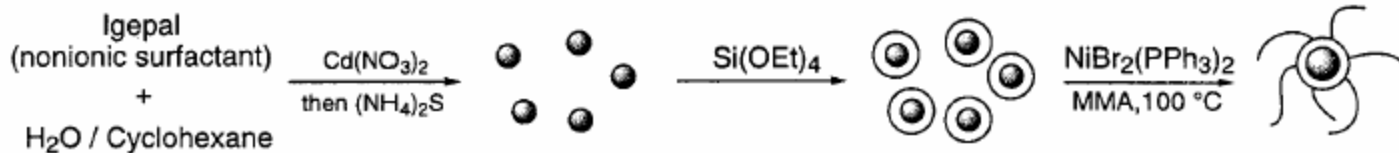
- Synthetic scheme for the synthesis of CdS/SiO$_2$/PMMA nanocomposites
- Fluorescence image of the hybrid materials on a glass slide under ambient light (left) and under 365 nm UV light (right).
- TEM micrographs of agglomerates of CdS/SiO$_2$/PMMA composite nanoparticles: (A) small nanoparticle aggregated cast from dilute solution showing inorganic cores surrounded by an outer layer of PMMA (B)(C) large agglomerates from more concentrated solutions.
- Patten et. Al. Chem. Of Mater. 2001, 13, 3920

ATRP on Silica Nanoparticles
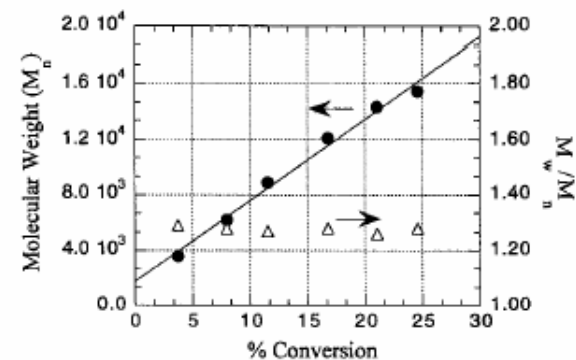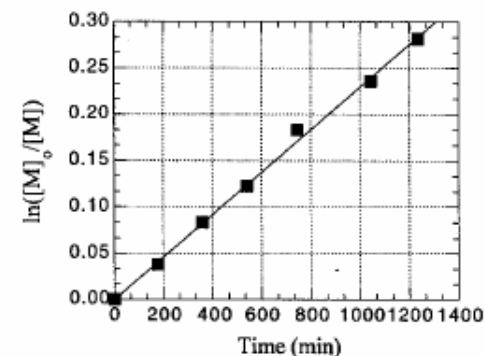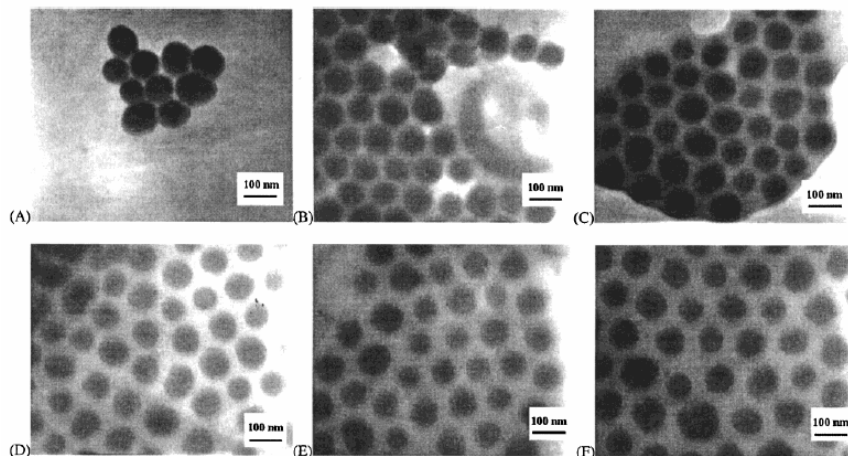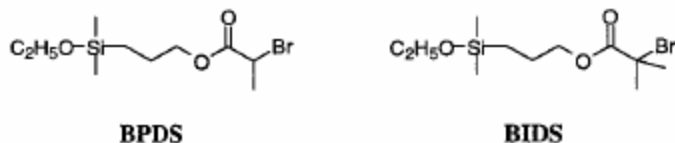
- ATRP from Nanoparticles: Preparation of well-defined hybrid nanostructures and for investigating controlled/living radical polymerization from surfaces
- Structure of monosilane initiators used.
- First order kinetic plot and molecular weight versus conversion plot for the ATRP of styrene from the surface of 75 nm functionalized silica
- TEM of products at various percent conversions
- Patten et.al. J. Am. Chem. Soc. 2001, 123, 7497

Topic 3: Core-Shell Colloids by ATRP: Differentiation of Blocks by AFM

$SiO_2\text{-}g\text{-}[pBA_{94}\text{-}\text{-}b\text{-}pMMA_{352}]_{1000}$
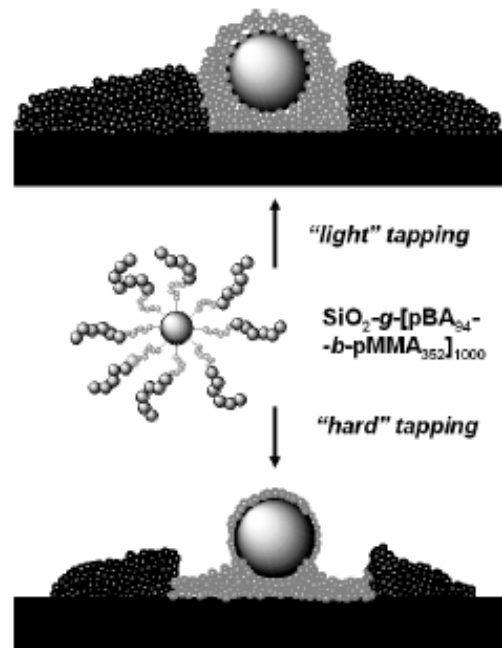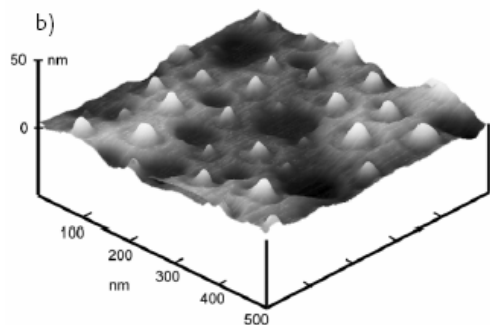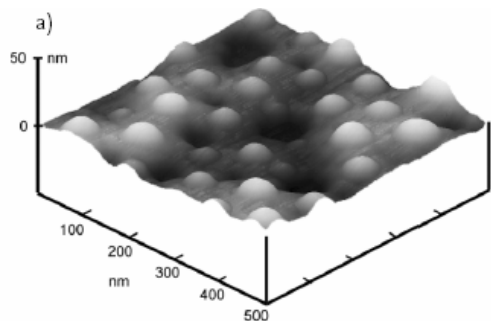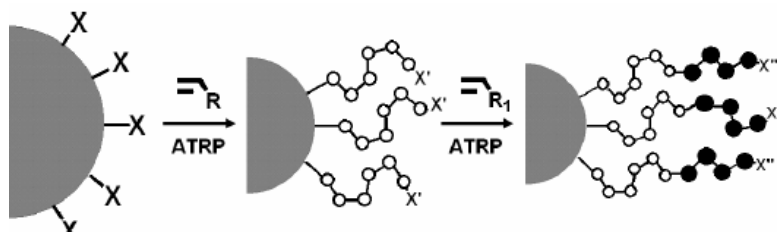
(a) Tapping mode AFM os SiO2-g-(pBA-b-PMMA)core shell colloid with rubbery inner segment and glassy outer shell
(b) the same material imaged with increasing applied tapping force. Regions of different contrast assigned to silica core (bright spots), pBA inner segment and PMMA dark halo or continuous matrix..

Pyun, J.; Jia, S.; Kowalewski, T.; Patterson, G.; Matyjaszewski, K. Macromolecules 2003, 36, 5094

Atomic Force Microscopy Images of SIP-Nanoparticles
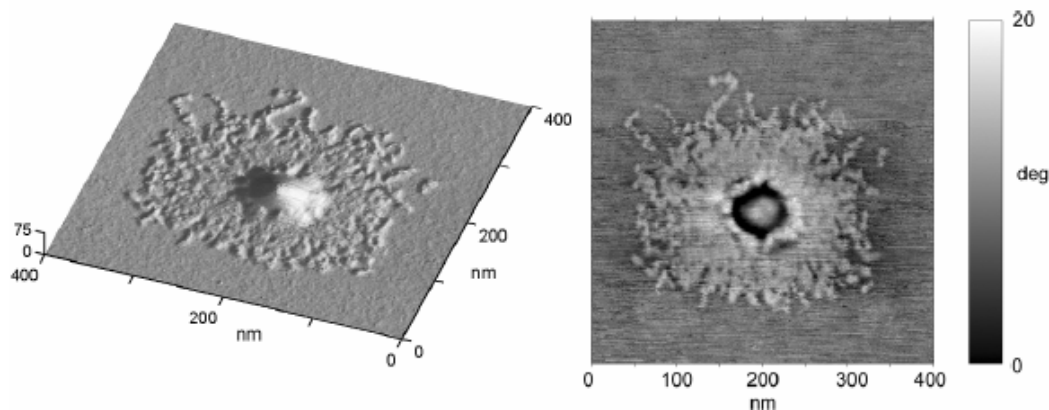
- Tapping mode AFM height (left) and phase image (right) of an individual SiO2-g-(pBA-b-pMMA) core-shell nanoparticle
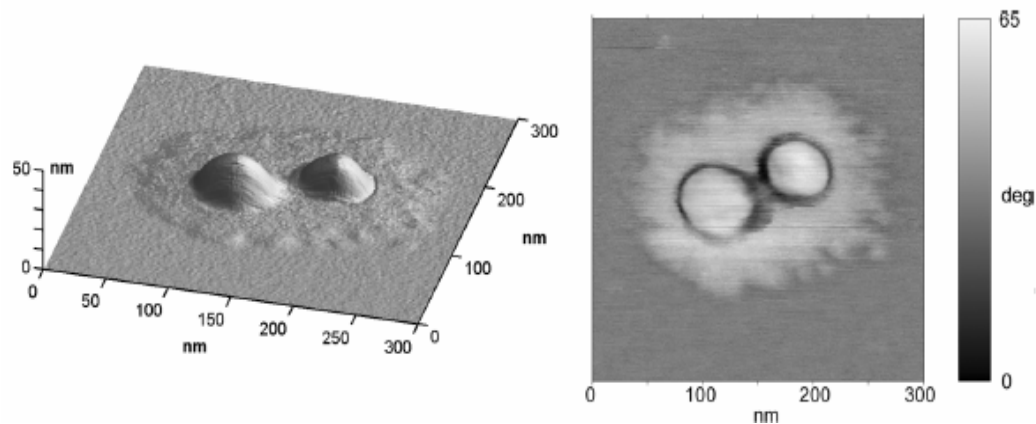
- Tapping mode AFM height (left) and phase image (right) of an individual SiO2-g-(pMMA) core-shell nanoparticle

TEM Images
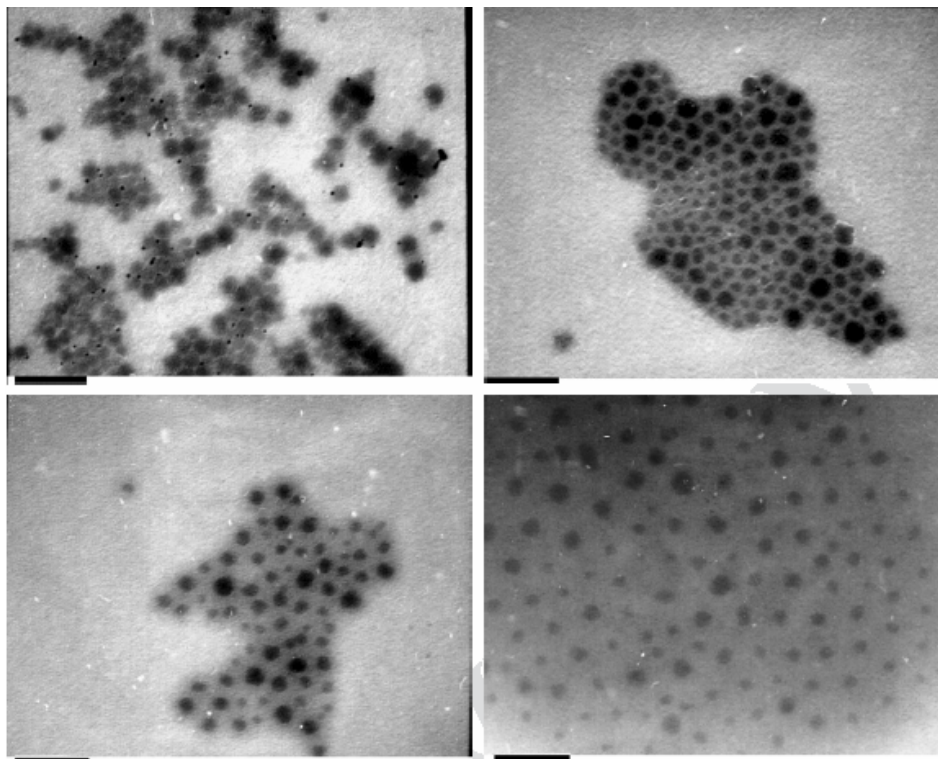
- Transmission Electron Microscopy images of silica colloidal initiator and Silica grafted with polystyrene. Scale is 100 nm.

