Techniques for Synthesizing Polymer Particles

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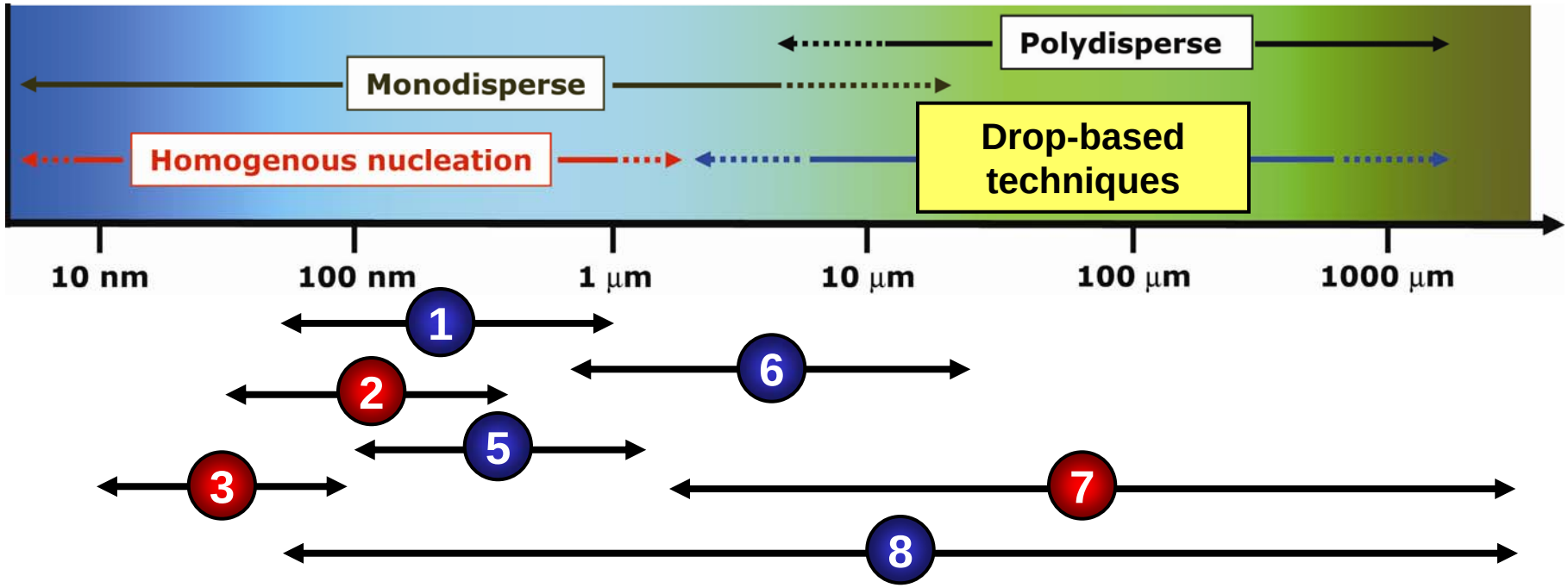
Current techniques

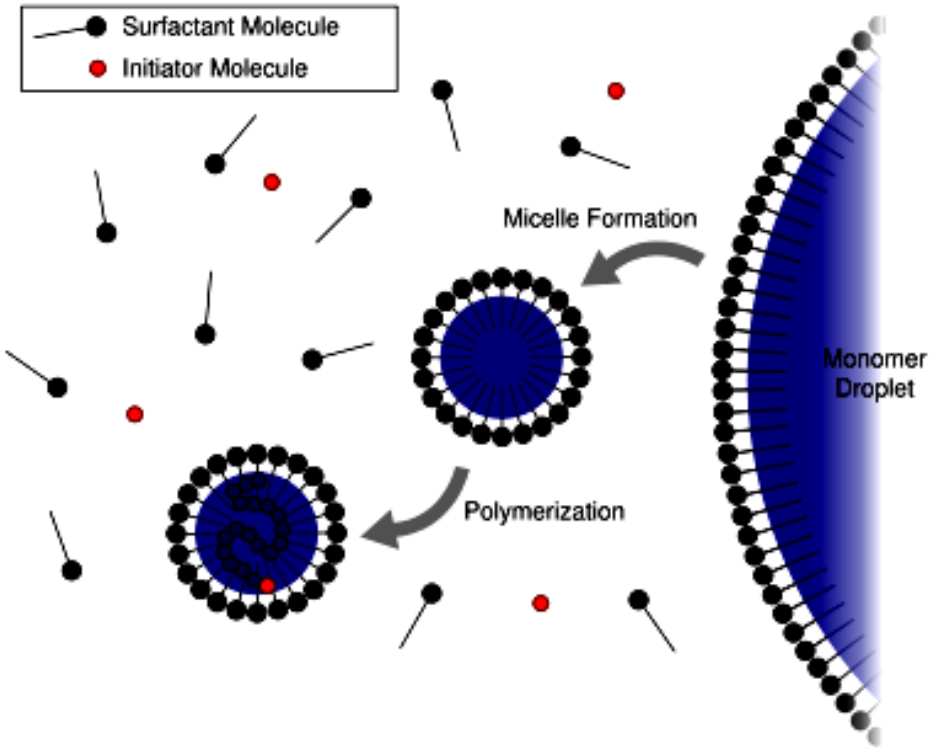
1. Emulsion polymerization
2. Miniemulsion polymerization
3. Microemulsion polymerization
4. Precipitation polymerization
5. Dispersion polymerization
6. Suspension polymerizations
7. Seeded polymerization

