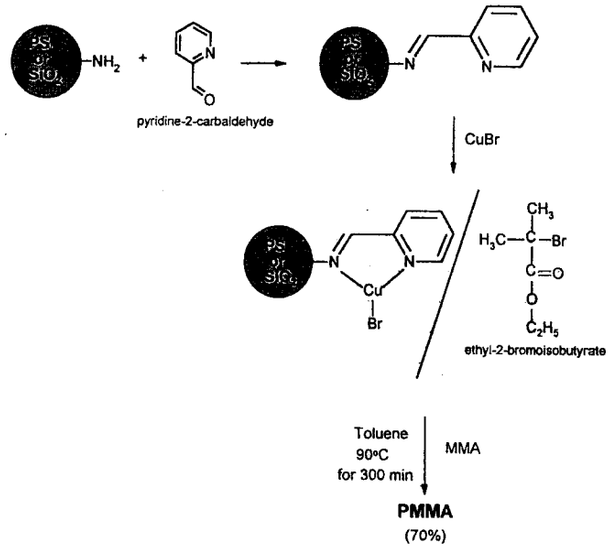
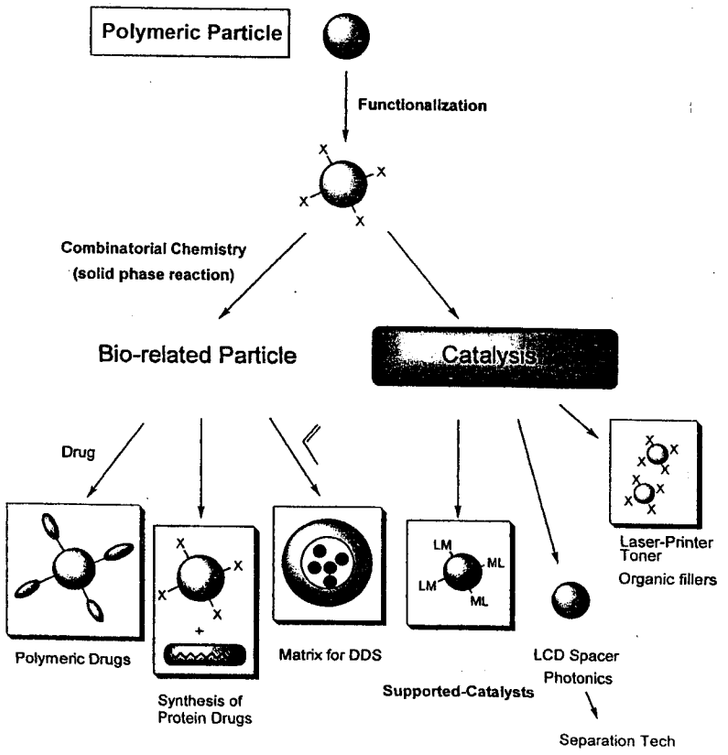
Supported ATRP Catalysis

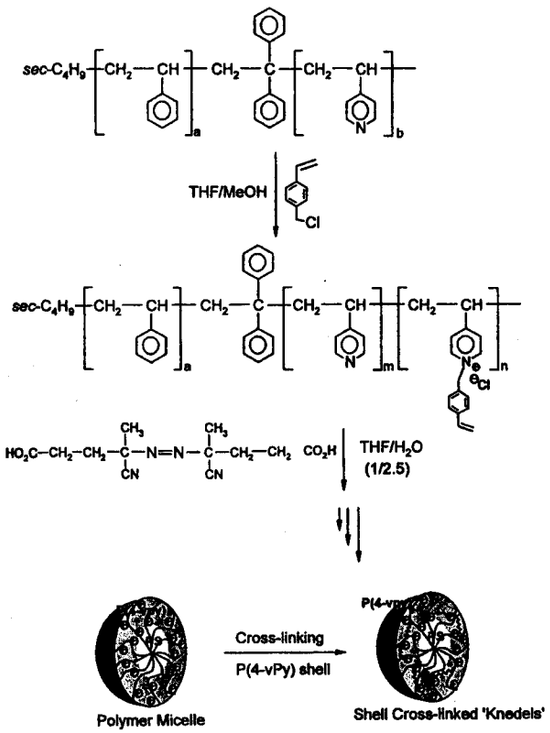


ref) Haddleton, D. M.; Kukulj, D.; Radigue, A. P. *Chem. Commun.* **1999**, 99.