- Savin, D.A., Pyun, J., Patterson, G.D., Kowalewski, T.; Matyjaszewski, K., J. Polym. Sci. Polym. Phys. 2002, 40, 2667.

Topic 4: Gold nanoparticles coated with PMMA by ATRP

Scheme 1. Schematic Representation for the Synthesis of Polymer-Coated AuNP by Surface-Initiated LRP
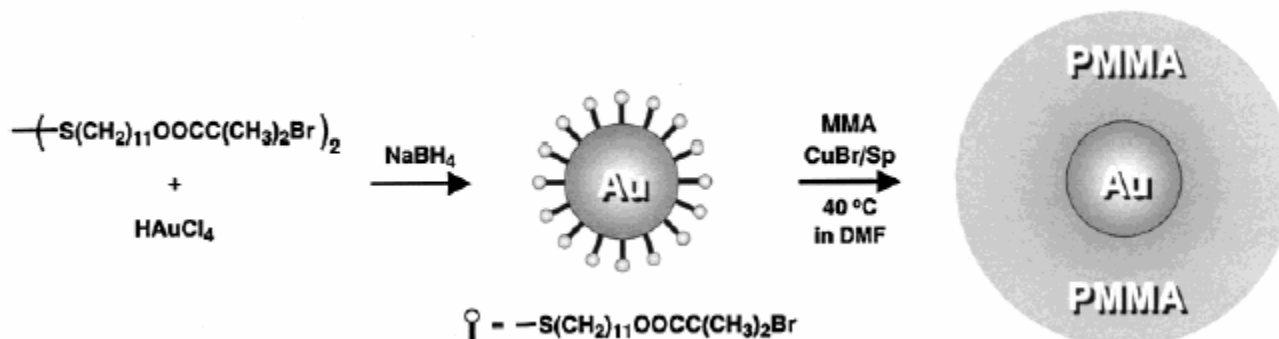
- Synthesis of Gold nanoparticles coated with well-defined high density polymer brushes by surface initiated living radical polymerization
- Evolution of the Mn and Mw/Mn of the graft and the free polymers as a function of monomer conversion for the solution polymerization of MMA in DMF with initiator coated Au nanoparticles.
- Fujkuda et. Al. Macromolecules 2002, 35, 8089-8993.
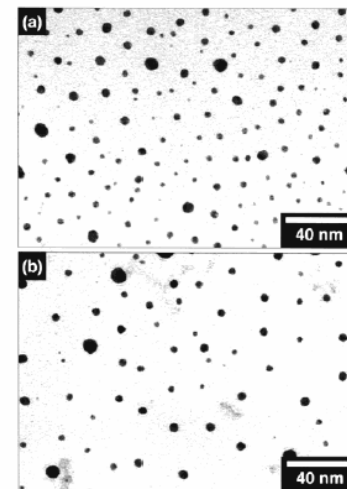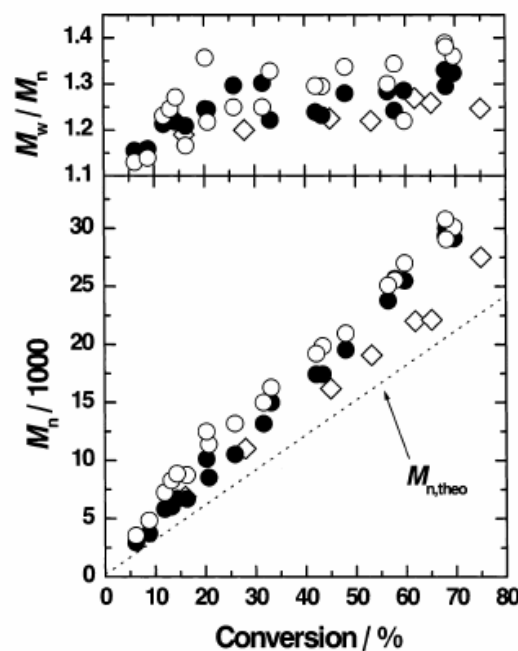
Topic 5: Aqueous ATRP on silica nanoparticles
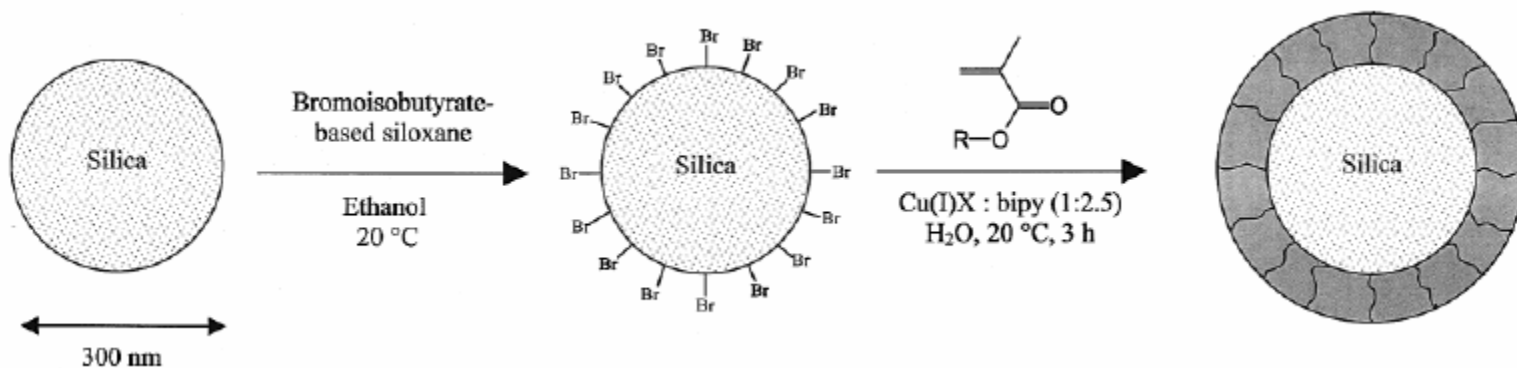
- Synthesis of well-defined polymer-grafted silica particles by aqueous ATRP
- Reaction scheme for the synthesis of polymer grafted silica particles via aqueous ATRP
- SEM of the uncoated and then coated silica particles.
- Armes, S. and Patten,T. et. Al. Langmuir 2001, 17, 4479.
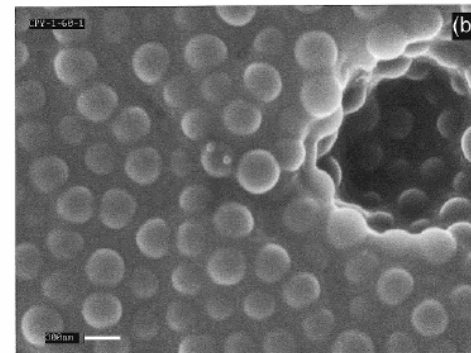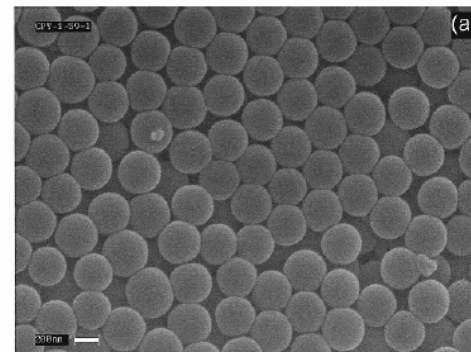
Topic 6: Ring opening metathesis polymerization (ROMP) on Au nanoparticles
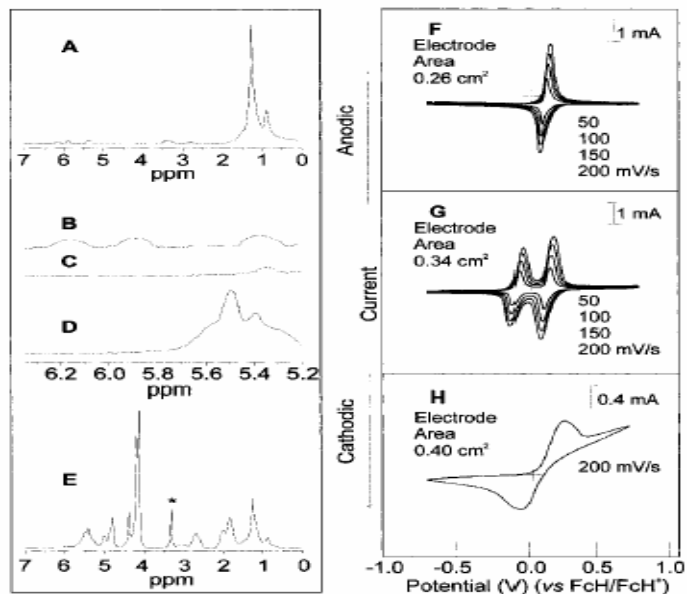
Figure 1. ¹H NMR spectrum (line broadening = 1 Hz) of (A) GNPs functionalized with a 3:1 mixture of 1-dodecanethiol and **2** (δ 7 to 0 ppm), (B) GNPs functionalized with a 3:1 mixture of 1-dodecanethiol and **2** (δ 6.3 to 5.2 ppm), (C) **2**-modified GNPs after treatment with **1** equiv of **1** (δ 6.3 to 5.2 ppm), (D) **2**-modified GNPs after the addition of 20 equiv of **3** to the ROMP-activated GNPs (δ 6.3 to 5.2 ppm), and (E) the GNP−poly**3**−poly**4** hybrid system (δ 7 to 0 ppm). Cyclic voltammetry of (F) the GNP−poly**3** system, (G) the GNP−poly**3**−poly**4** hybrid, and (H) poly**3**.
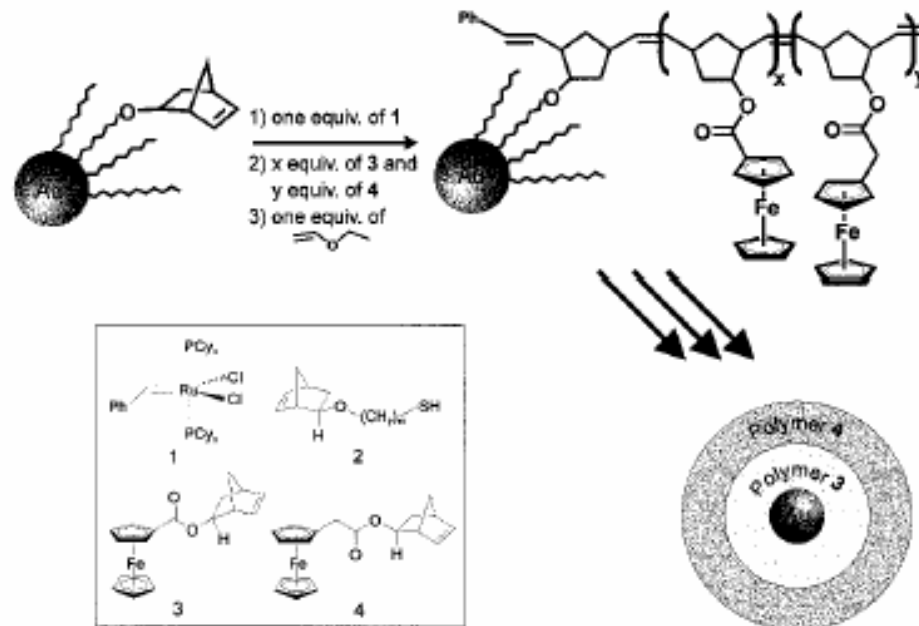
- Hybrid Nanoparticles with Block Copolymer Shell Structures:
- Examples of metal nanoparticles coated with polymer brushes.
- Mirkin et. Al. J. Am. Chem. Soc. 1999, 121, 462-463

Topic 7: Hyperbranched grafting: self-condensing ATRP on nanoparticles

Scheme 1. SCVP of an AB* Inimer (BPEA) from a Functionalized Silica Particle (B*f)ᵃ
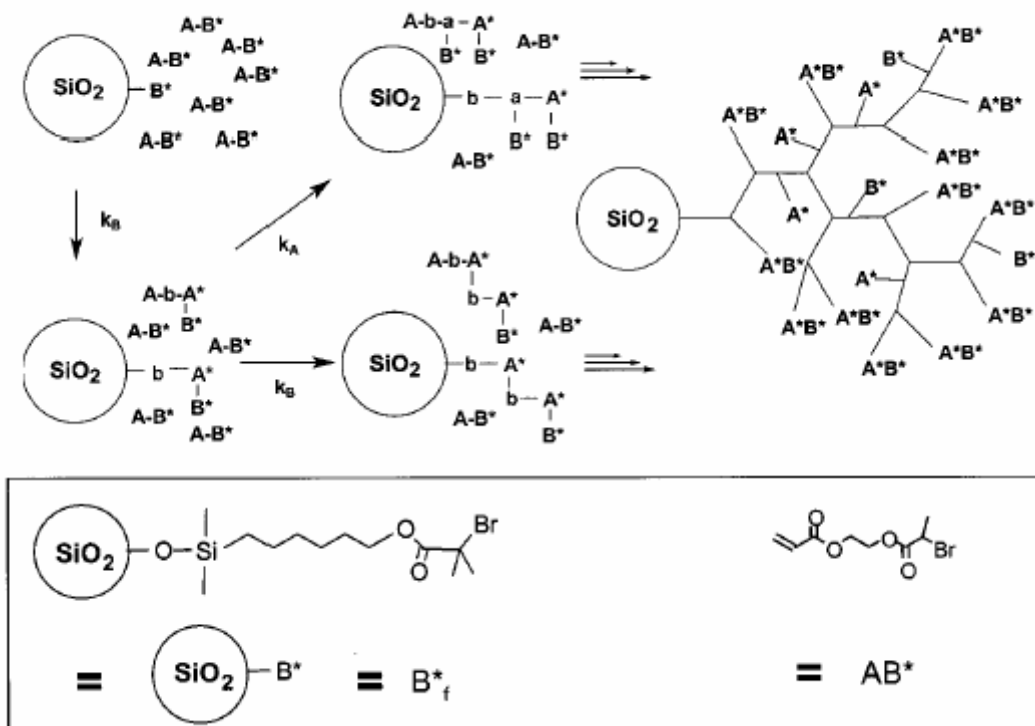
- Hybrid Nanoparticles with Hyperbranched Polymer shells via self-condensing ATRP from silica surfaces. Capital letters: vinyl groups (A) and active centers (A*,B*) and lower case letters stand for reacted ones (a,b)
- SCVP of an AB+ inimer (BPEA) from a functionalized silica particle.
- Examples of functional groups incorporated in polymer brushes.
- Muller, et. al. Langmuir 2002, 18, 3682