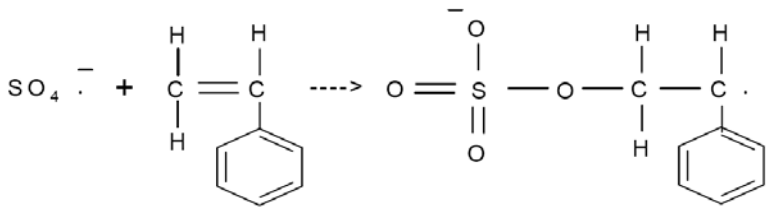
Basic considerations

- A batch process
- Radical polymerization
- Monodispersity: <30%



(Macro)emulsion polymerization





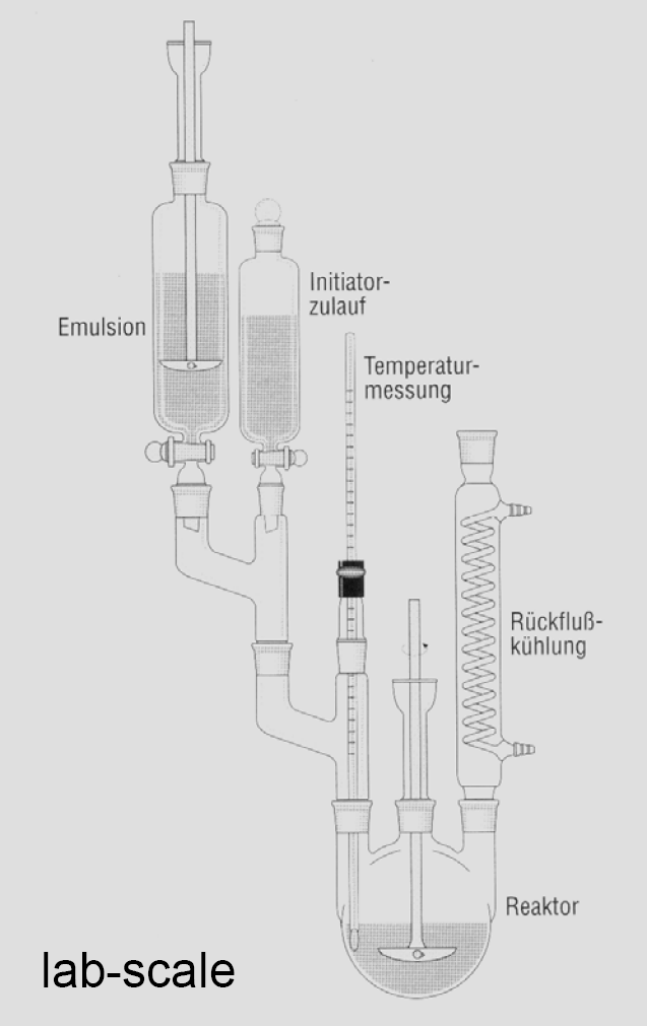
Features

- Heterogeneous system
- Nucleation site: water (in micellar or homogeneous)
- ~20nm – ~1μm
- Monodisperse
- Polymerization time: fast
- High MW
- Surfactant-free is possible