Map for Applications of Polymeric Particles

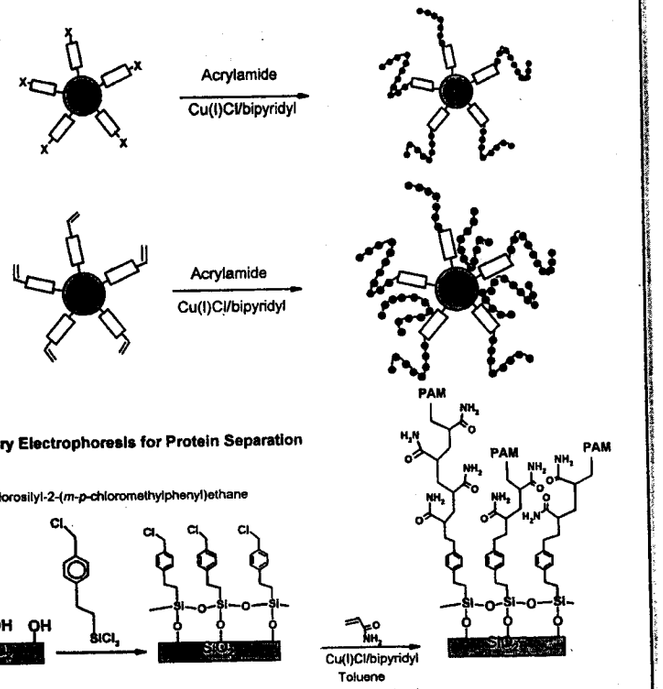


Shell Cross-linked Knedels



ref) Thurmond, II, K. B.; Kowalewski, T.; Wooley, K. L. *J. Am. Chem. Soc.* **1997**, *119*, 6656-6665.

Surface-Confined ATRP for Coatings



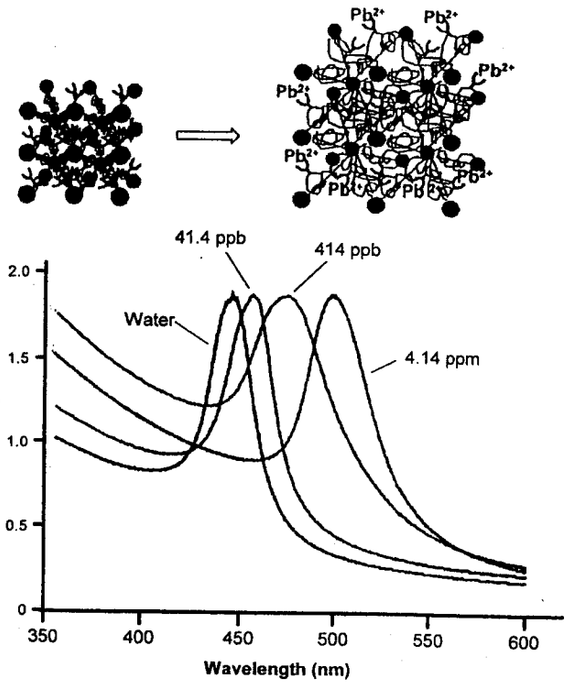
ref) Huang, X.; Doneski, L. J.; Wirth, M. J. *Anal. Chem.* **1998**, *70*, 4023.

Application of Dispersed Polymers

Particle Size: 0.01 ~ 10 μm
Solid Contents: 20 ~ 70 %

1. Impact Modifier
2. Surface Coating: Automotive Coating
3. Cosmetics & Polishes
4. Encapsulation: Pigments, Insecticides, and Metal salts
5. Lacquers or Dry-inks: High Solid Content
   - Electrostatic Developer
   - Adhesives
   - Printing Inks
6. Elastomers
7. Immunoassay: 2 μm; hydroxylated dispersion
   - Radioimmunoassays (RIA)
   - Immunoradiometric Assays (IRMA)
8. Template for 3-D arrays of spheroidal voids
   - Optoelectronics
   - Porous membranes
9. Diffractive element ← 3-D crystalline assemblies
   - Optical filters
   - Sensors

Visible Spectra of Acrylamide Crystalline Colloidal Arrays (CCA) Pb^{2+} Sensor

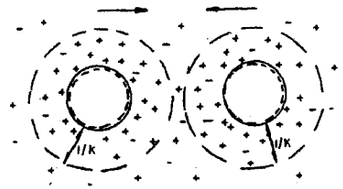


ref) Holtz, J. H.; Asher, S. A. *Nature* **1997**, *389*, 829.