Hyperbranched grafting

Scheme 2. Synthetic Route for the α-Bromoester Type Initiator Grafted on a Silica Particle

Scheme 3. Initial Steps in Copolymerization of an AB* Inimer with a Conventional Monomer (M) from a Silica Particle[a]

- Schematic representation of (a) a core shell morphology of branced polymers grafted on silica particles and comparison of isolated and aggregated forms of the branched polymer-silica particles
- Examples of functional groups incorporated in polymer brushes.
- Muller, et. al. Langmuir 2002, 18, 3682
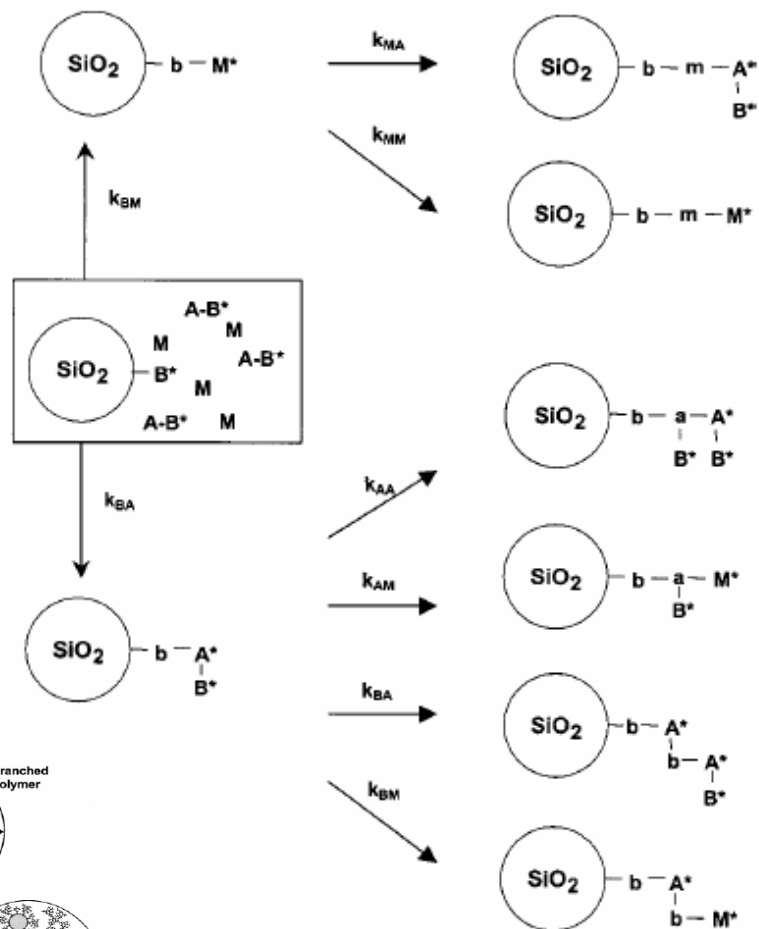
SPM and SEM probe of hyperbranched grafted nanoparticles
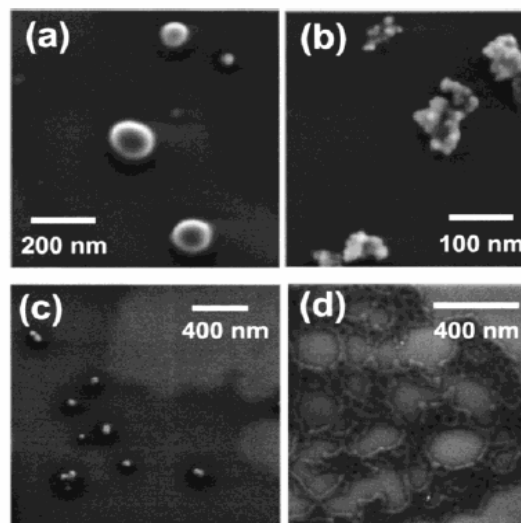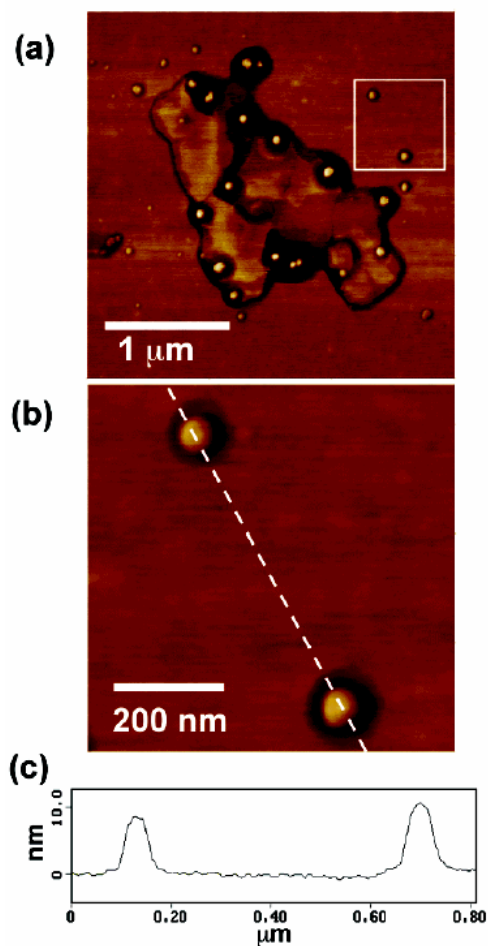
- Representative SFM images of the branched PtBuA silica hybrid particles obtained by SCVP (phase image)
- Representative FE-SEM images of the branched PtBuA-silica hybrid particles obtained by SCVP

Topic 8: Cationic Polymerization on Gold Nanoparticles
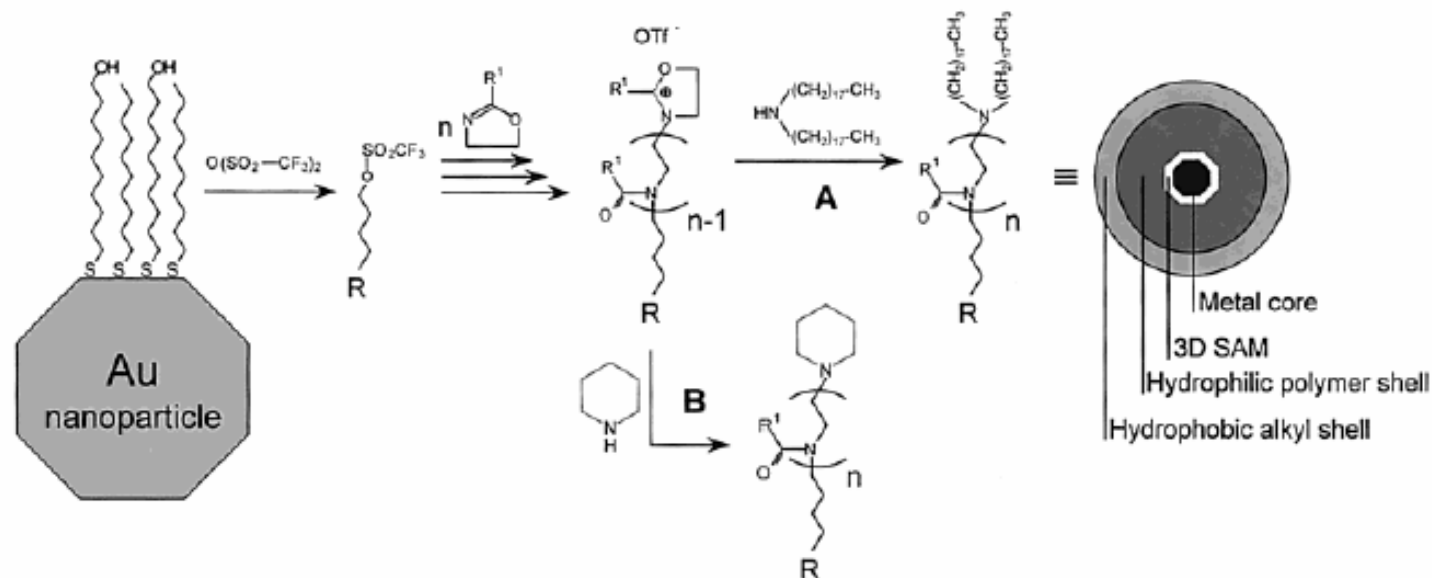
A (amphiphilic core-shell): $R^1=C_2H_5-$; Terminating agent: *N,N*-di-*n*-octadecylamine; polymerization time: 72h
B (*ex situ* kinetics): $R^1=C_6H_5-$; Terminating agent: piperidine; polymerization time: 2, 8, 24, 79h

- Nanocomposites by Surface-Initiated Living cationic polymerization of 2-oxazilines on functionalized gold nanoparticles
- Reaction scheme of the surface initiated polymerization of oxazilines. For the preparation of the amphiphilic nanocomposite 2-ethyl-2oxaziline and N,N-di-ocatadecylamine were used as monomer and terminating agent, respectively.
- Jordan et. Al. Macromolecules 2001, 34, 1606.
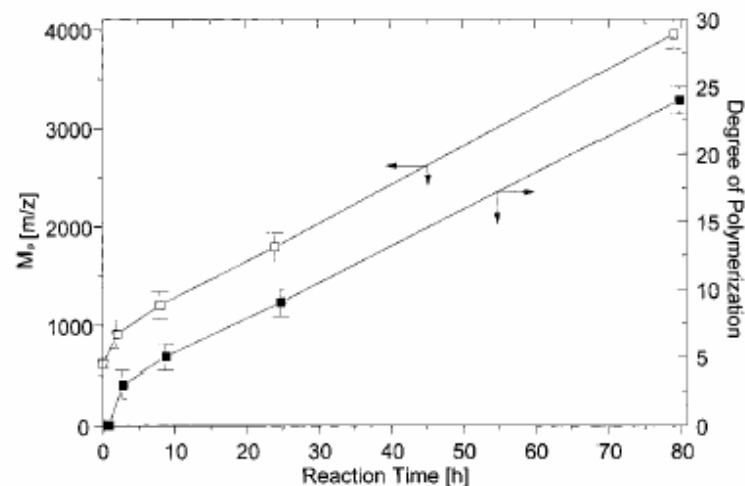
Topic 9: Living Anionic Surface Initiated Polymerization (LASIP)
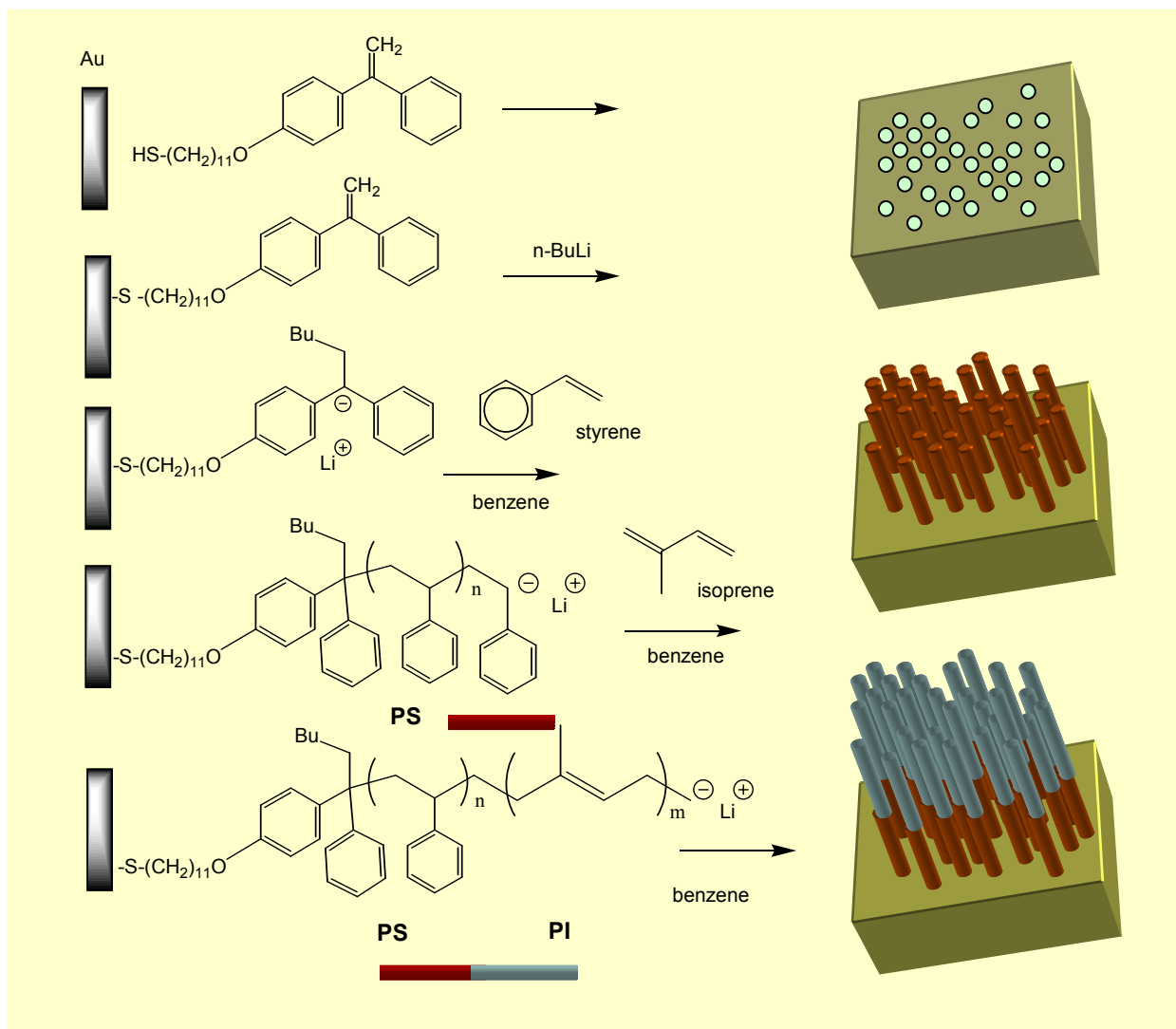
Anionic Polymerization in general