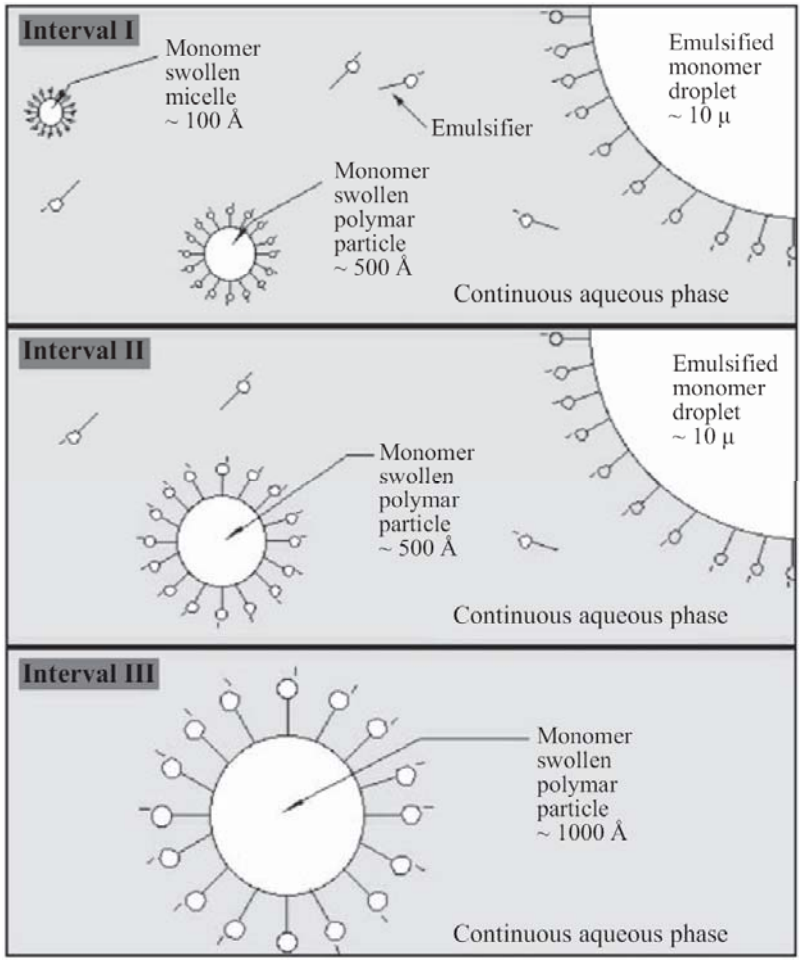
Components

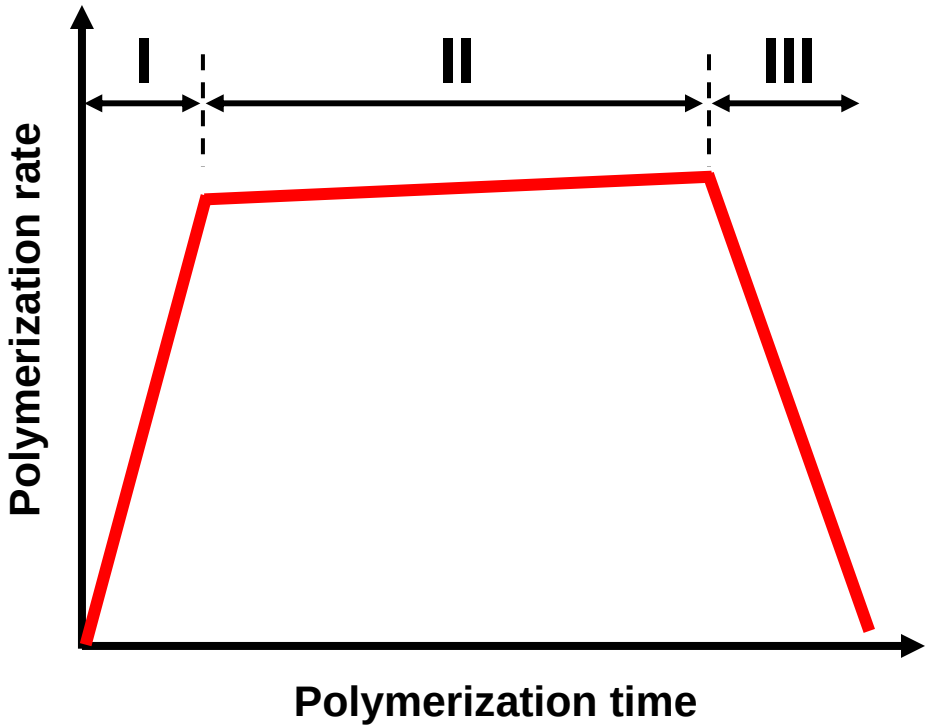
- Monomers
- Water
- Water-soluble initiator
- Surfactant

Reactors


Emulsion
Initiator-
zulauf
Temperatur-
messung
Rückfluß-
kühlung
Reaktor
lab-scale

Stage of emulsion polymerization





Interval I

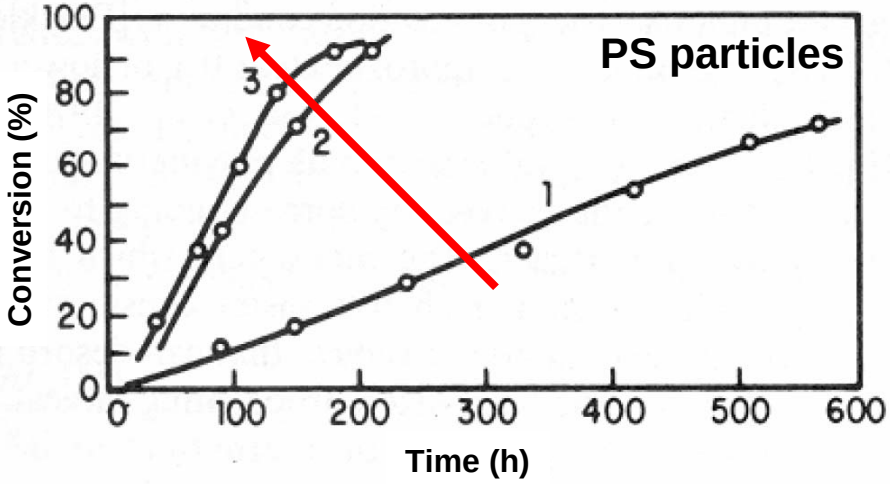
- 2-15% conversion
- Radical capturing and # of particles increase (rate increase)
- As particle grow, more surfactants adsorb
- Surfactant concentration falls below CMC
- All the surfactant adsorb to the particles at the end of interval 1