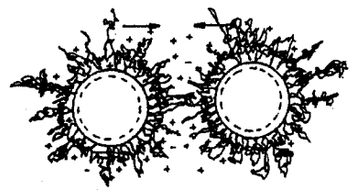
Examples of Dispersed Polymers (Addition Polymerization)

Stabilizing Polymer	Disperse Polymer	Medium
Natural Rubber	PMMA, PVAc	Alkane
Butyl Rubber	PMMA	
Polyisobutylene	PMMA	
Poly(lauryl methacrylate)	PVC, PMMA, Polyacetal	
Poly(ethyl hexyl acrylate)	PVAc	
Poly(12-hydroxystearic acid)	PMMA, PAN, PVDC, PVAc, PVP	
Poly(dimethylsiloxane)	PMMA, PS, PAN, poly(a-methylstyrene)	
Poly(*t*-butylstyrene)	PS	
Polystyrene	PAN	Toluene
Poly(ethylene terephthalate)	Poly(acrylic acid)	Chloroform
Poly(vinylpyrrolidone)	PS	Ethanol
Hydroxypropylcellulose	PS	Methoxyethanol Ethanol

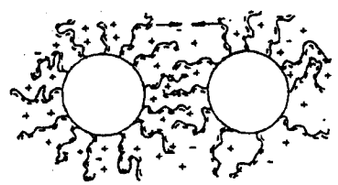
Concept of Stability of Polymeric Particles



Electrostatic Stabilization

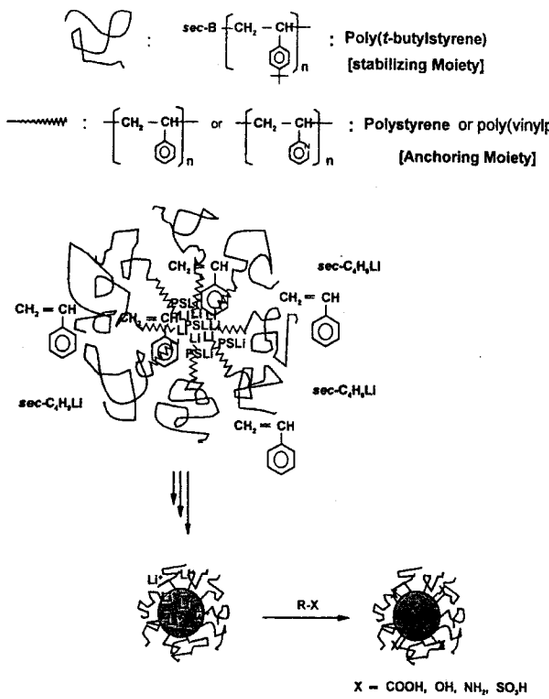


Steric Stabilization



Electrosteric Stabilization

Schematic Diagram of Living Dispersion Polymerization

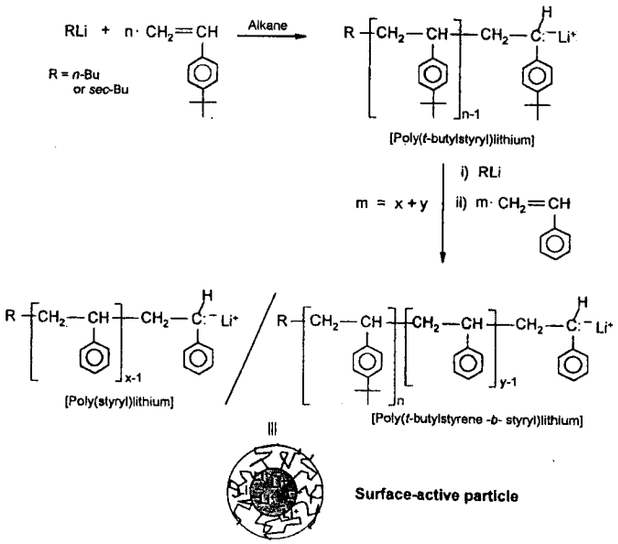


Living Dispersion Polymerization ???

Definition

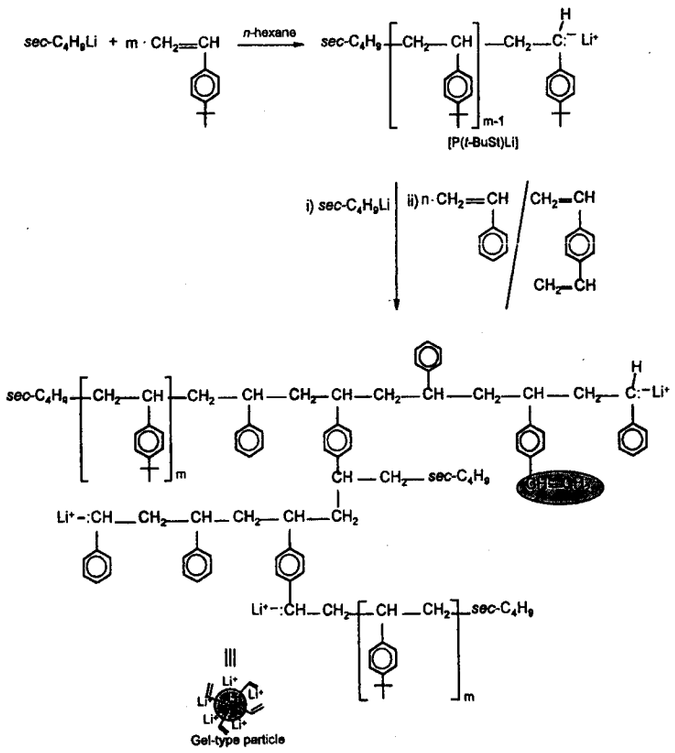
A dispersion polymerization *in which both steric stabilizer and core are simultaneously formed by a mixture of the growing steric stabilizing moiety and a simple initiator leads to the generation of particle retaining the surface-living nature.*