Propagation

- Dependent on nature of the ion pair

-
  1. Anion
  2. Cation or Gegen ion
  3. Solvent polarity

Solvents

- Aprotic to prevent transfer to solvent and termination

- Free of electrophilic impurities which will react with ionic sites

- Dissolve both monomer and polymer allowing heterogeneous polymerisation

$$B: + CH_2=CHR \rightarrow BCH_2C{:}^-HR \quad \text{carbanion}$$

- The strength of the base depends upon monomer reactivity.

- Monomers with strongly electron-withdrawing substituents require relatively weak bases (low pK_a).

- Ability of substituents to stabilize carbanions decreases as:

$$-NO_2 > -C=O > -SO_2 > -CO_2 \sim -CN > -SO >$$

$$\hexagon \sim -CH=CH_2 >>> -CH_3$$

$$N_n = \frac{\text{Number of anions containing n monomers}}{\text{Number of anions}}$$

$$N_n = \frac{[AM_{n-1}M^-]}{[GA]o}$$

This is a Poisson distribution.

$$N_n = \frac{v_\infty^{n-1}\exp(-v_\infty)}{(n-1)!} = \frac{1}{(n-1)!}\left\{\frac{[M]_o}{[GA]_o}\right\}^{n-1}\exp\{-[M]_o/[GA]_o\}$$

R.C. Advincula/ University of Houston
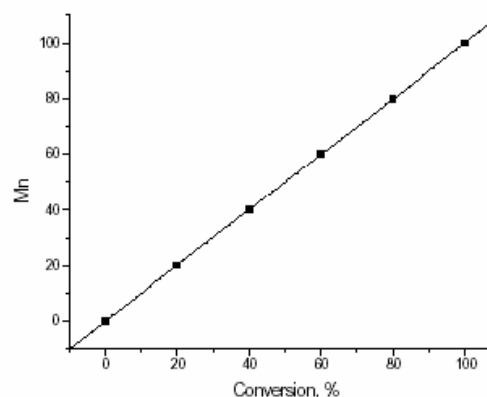
Remember…

Overview of Ionic Polymerization: Ion-pair Binding

There are four states of ion-pair binding:

I	II
$\sim\sim\sim BA$ covalent bond	$\sim\sim\sim B^+A^-$ tight or contact ion pair, intimate ion pair
III $\sim\sim\sim B^+\|A^-$ solvent-separated, loose ion pair	$\sim\sim\sim B^+ + A^-$ **IV** free ion, very reactive but low concentration

Most ionic polymerizations have equilibrium between ion pairs (II or III, depending upon solvent) and free ion (IV).

Effect of Reaction Medium: Solvent

Solvent	Dielectric Constant	k_p (liter/mole sec)
Benzene	2.2	2
Dioxane	2.2	5
Tetrahydrofuran	7.6	550
1,2-Dimethoxyethane	5.5	3,800

Data from G. Odian, Principles of Polymerization, 3rd Ed., Table 5-9, p 383.

• As the dielectric constant increases, the solvating power of the reaction medium increases and there is an increased fraction of free ions (which are highly reactive).

Remember…

Effect of Reaction Medium: Counterion

The separation between the counterion and the carbanion end group on the polymer is the major factor determining the rate, equilibrium, and stereochemistry.

	Counterion	k_p, liter/mole sec	
		in tetrahydrofuran	in dioxane
Cation size	Li+	160	0.94
	Na+	80	3.4
	K+	60-80	19.8
	Rb+	50-80	21.5
	Cs+	22	24.5
	Free anion	65,000!	

Data from R.W. Lenz, Organic Chemistry of Synthetic High Polymers, 1967, p 425.

Tetrahydrofuran is a good solvating solvent ($\varepsilon = 7.4$)
Dioxane is a poor solvating solvent ($\varepsilon = 2.2$)

Termination

By impurities and transfer agents:

• Oxygen and carbon dioxide can react with propagating anions, and water will terminate the chain by proton transfer. Thus, the reactions must be carried out under high vacuum or in an inert atmosphere.

By nucleophilic attack of initiator on polar monomer:

• Polar monomers such as methyl methacrylate, methyl vinyl ketone, and acrylonitrile have substituents that will react with nucleophiles. These side reactions broaden the molecular weight distribution. To minimize the effect, use a less nucleophilic initiator, lower reaction temperatures, and more polar solvents.

In order to understand more, we need more samples or higher surface areas.

Complex Macromolecular Architectures

Block Copolymer Architectures

Linear — AB Diblock, ABA Triblock

Star — A_2B 3-miktoarm, ABC 3-miktoarm, A_2B_2 4-miktoarm, A_3B 4-miktoarm, $(AB)_4$ 4-miktoarm

Multifunctional Initiator — Living Polymerization

Multifunctional Coupling Agent — Coupling Reaction

Linking Reaction
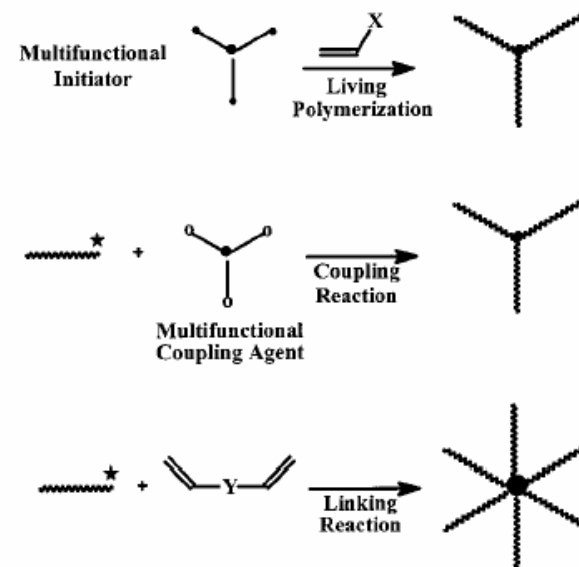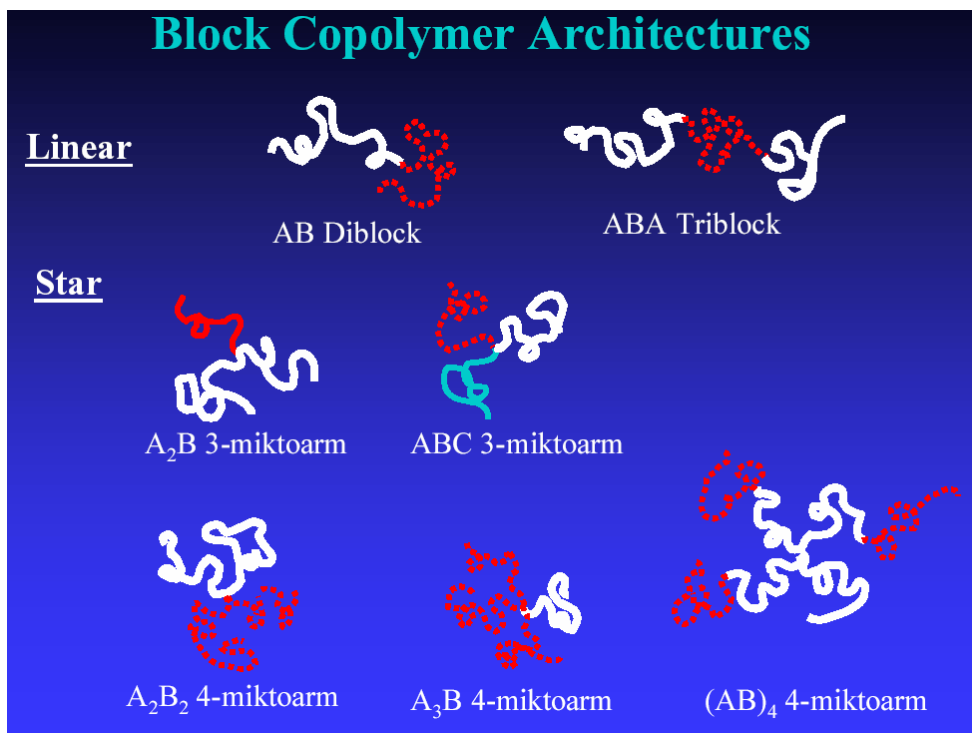
- Anionic Polymerisation
- Cationic Polymerisation
- Ring Opening Polymerisation
- Living Radical Polymerisation
- Group transfer Polymerisation

Living Anionic Polymerization : Model Studies on Surfaces

Chemistry of Anionic Polymerization in general:

-Living Polymerization
-Poisson type of distribution for MW
-Block copolymer preparation
-Complex Macromolecular Architectures

Model studies for living anionic SIP and theoretical predictions:

- *Entropic vs. enthalpic considerations*
- *Initiator activity and monomer diffusion*
- *polymer brush properties: conformation, χ parameter, Kuhn length, radius of gyration (Rg),etc.*

Need?

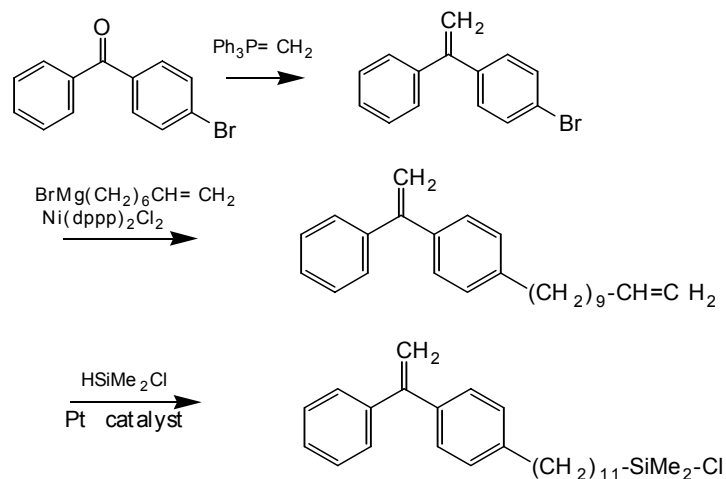- Develop the initiator system and polymerization method

- Analysis methods on surfaces

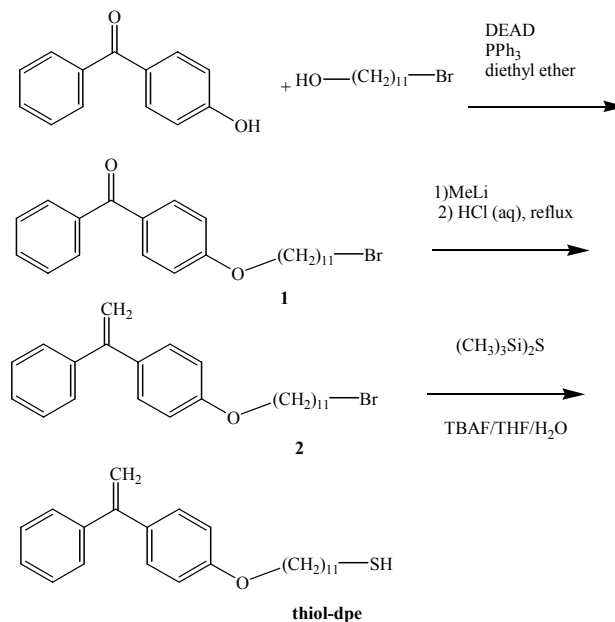- Design of experiments to differentiate surface from solution