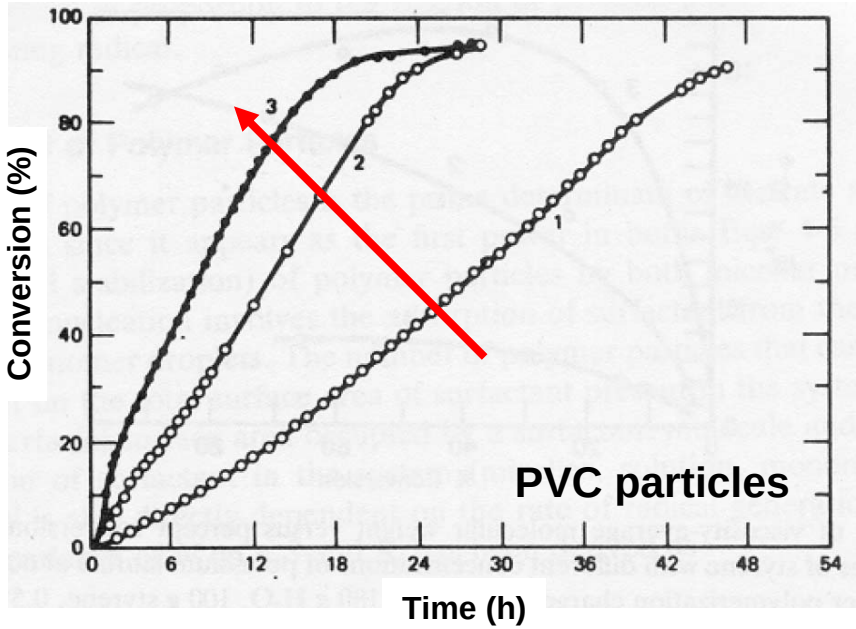
Interval II

- # of particles remains constant
- Slight increase due to Trommsdorf effect
- Interval II ends when all the monomer droplets disappear

Interval III

- # of particles remains constant
- [M] decreases (rate decrease)





- **Increasing surfactant**
- **Increasing # of particles**

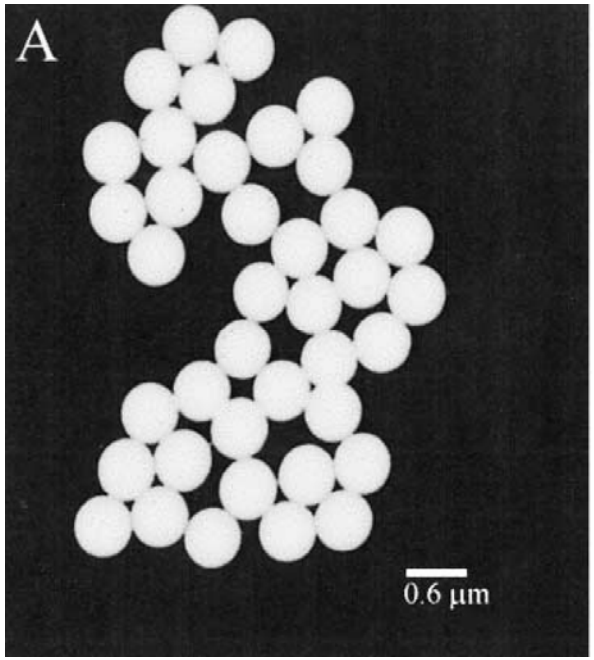
- **Increasing initiator concentration**
- **Increasing # of particles**