❖ **Anionic Scheme**



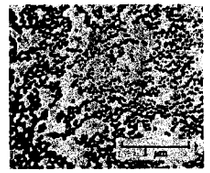
ref) Kim, J.; Jeong, S. Y.; Kim, K. U.; Ahn Y. H.; Quirk, R. P. *J. Polym. Sci ; Part A; Polym. Chem.* **1996**, *34*, 3277.

Microgel by Living Dispersion Copolymerization

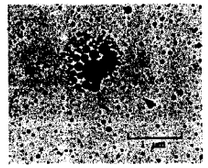


ref) Kim, H. J.; Ryu, H.; Kim, K. H.; Kwak, S.; Hwang S. S.; Kim, K. U.; Kim, J.; Ihm, S. S. *Korea Polym. J.* **1999**, *7*, 64.

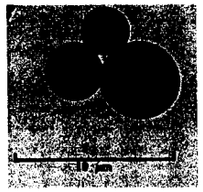
Control of Particle Size of Dispersed Polymers



DSP 7

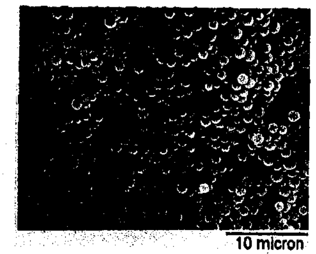


DSP 8

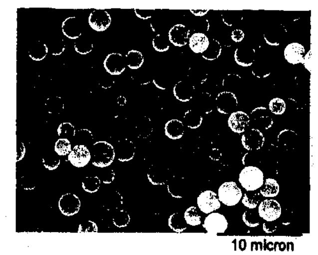


DSP 9

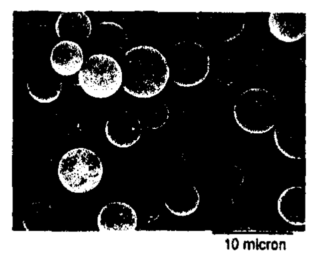
Control of Particle Size of Disperse Poly(styrene -co- DVB)



LDP 2
(1.2 ± 0.003 μm)



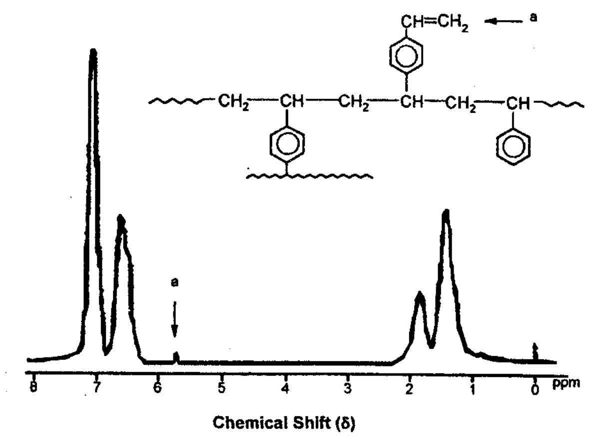
LDP 3
(2.7 ± 0.025 μm)



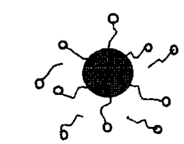
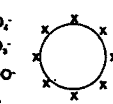
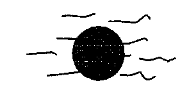
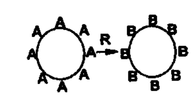
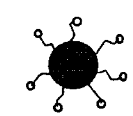
LDP 5
(6.3 ± 0.500 μm)

¹H NMR Spectrum of Microgel (LDP 6)