Synthesis of DPE Initiator for surfaces: SAM

Silane initiator

thiol initiator

- anionic polymerization based on 1,1-diphenylethylene (DPE)
- surface grafting of initiator important: SAM
- activation in the absence of side-reactions and stability

Grafting of the Initiator and Polymerization of Styrene
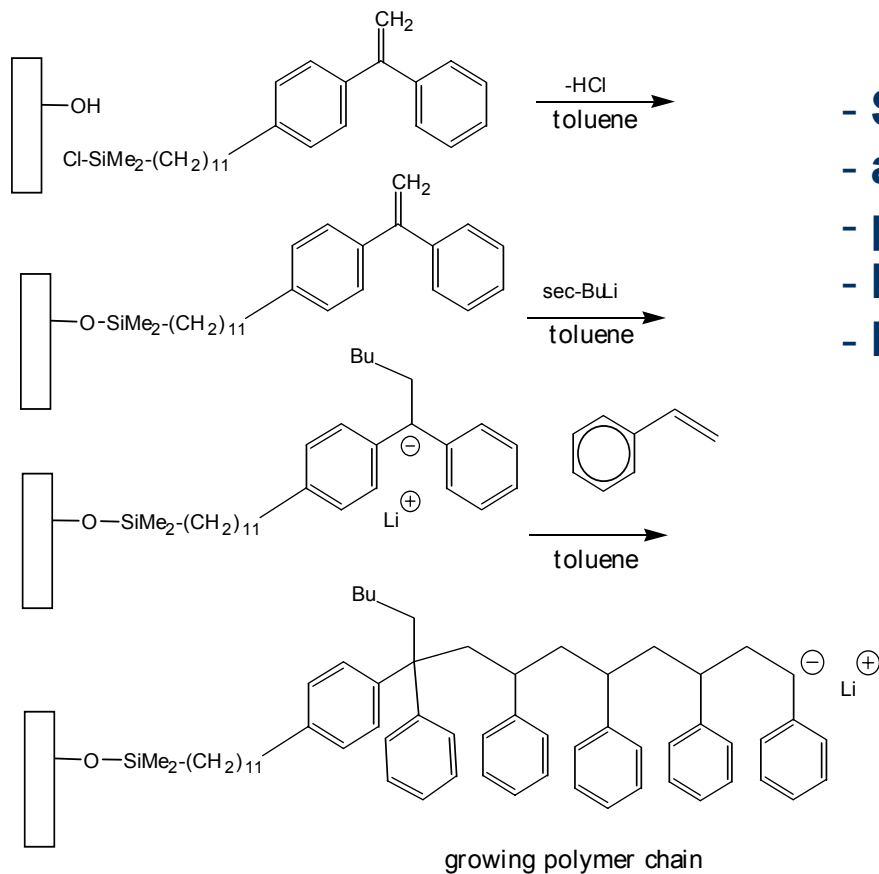
- **SAM of initiator on surfaces**
- **activation**
- **propagation**
- **living mechanism**
- **Polymerization under high vacuum**

growing polymer chain

Advincula, R.; Zhou, Q.; Park, M.; Wang, S.; Mays, J.; Sakellariou, G.; Pispas, S.; Hadjichristidis, N.; "Polymer Brushes by Living Anionic Surface Initiated Polymerization on Flat Silicon (SiO*x*) and Gold Surfaces: Homopolymers and Block Copolymers" *Langmuir* **2002***; 18(22);* 8672-8684.

Apparatus for Polymerization

A: Styrene
B: MeOH
C: THF
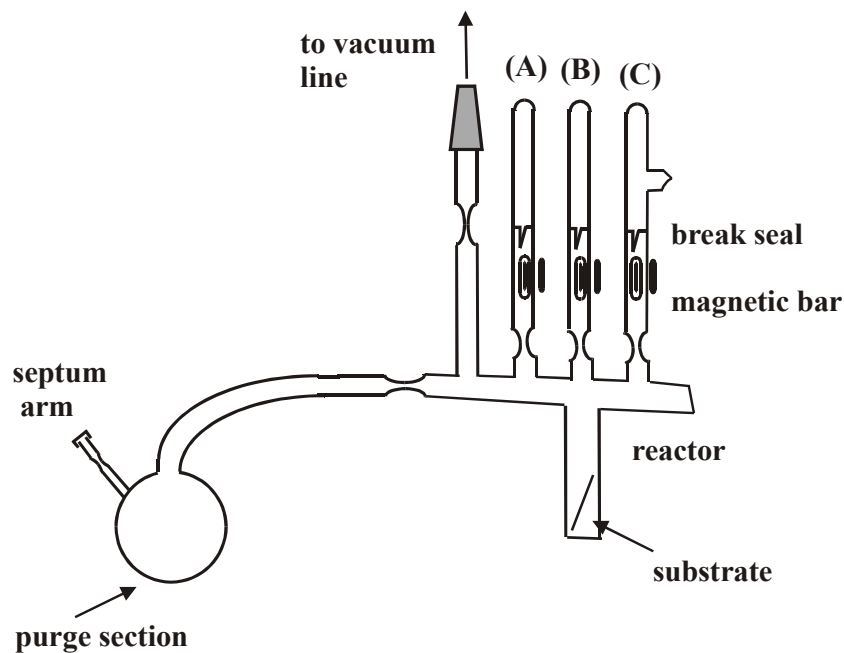
- polymerization under high vacuum
- Selective washing and introduction of monomer solution
- termination and removal of polymer

Results from Surface Polymerization

SAMPLES	ACTIVATION	ADDITIVE (1% V/V)	THICKNES (nm)	CONTACT ANGLE
SIP-B-3 (3 DAYS)	s-BuLi	NONE	6.8	85
SIP-B-4 (5 DAYS)	n-BuLi	THF	10.8 (16%) 16.1 (100%)	70 76
SIP-B-5 (5 DAYS)	n-BuLi	THF	13.4 (16%) 13.7 (100%)	85 89
SIP-S-3 (3 DAYS)	S-BuLi	BuOLi	3.8 (16%) 3.9 (100%)	50 72
SIP-S-4 (4 DAYS)	n-BuLi	THF	6.3 (16%) 8.2 (100%)	61 64
SIP-B-9 (4 DAYS)	n-BuLi	THF	8.9 (100%)	82
SIP-TMEDA (5 DAYS)	n-BuLi	TMEDA/ Au substrate	23.4	94

Concentration:

2-15 g styrene/ 100 mL benzene solvent

Brackets indicate % of DPE with alkydimethyl chlorosilane solution (0.0001M) for SAM

Bulk vs. solution?

SiOx vs. Au?

Polymer brush thickness and contact angle

NOTE: All polymerizations were done at room temperature, 24-25 ºC. The volume of benzene solvent is 100 mL. Termination was done by the addition of 2 mL of methanol.
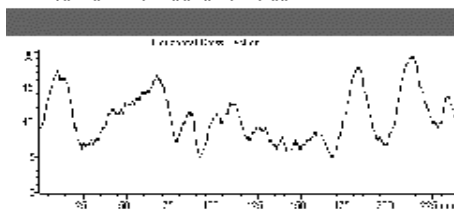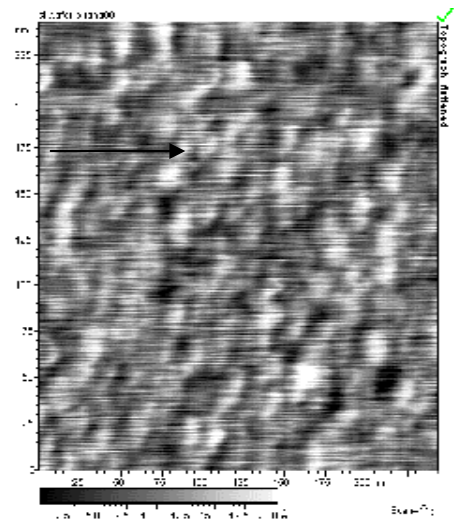*brackets indicate % of DPE initiator with alkydimethylchlorosilane solution (0.0001M) for
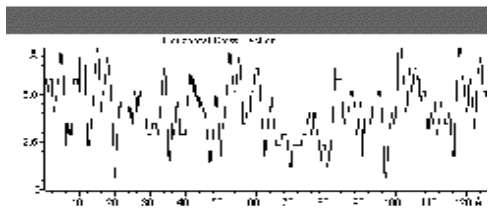[c]free polymer from solution Mn = 1.10 x 10^6 , P.D.=1.44, by SEC.
[d]free polymer from solution Mn = 1.08 x 10^4 , P.D.=1.24, by SEC.
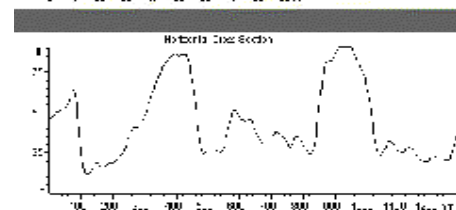
AFM Images: Si-wafer – SAM- Polymer

Si-Wafer
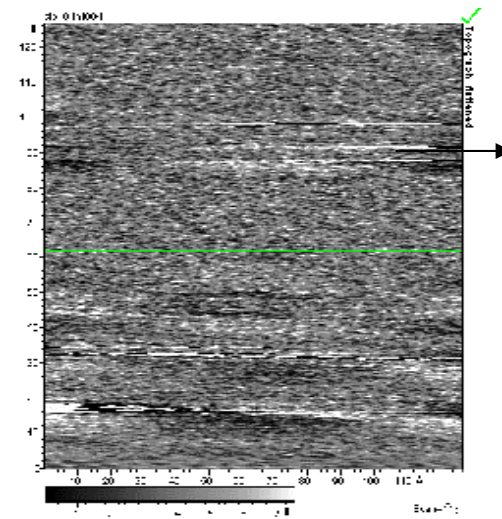
**DPE Functionalized
Si Wafer**
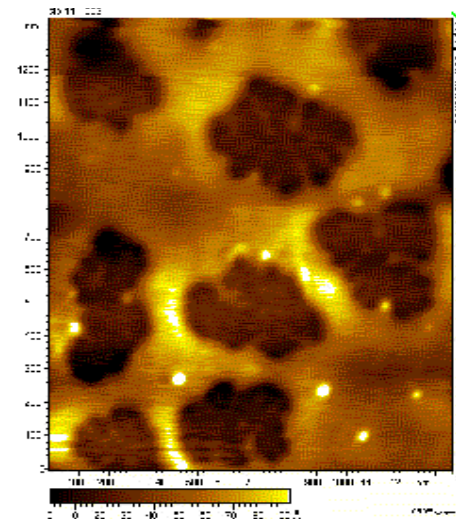
**Polymer Brush
on Si-Wafer**

AFM: Different conditions
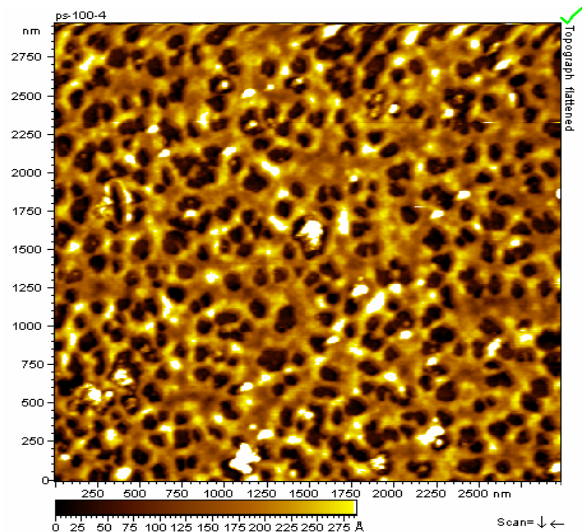
SIP-B-5
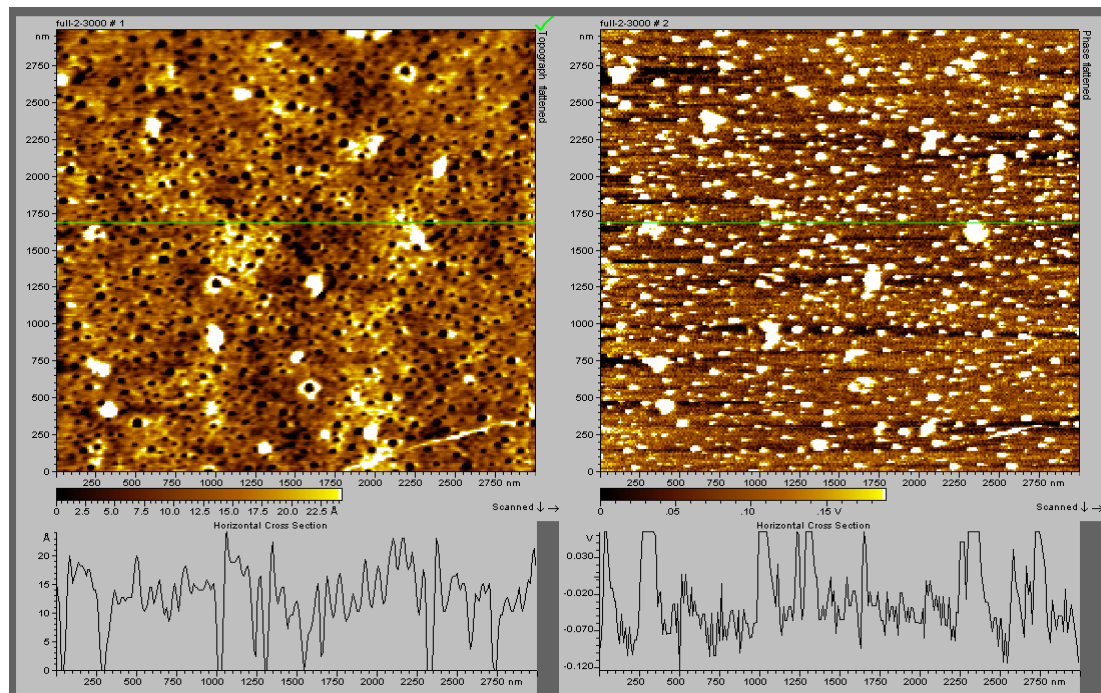
SIP-TMEDA/Au