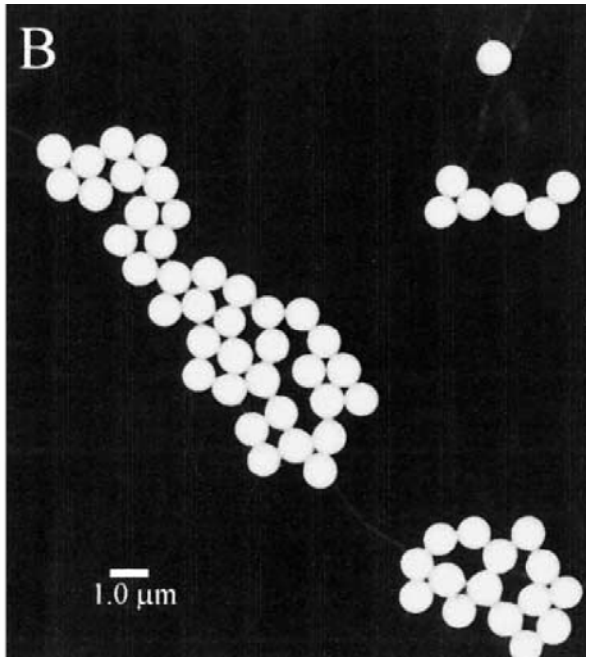
$$R_p = k_p[M]_p N_p \bar{n}/N_A$$

$$DP = r_p/r_i = N\ kp\ [M]\ /\ R_i$$

$$N_p \propto [\text{initiator}]^{0.4}\ [\text{emulsifier}]^{0.6}$$

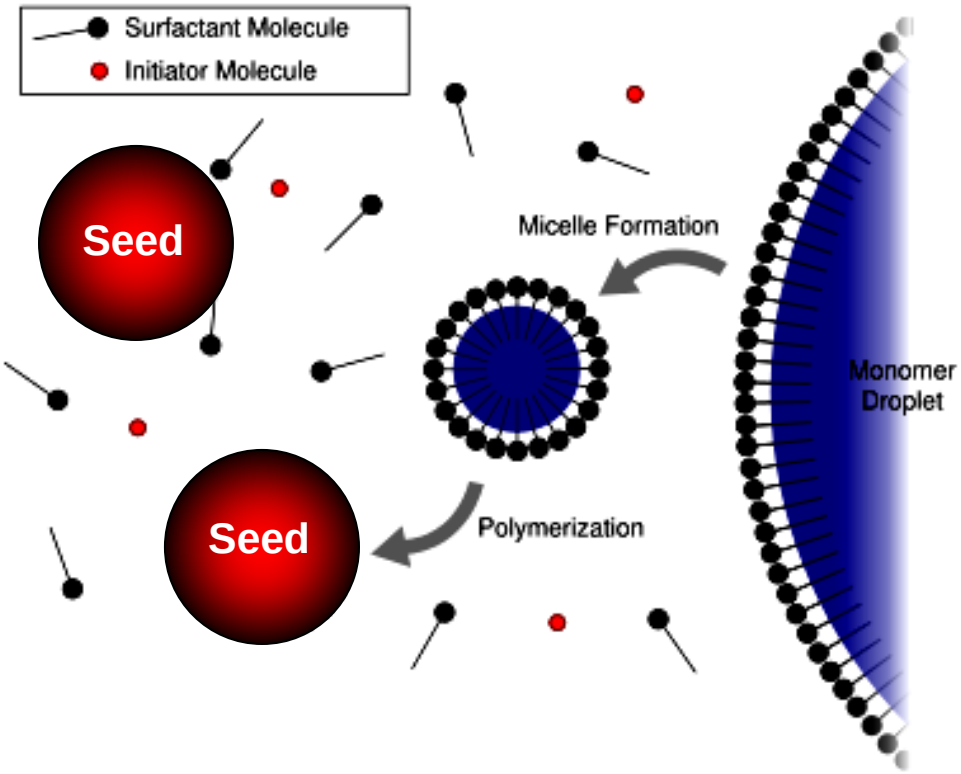
Polymer particles





PS particles

Seeded emulsion polymerization



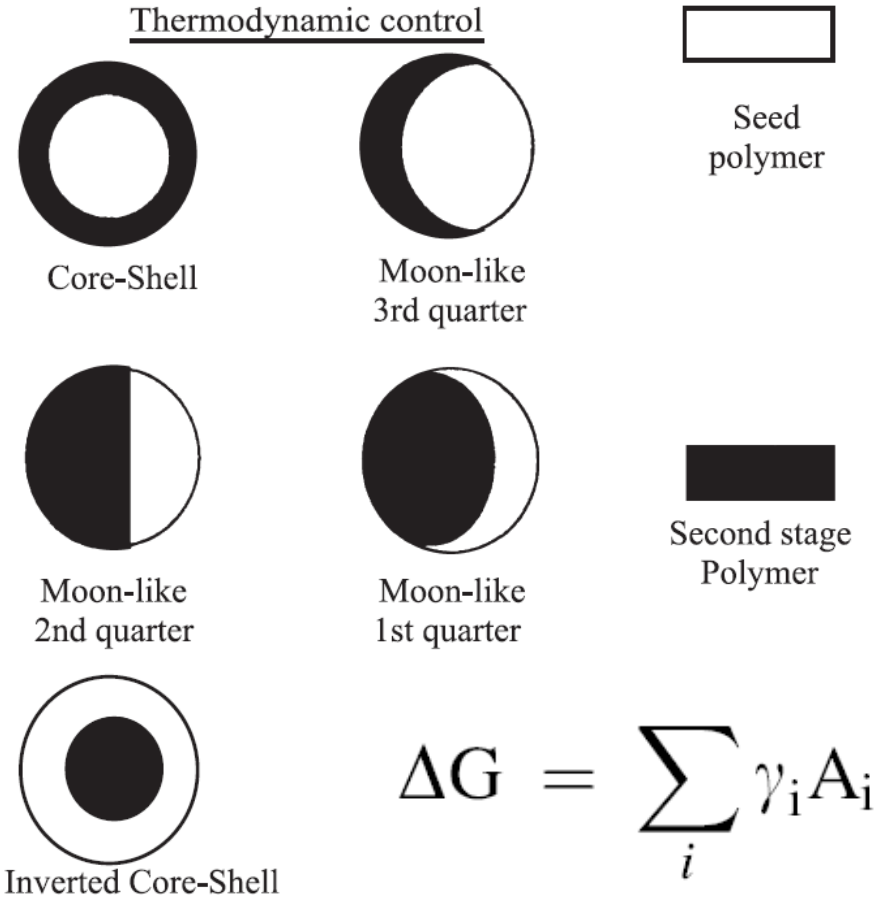
Features

- Heterogeneous system
- Nucleation site: water
- Bigger than seed particles
- Monodisperse
- Good for controlling morphologies

Components

- Seed polymer particles
- Monomers
- Water
- Water-soluble initiator
- Surfactant