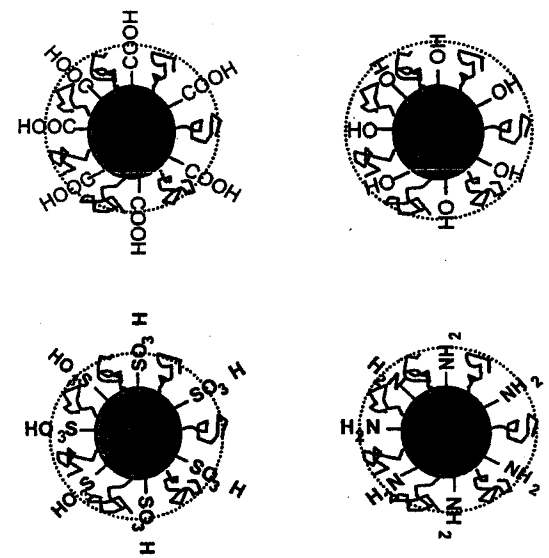
Precipitation in MeOH → Drying → Grinding → Dissolving → Filtration



Surface-Functionalizations of Latex Particles

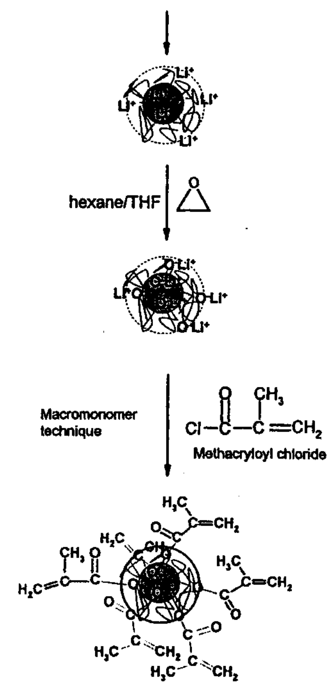
Method	Structure	Remarks
Conventional Emulsifier ionic nonionic zwitterionic		∘ Physical Adsorption of Emulsifier (Desorption) ∘ Effect of the polarity of the polymer on the emulsifier adsorption
Initiator ionic ⎤ Charges nonionic ⎦	x = SO_4^- SO_3^- COO^- etc. 	∘ Covalently bound surface groups ∘ Model colloids ∘ Low solids (< 20%)
Functional Monomer ionic nonionic		∘ High solids ∘ Distribution of the monomer in the various phase ∘ Complex surface morphology
Post reaction in latex		∘ Modification of the surface end group functionality
Surface Active Monomer		∘ Control of surface charged density ∘ Low level of water soluble Polymers

Functionalized Disperse Polymer

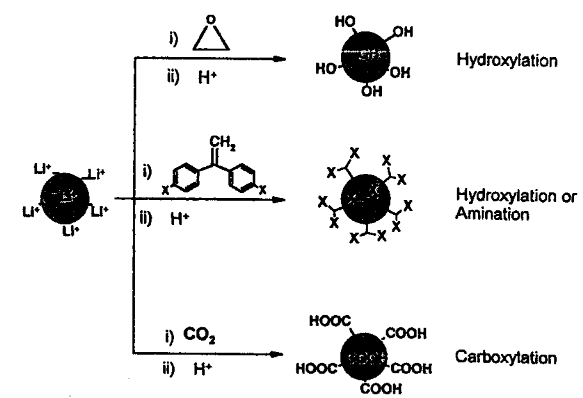


Macromonomer Type of Disperse Polymer

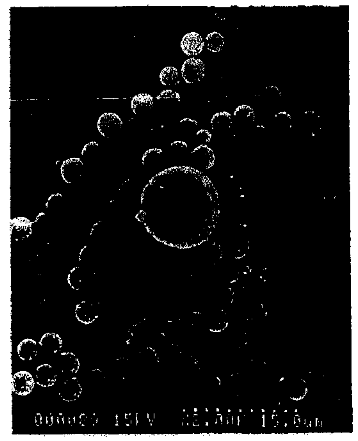
Living Dispersion Polymerization



Functionalizations of Living Disperse Polymers

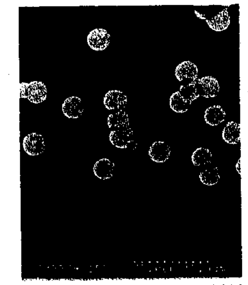


3-D Crystalline Assembly of Multi-macromonomeric Disperse Polystyrene

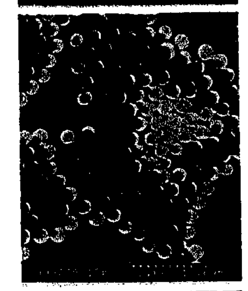


Bi-layer Assembly

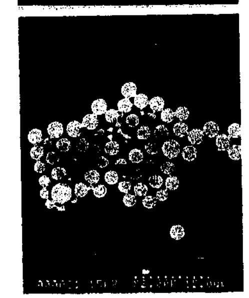
Comparison of SEM Photogaphs of Unfunctionalized, Hydroxylated, and Multi-macromonomeric Disperse Polystyrenes