AFM Images based on different polymerization conditions
- **SIP-B-5- 5 days, 100%, n-BuLi, THF added, bulk: 13.7 nm**
- **SIP-TMEDA/Au- 5 days, 100%, n-BuLi, TMEDA added, bulk: 23.4 nm**

Other Observations

- MW range from **360,000 to 1,000,000**, from solution much higher than that possible from surface **10,000 to 50,000***

- The polymers in solution showed very **broadened molecular weight distribution**

- FT-IR confirms presence of PS and Surface Plasmon Spectroscopy (SPS) confirms thickness
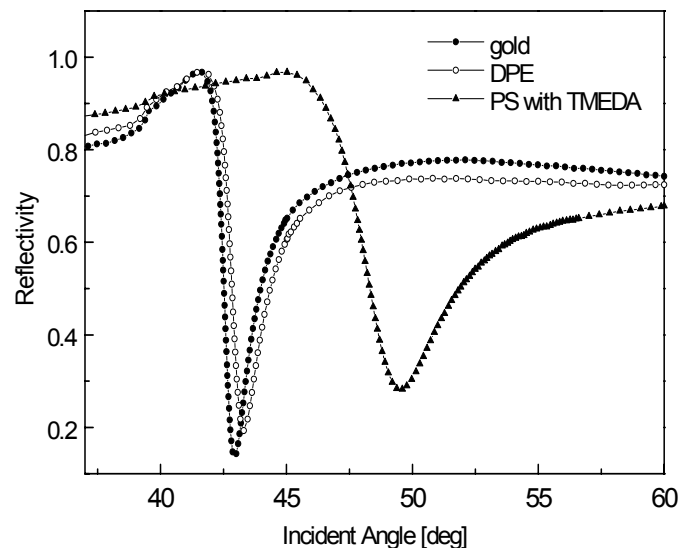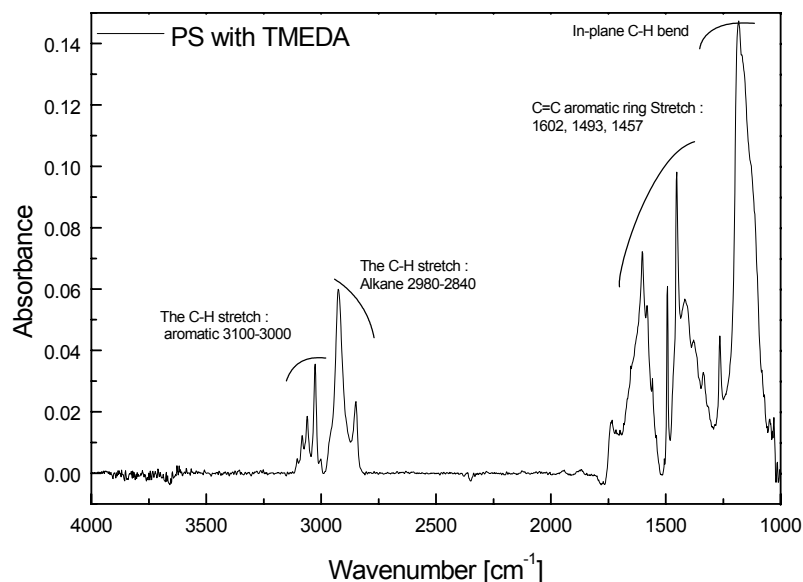
XPS spectra of the Si-wafer and Au-substrate
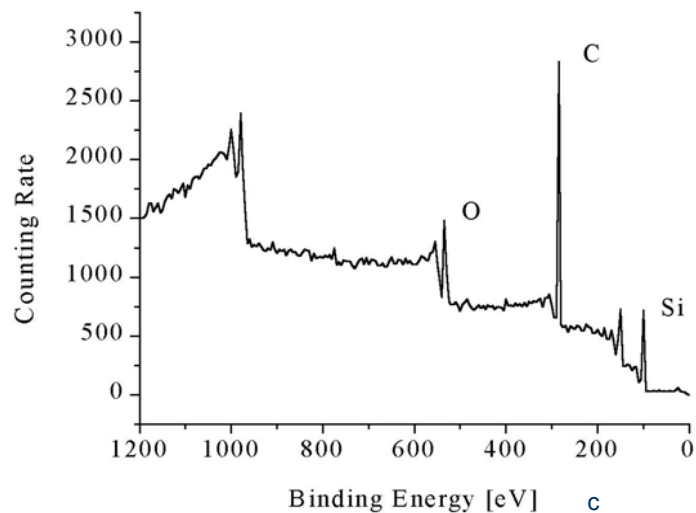
Si-wafer
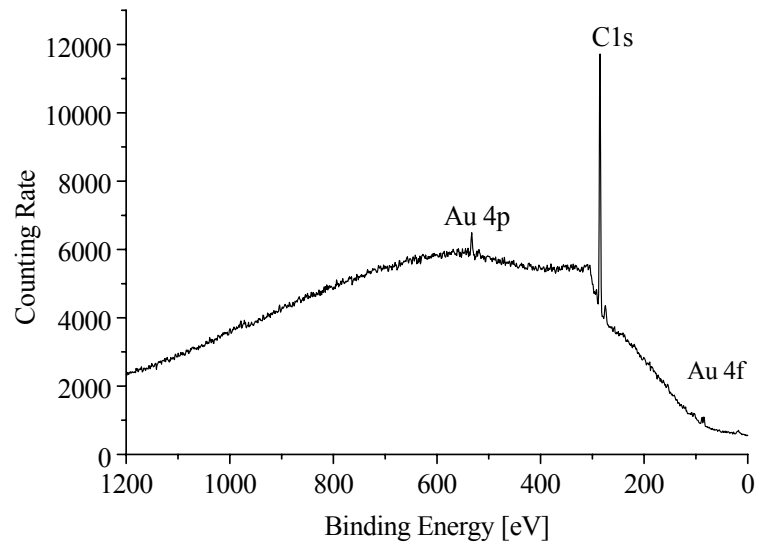
Au-coated substrate

Consistent with morphology and thickness

Degree of Polymerization and MW of Polystyrene Brush

Degree of polymerization (*N*) and molecular weight (MW) Estimation by Ulman et al.

Solvent Swelling Experiment

The height *h* of a brush in a good solvent is given by: $h = (12/\pi)^{1/3} N\sigma^{1/3}(\omega/v)^{1/3}$

Where ω is the excluded volume parameter, approximately $(2\text{Å})^3$, *N* is the number of monomers, and $v = (a^2/3)^{-1}$, with *a* = 6.7 Å (the Kuhn length for a polystyrene monomer unit. The degree of polymerization can be expressed as:

$$N = [1.074(h_{swollen})^{2/3}]/[h_{dry}(\text{Å}^2))^{1/2}]$$

When the thickness is 18nm, the N= 382, MW calculated, Mn= 39,728 g/mol.

- Jordan, R.; Ulman, A.; Kang, J.F.; Rafailovich, M.H.; Sokolov, J. *J. Am. Chem. Soc.* **1999,** *121*, 1016

OTHERS:

Theoretical Calculations: Milner, S.T. *Europhys. Lett.* **1998***, 7,* 695

Chain Stretching of tethered Polymer by AFM: Walker, G. et.al., *J. Phys. Chem. B* **2001,** *105,* 3965.

Efficiency of polymerization and mechanism

- Consistent with previous results on thickness and efficiency

- 5.6% in Anionic Polymerization of Styrene

  Ulman, A., et. al. *J. Am. Chem. Soc.* **1999**, *121*, 1016.

- time of polymerization, concentration, bulk vs. solution, % DPE on surface did not show any particular trend with thickness

- Presence of more polar additive improves thickness (TMEDA).

- **Why the low grafting density?** Hypothesis: polarity at the interface, entropic vs enthalpic considerations, desorption of initiator, activation of initiators or reaction of Si-O-Si linkage, polarity of solvent, surface energy and the propagating anion at the interface, diffusion of monomers.

- *Design of initiator and polymerization conditions needs to be reexamined*

Living Anionic Polymerization: Silica Nanoparticles
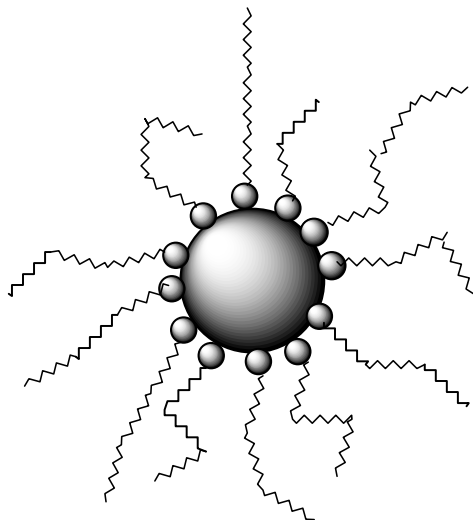
Polystyrene grafting from Si-nanoparticle surface approaches. Small spheres represent reactive initiator.

-Silica (Aerosil A200, Degussa) with a specific surface area of 200 ± 15 m^2/g

-was dried overnight at 120°C under vacuum.

12-20 nm diameter

Zhou, Q.; Wang, S.; Fan, X.; Advincula, R.; Mays, J.; "Living Anionic Surface-Initiated Polymerization (LASIP) of a Polymer on Silica Nanoparticles", *Langmuir* **2002**; *18(8);* 3324-3331.

Immobilization of the DPE-Precursor

ClSi(CH$_3$)$_2$(CH$_2$)$_8$-DPE

Tolune

Si-gel

+ excess DPE

Stirring 3 days / centrifuge

redissolving / centrifuge
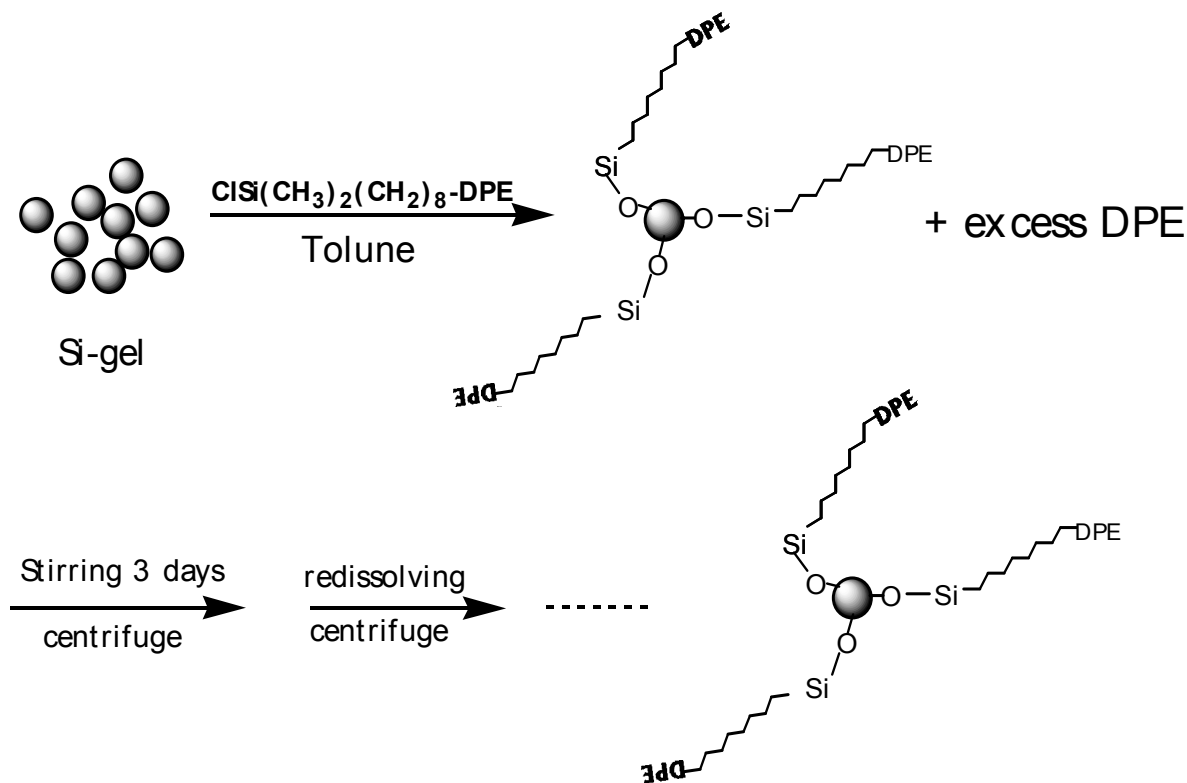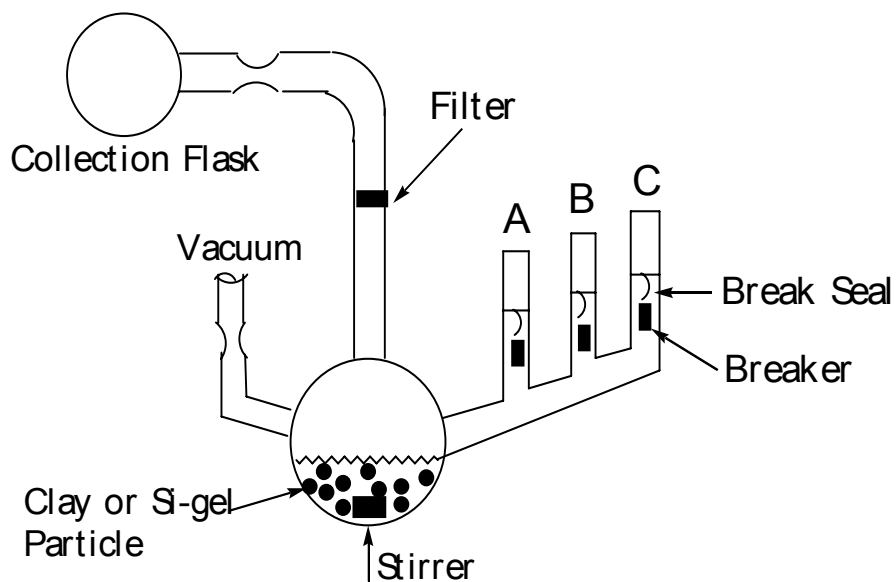
-grafting from Si-gel surface by silane coupling reaction.