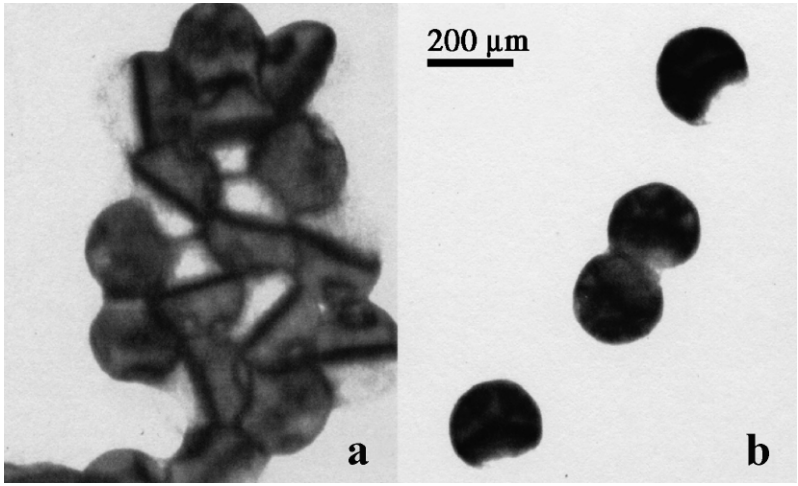
Thermodynamic effect



$$\Delta G = \sum_i \gamma_i A_i$$

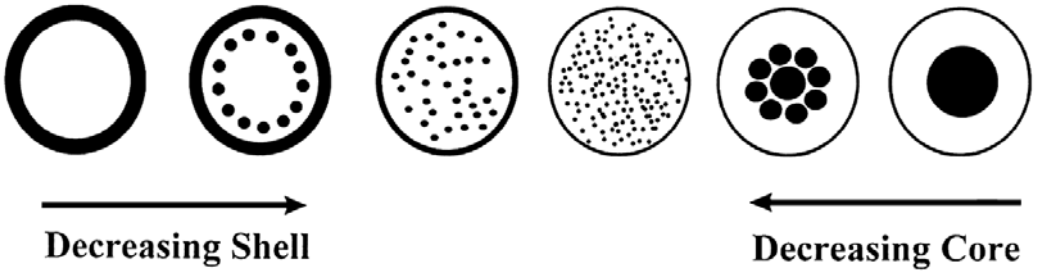
PS

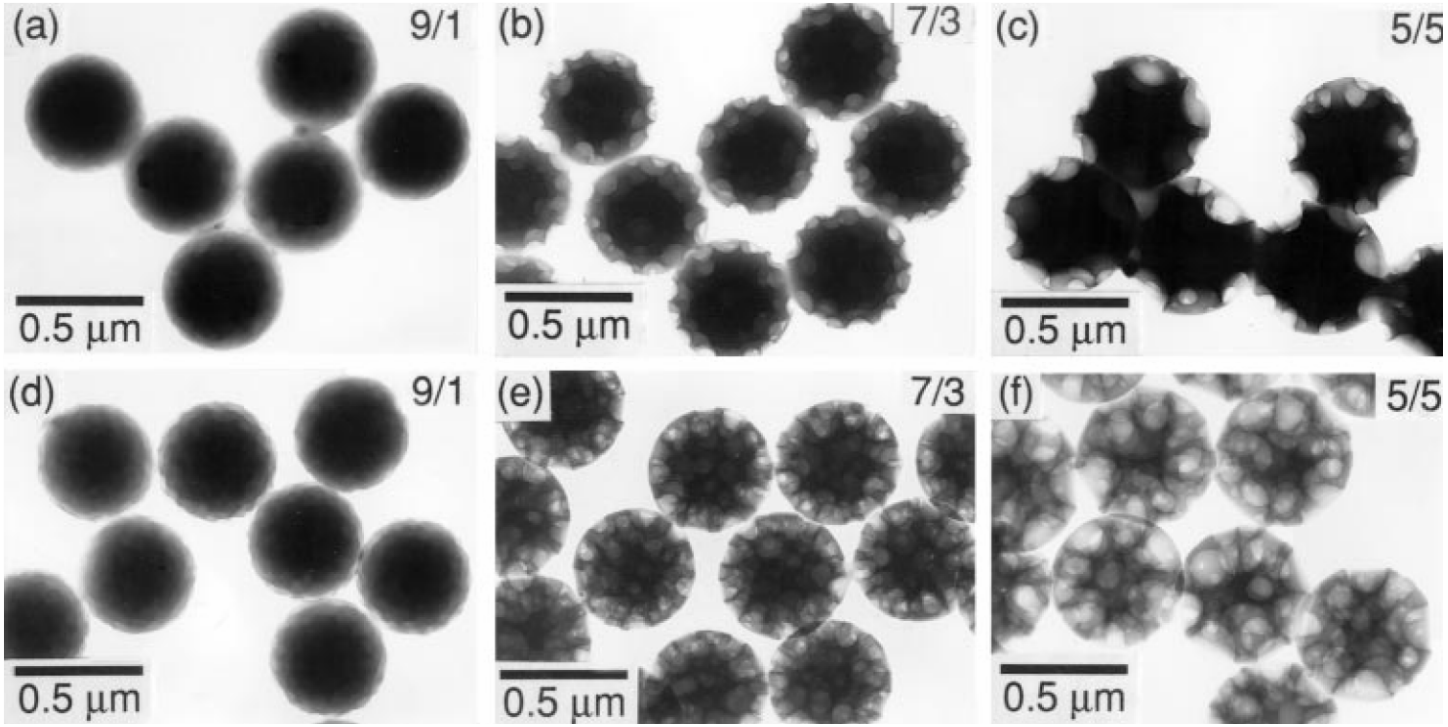
PMMA



PS/PBMA composite particles

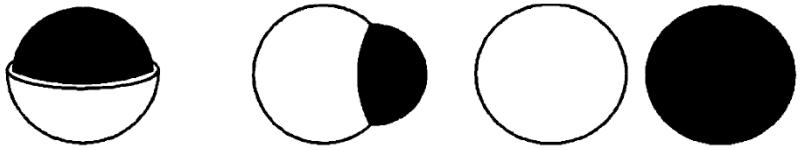
Penetration depth





PS/PBA composite particles

Entropy and Spreading coefficient effects

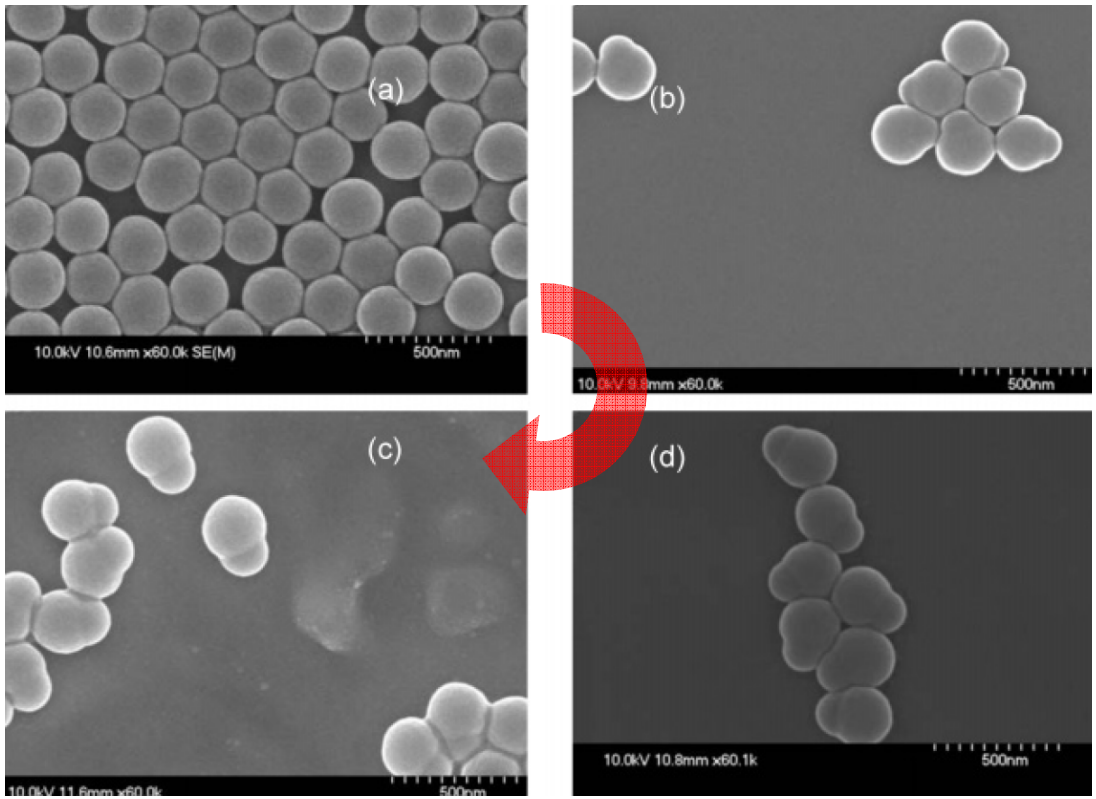


Complete engulfment