Unfunctionalized Disperse Polystyrene



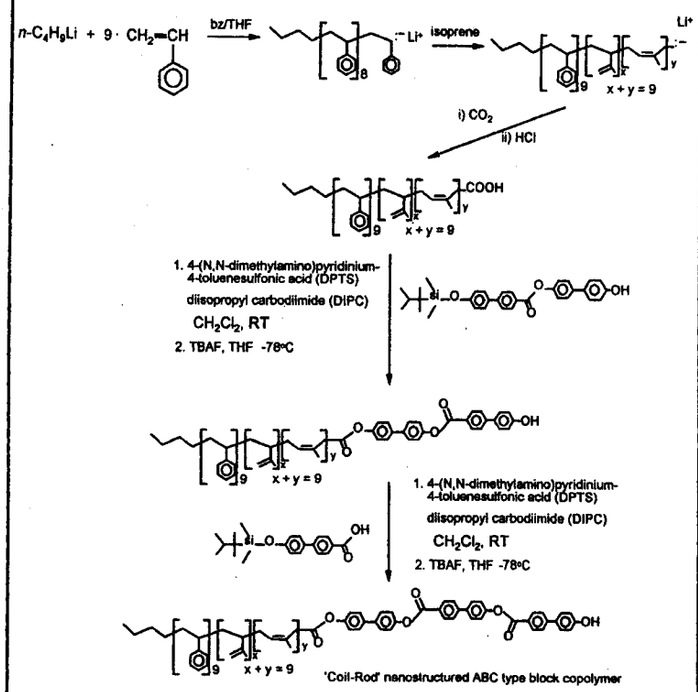
Hydroxylated Disperse Polystyrene



Multi-macromonomeric Disperse Polystyrene

Supramolecular Materials
Coil-Rod Nanostructures

Function: Geometry & Symmetry



ref) Stupp, S. I.; LeBonheur, V.; Walker, K.; Li, L. S.; Huggins, K. E.; Keser, M.; Amstutz, A. *Science* **1997**, *276*, 384.

Applications of Block Copolymers

- **Emulsifier** ⟶ **surfactant in dispersion polymerization**
- **Dispersants** ⟶ **stabilization of pigments, cosmetics, and drugs**
  Hybridization of inorganic salts
- **Foamer**
- **Thickeners**
- **Rinse aids**
- **Compatibilizers** ⟶ **polymer blends**

Principle & Application

- Hydrophobic & Hydrophilic effecs
- Hydrogen bonding
- Coulombic interaction
- van der Waals interaction

↓

Self-organization ⟶ Phase / Microphase ⟩ separation
Mesophase formation
Adsorption
Crystallization

↓

- Morphology control
- Micellar aggregation ⟶ nanoreactor
  template for mesophase
- Rearrangement of the aggregates ⟶ compatibilization
  surface stabilization

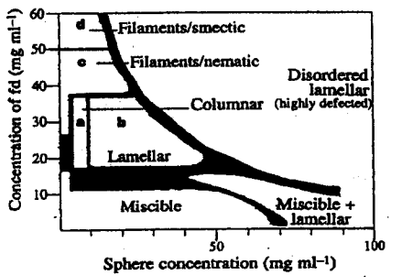
↓

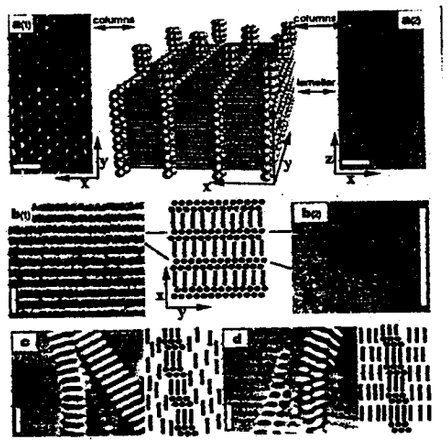
Polymer/Inorganic salts Hybrids ⟶ (size-controllable supramolecular assembly) ⟶ opto-electronics

Phase Diagram of Rod/Sphere Mixtures

(Bacteriophage fd Virus / Dilute PS Spheres)