-The immobilization of the DPE derivative on silica surface was done by mixing excess DPE derivative with dried toluene and pyridine and dispersing silica with vigorous stirring for several days in a glove box.

Apparatus for Polymerization of Nanoparticles

Schematic diagram of the
polymerization set-up under vacuum
A: ampoule containing styrene,
B: ampoule containing n-BuLi,
C: ampoule containing MeOH

-*a key design is the inclusion of a
filter unit*

- *polymerization may be followed based
on red-color of the Li-DPE complex*

Polymerization: Step-by-step
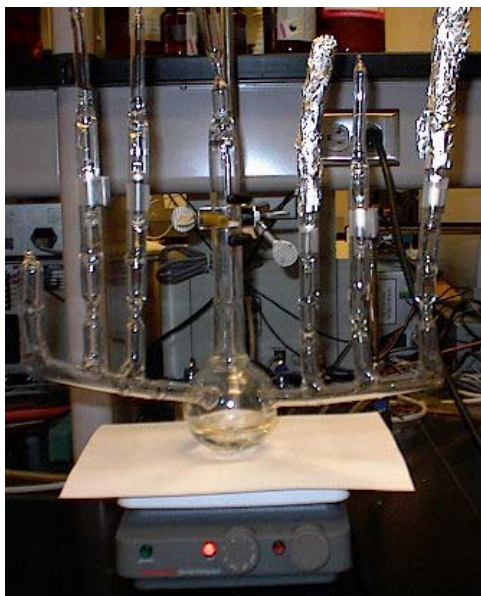
(A)   DPE initiator coated
Si-gel particles suspension

(B) Adding n-BuLi

Continued ...

(C) DPE reacted with n-BuLi

(D) DPE further reacted with n-BuLi

Continued...
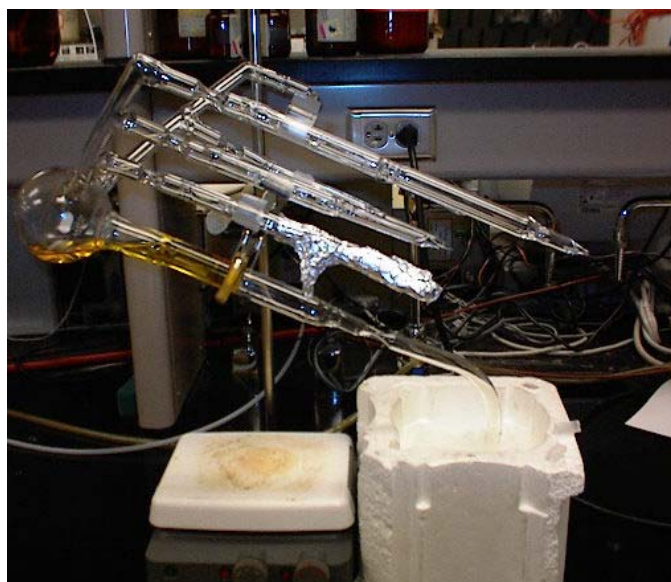
(E) Separation of initiated Si-gel
from solution

(F) Initiated Si-gel stored
on the filter

Continued...

(G) The solution in the collection flask with yellow color

(H) Initiated Si-gel redissolved in Benzene

Continued...

Free DPE initiator could be washed away from the Si-gel surfaces, the amount of initiator determined by TGA may be over estimated

(I) Termination of polymerization by MeOH

Cleavage of bound polymers and analysis
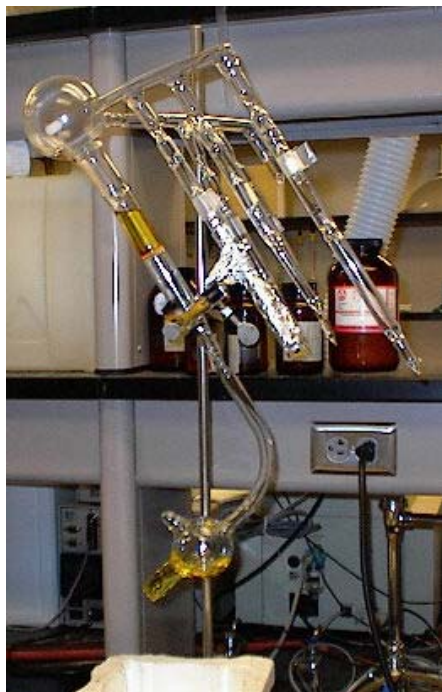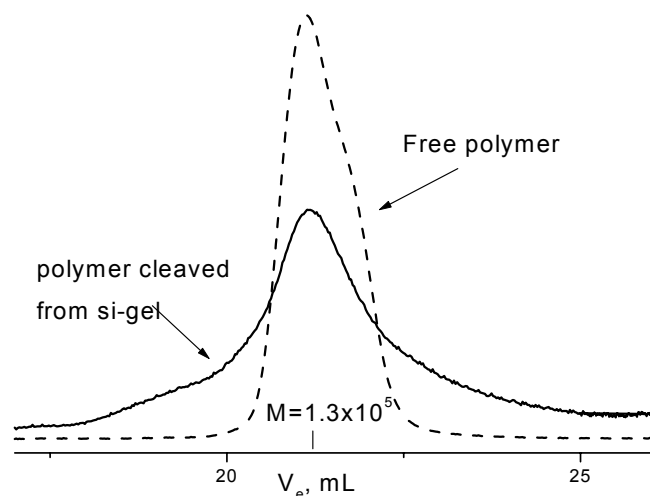
SEC analysis

Free polymer

polymer cleaved
from si-gel

$M=1.3 \times 10^5$

20   V_e, mL   25

REMOVAL: Si-gel with bound polymers was mixed with KOH, Alcohol and THF, and fluxed overnight. The solution was centrifuged to remove the particles from polymer.

Monomer content (g styrene/g si-gel)
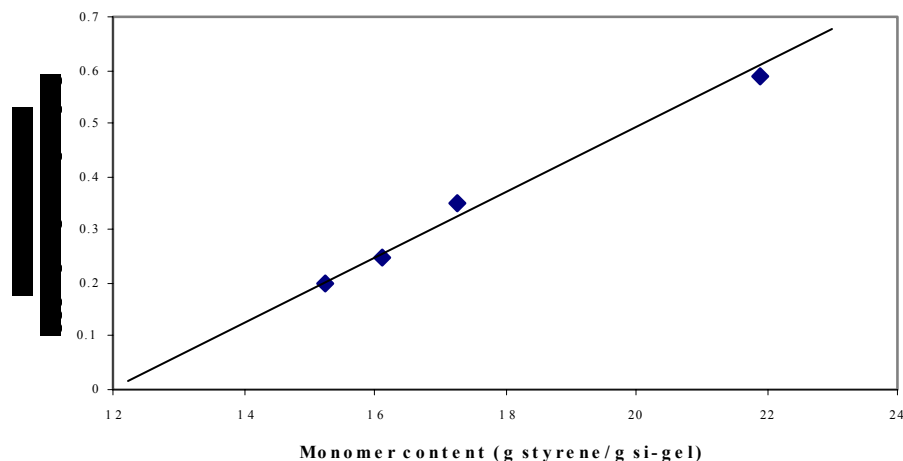
SEC traces for toluene-soluble and bound polymers on Si-gel (SP-3) : A Linear relationship of MW with monomer concentration demonstrates a "living" nature of LASIP.

Polymerization Results

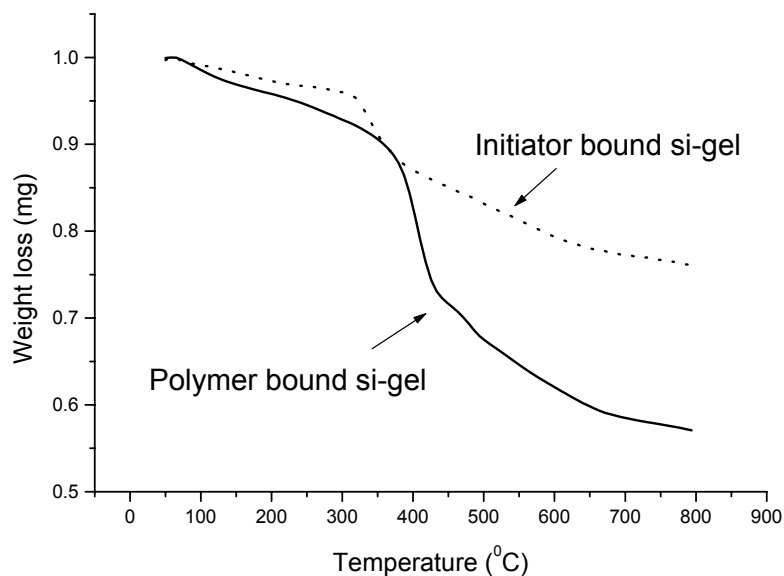| SAMPLE	INITIATOR	ADDITIVE	MONOMER	AMOUNT g styrene/ g Si-gel	Mn (C) [Mw/Mn]	Mn (s) [MW/Mn]
S-7	n-BuLi	THF	styrene	21.89	397,000 [1.79]	433,000 [2.02]
SP-2	n-BuLi	THF	styrene	15.23	101,000 [1.21]	190,000 [1.18]
SP-3	n-BuLi	THF	styrene	17.28	135,000 [1.19]	126,000 [1.14]
SP-4	n-BuLi	THF	styrene	16.10	110,000 [1.25]	133,000 [1.20]

Mn(C):molecular weight of polymer cleaved from Si-gel

Mn(s):molecular weight of polymer formed in the solution

[ ]: polydispersity

Characterization of Bound Polymer

Weight loss (mg) vs Temperature (°C)

Initiator bound si-gel

Polymer bound si-gel

TGA results of SP-3 show:

6.3% (0.95x 10-3 mol initiator/g Si-gel) efficiency on the Si-gel surfaces.

80g of bound polymer would be expected if each site had a chain attached with 1.3x105 molecular weight

30% bound polystyrene in the PS/Si-gel system from our experiment

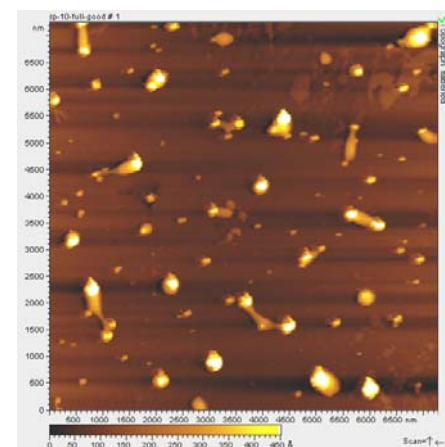Meier, L.P.; Shelden, R.A.; Caseri, W.R.; Suter, U. *Macromolecules,* **1994***, 27,*1637.