$S_1<0,\ S_2<0,\ S_3>0$

Partial engulfment
$S_1<0,\ S_2<0,\ S_3<0$

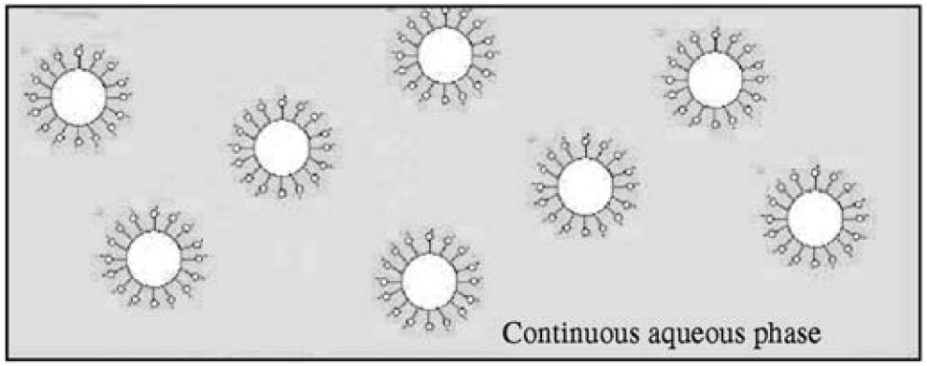
No engulfment
$S_1<0,\ S_2>0,\ S_3<0$

$$S_i = \gamma_{jk} - (\gamma_{ij} + \gamma_{ik})$$



Hydrophilicity of seed particles increases

Miniemulsion polymerization



Features

- Heterogeneous system
- Droplet nucleation (no micelles in water)
- Initiation by radial entry (prepolymeric or oligomeric)
- Fairly monodisperse