Entropically driven microphase control

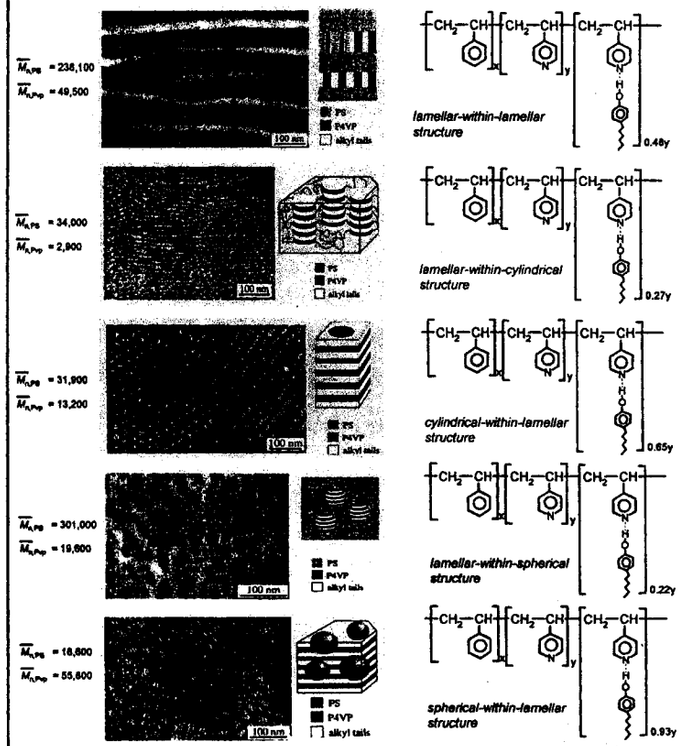




ref) Adams, M.; Dogic, Z.; Keller, S. L; Fraden, S. *Nature* **1998**, *393*, 349.

Control of Nanostructures Using Polymer/Amphiphile Complexes

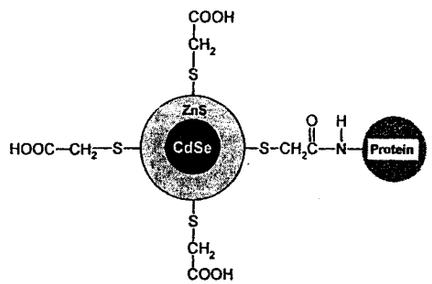
p-nonadecylphenol = 4-*n*-$C_{19}H_{39}$-C_6H_4-OH



ref) Ruokolainen, J.; ten Brinke, G.; Ikkala, O. *Adv. Mater.* **1999**, *11(9)*, 777.

Quantum Dot Bioconjugates for Ultrasensitive Nonisotropic Detector

Highly luminescient semiconductor quantum dots
(zinc sulfide-capped cadmium selenide)



- DNA sequencing
- Clinical diagnostics
- Fundamental molecular biology

ref) Chan, W. C. W.; Nie, S. *Science* **1998**, *281*, 2016.

Copolymers used in DDS

Composition	Mechanism	Application
Methyl methacrylate, and 2-Hydroxyethyl methacrylate		
Methyl methacrylate, 2-hydroxyethyl methacrylate, methacrylic acid, and ethyleneglycol dimethacrylate		
Methyl methacrylate, 2-hydroxyethyl methacrylate, methacrylic acid, acrylamide, and ethyleneglycol dimethacrylate	emulsion or γ-irradiation polymerization	Attachment of antibodies, radioactive amino acids, and fluorescent molecules
2-Hydroxyethyl methacrylate, methacrylic acid, and *N,N'*-bis-methyleneacrylamide		
2-Hydroxyethyl methacrylate, methacrylic acid, acrylamide, and *N,N'*-bismethyleneacrylamide		
Styrene	Emulsion	not biodegradable immunosorbent Vaccination
4-Vinylpyridine or 2-vinylpyridine *N,N'*-bismethyleneacrylamide	radical	Binding metals
4-Vinylpyridine or 2-vinylpyridine 2-hydroxyethyl methacrylate		
Acrolein	γ-irradiation polymerization	Attachment of protein drugs, enzymes, antibodies
Glutaraldehyde	aldol condensation	Magnetic properties (Fe content) fluorescent
Dialkyl methylidenemalonic acid ester	cationic polymerization	intraveneous injection
Alkyl cyanoacrylate	interfacial polymerization or anionic polymerization	nanocapsules

Polymer Coated Inorganic Salts

Hard-Soft Acid-Base (HSAB) Principle

$$d = \left(\frac{6\, f\, m\, Z}{\pi\, \rho\, N_A} \right)^{1/3}$$

N_A = Avogradro's number

- d = diameter of colloid
- $f = \frac{[M]}{[A]}$ — [M] → metal precursor; [A] → Monomer
- m = molar mass
- ρ = density of metal

(1) Co-colloid → Paramagnetic → Superparamagnetic → Ferromagnetic

Control of morphology within block copolymers

ref) Platonova, O. A.; Bronstein, L. M.; Sododovnikov, S. P.; Yanovskaya, I. M.; Obolonkova, E. S.; Valetsky, P. M.; Wenz, E.; Antonietti, M. *Colloid Polym. Sci.* **1997**, *275*, 426.