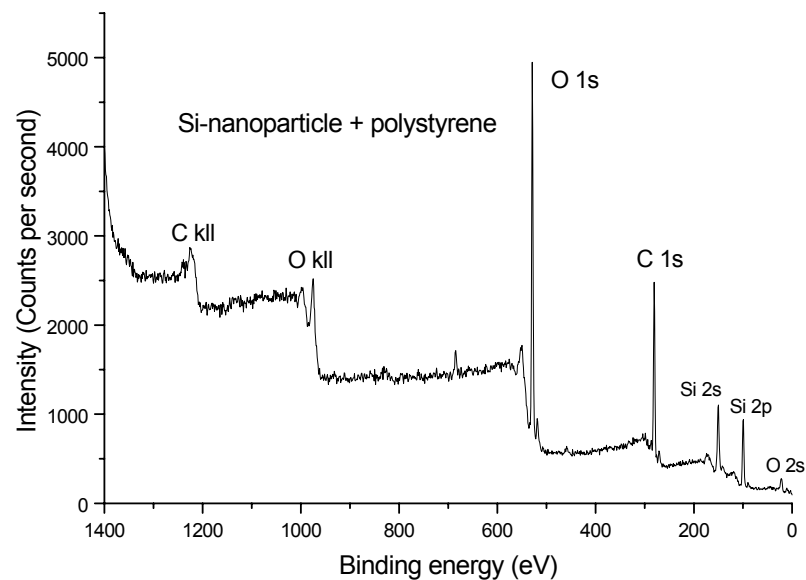- TGA results of initiator bound and polymer bound Si-nanoparticles (SP-3)
-Decomposition temperature of bound polymer increases to 418°C compared to 332°C of initiator
- Polymer weight composition of the "nanocomposite"

AFM

Further characterization…

IR spectrum of polymer cleaved from Si-nanoparticles

u(C-H)

u(C= C)
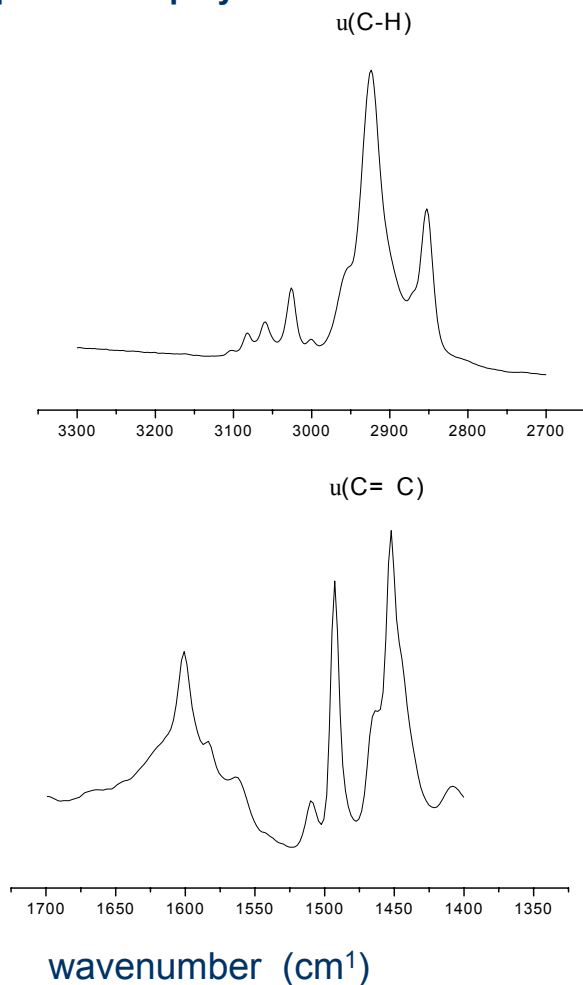
## XPS of pressed Powder

wavenumber (cm^1)

3061(cm^{-1}) and 3028 (cm^{-1}): polystyrene aromatic
CH stretching vibrations. 2925 (cm^{-1}) and 2852
(cm^{-1}):aliphatic CH stretch. 1600 (cm^{-1}), 1496
(cm^{-1}), and 1458 (cm^{-1}): polystyrene aromatic
ring vibrations

LASIP on Clay Nanoparticles ? Yes!

-direct initiation on the surface, lamellar or surface
- electrostatic interaction or covalent linkage
- aggregation and exfoliation
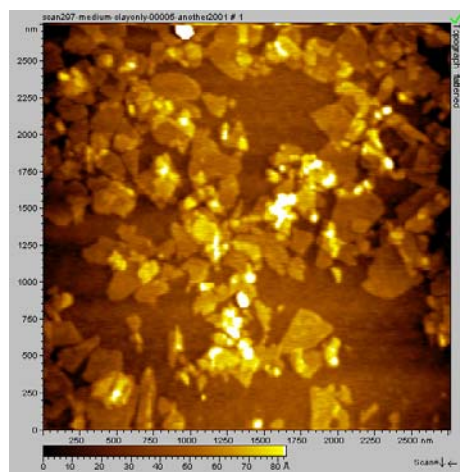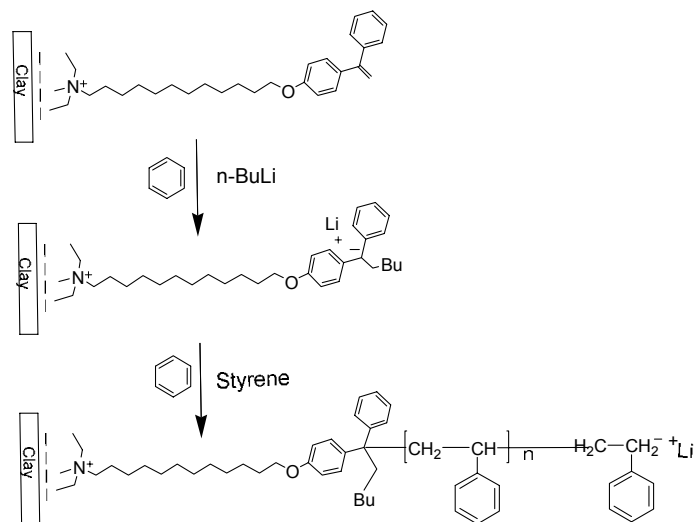
Weimer,W.; Chen, H.; Giannelis, E.; Sogah, D.
J. Am. Chem. Soc., **1999**, *121*, 1615.

Intercalation, activation, polymerization

Intercalation → Polymerization

Collection Flask
Filter
Vacuum
A B C
Break Seal
Breaker
Clay Particle
Stirrer
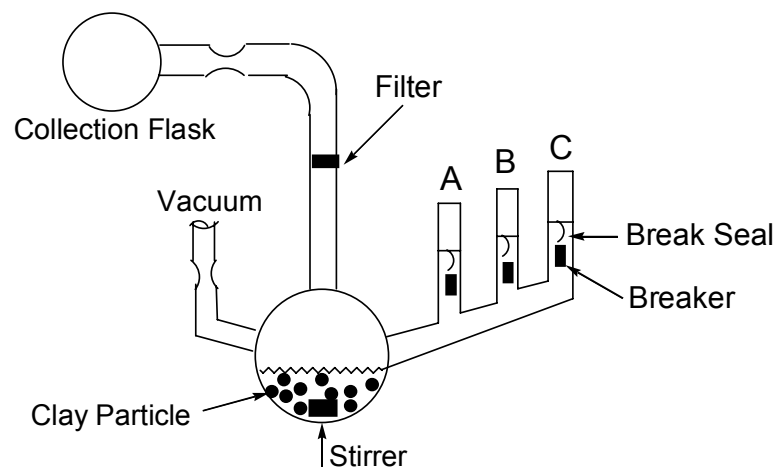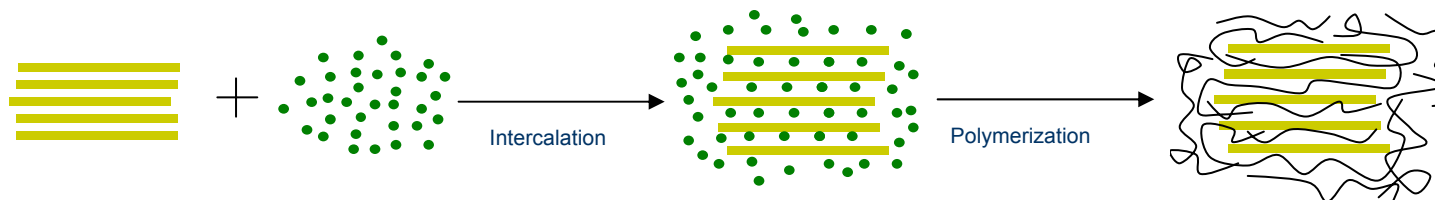
- exfoliation followed by DPE attachment
- **Drying and 120 °C heating important**
- introduction of n-BuLi, several washings
- introduction of monomer
- polymerization
- termination
- analysis of attached (composite) and detached polymers

Fan, X.; Zhou, Q.; Xia, C.; Cristofoli, W.; Mays, J.; Advincula, R.; "Living Anionic Surface-Initiated Polymerization (LASIP) of Styrene from Clay Nanoparticles Using Surface Bound 1,1-Diphenylethylene (DPE) Initiators", *Langmuir* **2002**; *18(11);* 4511-4518.

Polymerization results, SEC characterization

Batch	Styrene/ DPE (g/mmol)	Mn (SEC)[a] x 10^{-3} (s)[b]	PDI[c] solution[b]	Mn(SEC) [a,d] x 10^{-3} cleaved	PDI[c] (cleaved)[d]	Bound PS/clay (PS/g clay)
CP-1	14.6	78.6	1.09	11.9	1.44	0.62
CP-6	19.9	58.5	1.30	21.8	1.30	0.81
CP-3	9.6	35.5	1.20	7.4	1.31	0.45
CP-4[e]	21.8	100.1	1.10	23.6	1.40	0.79

[a] number average molecular weight (Mn) and weight average molecular weight (Mw) were determined by size exclusion chromatography(SEC) with PS standard. [b] Polymer formed in solution. [c] Polydispersity index, Mw/Mn. [d] Polymer cleaved from clay surfaces. [e] Cumyl potassium was used as initiator instead of n-BuLi

- consistent with anionic mechanism but higher polydispersity
- also linear relationship of MW with monomer concentration

IR Characterization, TGA and X-ray Diffraction
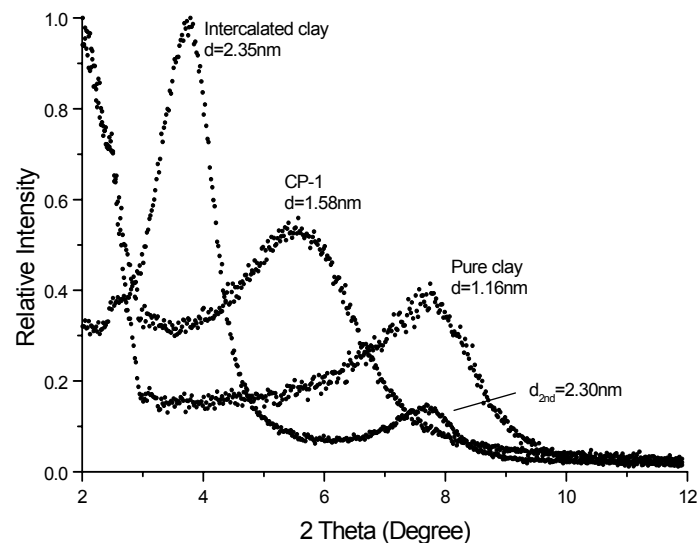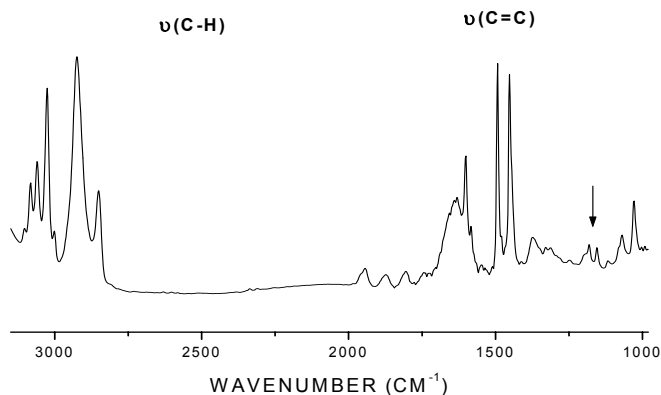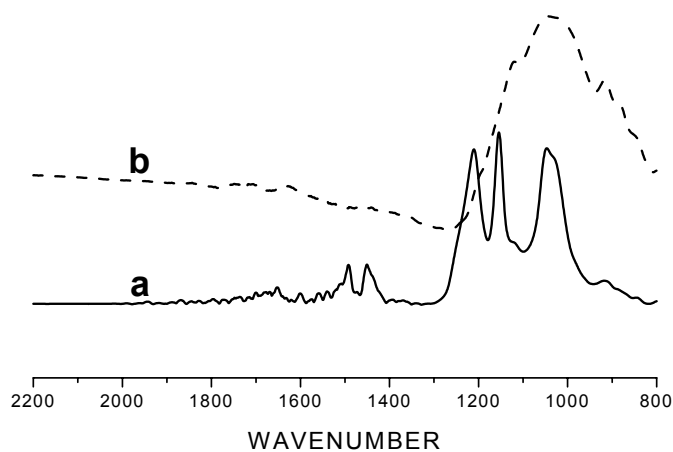
-**XRD**. basal spacing of the initiator- clay was is 2.34 nm, becauset pure clay is 1.14 nm, the initiator layer thickness ~1.2 nm.
-polymer-clay composite - a very broad peak centered at 1.58 nm.
- most polymerization occurred at the surface

-**TGA**, a two step decomposition of the clay-initiator at 330°C and the other one around 580°C. With bound polymer decomposition temperature increased to 418°C

- **IR:** *End group : ~C(C$_2$H$_5$)$_3$N$^+$Br$^-$ present on the attached and detached polymers.*
-*Spectra consistent of polystyrene*

Conclusions

- A general scheme for surface initiated polymerization involves tethering initiators at the surface of the nanoparticle: addition polymerization but also step-condensation polymerization schemes should be possible.

- Initiator control is critical as well as optimization of polymerization conditions with colloids.

- Formation of homopolymers, copolymers, and even hyperbranched polymer architectures possible. In the future, more complex graft copolymer and dendritic structures.

- Application of surface sensitive spectroscopic and microscopic methods are important both with ex-situ and in-situ methods of analysis.

- Nanoparticles are more processable with a polymer shell: processing conditions can be tailored. Nanocomposite properties must be studied.

- Active and passive role of the polymer shell with the nanoparticle property needs to be explored: optical, magnetic, spectroscopic, catalytic.

Acknowledgment