(2) CdS-colloid → core-block size (PS-*b*-PAAc) → redshift of absorption spectra

ref) Moffitt, M.; Eisenberg, A. *Chem. Mater.* **1995**, *7*, 1178

ZnO-colloid → UV-absorber in polymer film (λ < 350 nm)

ref) Forster, S.; Antonietti, M. *Adv. Mater.* **1998**, *10*, 195.

(3) Pd- or Au/Pd-colloid → Catalyst for hydrogenation of Heck coupling reaction

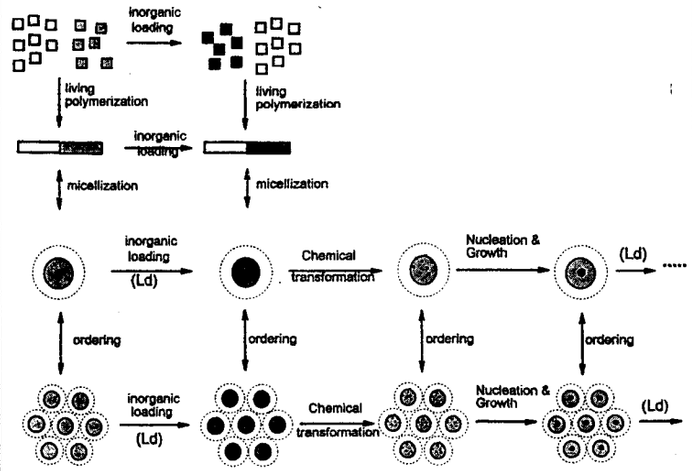
'highest' activity

'rasphery' morphology

Hybrid system → recyclable

ref) Mayer, A. B. R.; Mark, J. E. *Colloid Polym. Sci.* **1997**, *275*, 333.

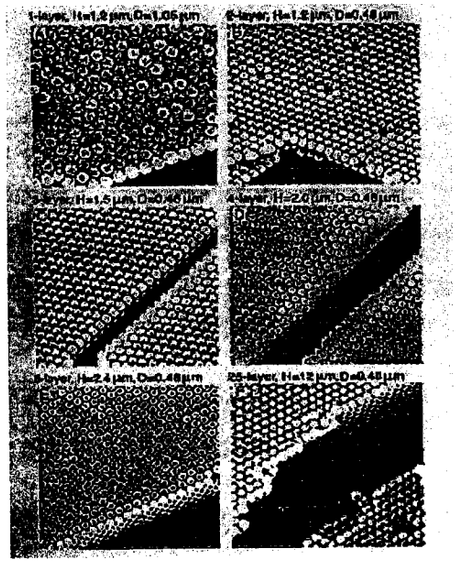
Scheme for Preparing Inorganic Colloids in Block Copolymers



ref) Forster, S.; Antonietti, M. *Adv. Mater.* **1998**, *10*, 195.

Assemblies of Polystyrene Particles in Fabricating Tunable Optical Filters

3-*D* Crystalline Assemblies of Particles → as Diffractive Elements → Sensor or Optical components



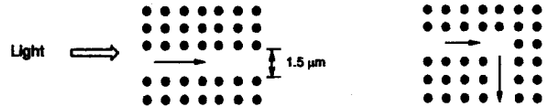
ref) Park, S. H; Xia, Y. *Langmuir* **1999**, *15*, 266.

Photonic Crystals

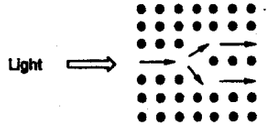
Defect Modes ⟶ **Waveguide, resonator, splitter**

⌘❖ Circuit Elements

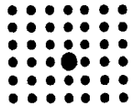
1) Waveguide ⟵ by line defects



2) Splitter/Combiner



3) Resonator ⟶ entrapping light ⟶ laser



Channel drop filter, All-optical switch

⌘❖ Fabrication Technology

- Electron beam lithography
- Imprinting technology

pinpoint photo polymerization tech.

Future Applications of Nanoparticles

✖ **One single Colloid per Microdomain** ⟶ For electro-optic Application (information data storage)

✖ **A large number of colloids within microdomain** ⟶ For catalysts (fuel cell ??)

❖ Nano-sized Colloids in Self-assembly

- Hexagonally ordered cylinder ⟶ Nanowire
- Lamellar structure ⟶ Nanocapacitor
- Nanocrystals ⟶ Photovoltaic / Electroluminescent) Device

  - Opal-like Crystal of CdSe nanocrystal
  - Porous Silica Thin Film
  - Liquid-Junction Porous TiO_2 Solar Cells (Gratzel cell)

Nano-structured particles ⟶ **Advanced Electronics**