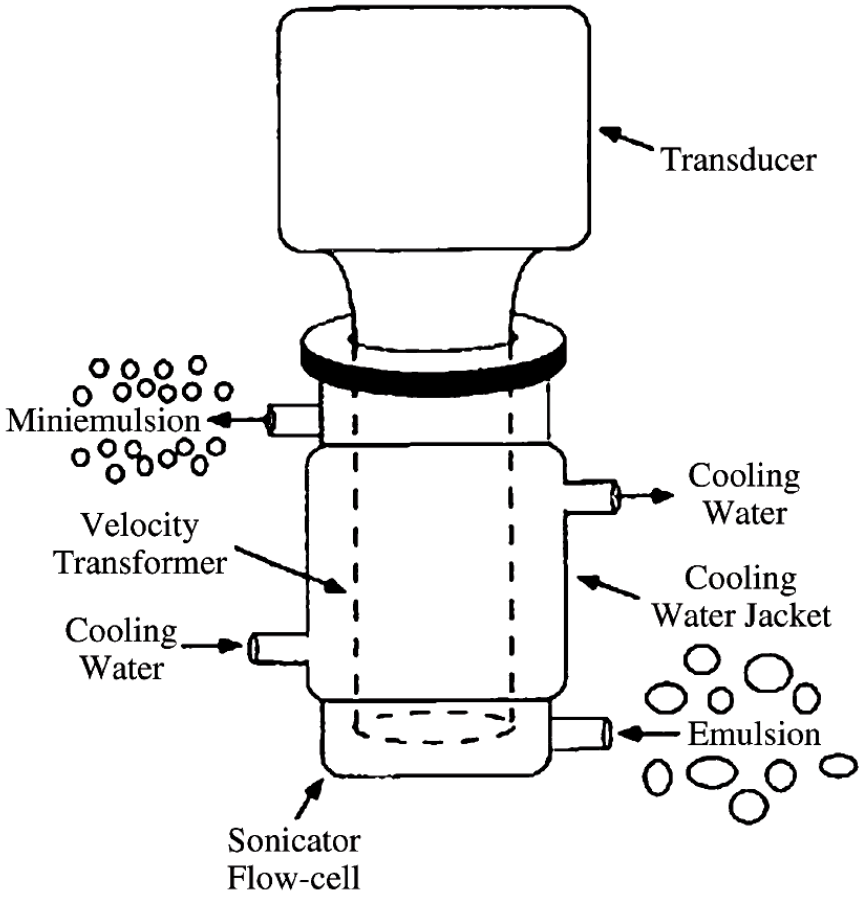
Role of costabilizers

- Highly insoluble in water; hexadecane, cetyl alcohol, polymers…
- Retarding monomer diffusion from the smaller droplets to the larger
- Preventing Ostwald ripening

Components

- Monomers
- Water
- Water-soluble initiator
- Surfactant and "costabilizer"

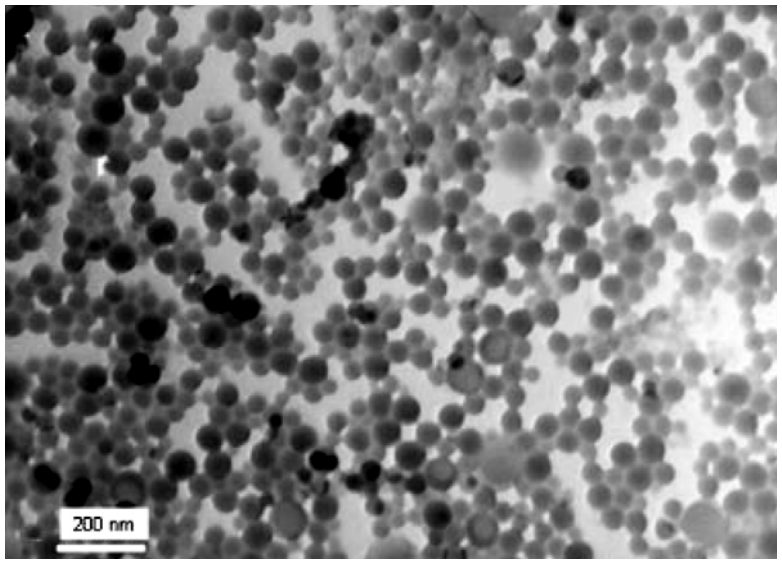
Emulsification



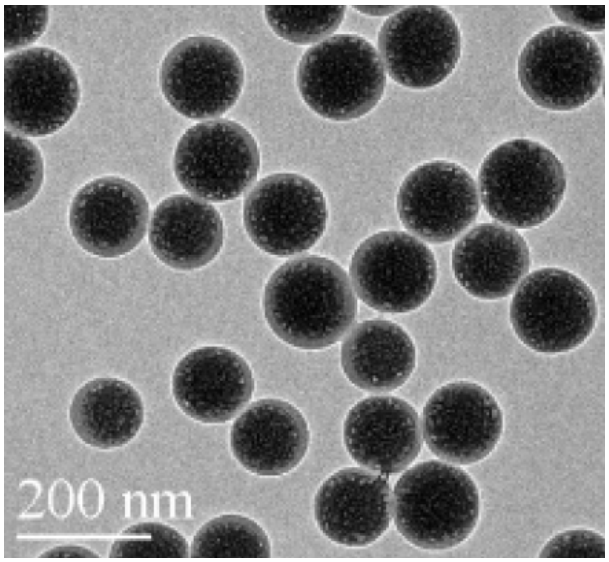
Mechanically emulsified

Macroemulsion and miniemulsion after 3 hours

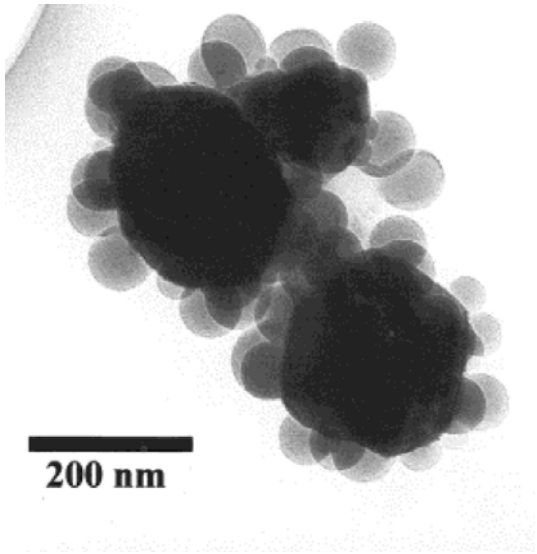
Polymer particles



PS particles

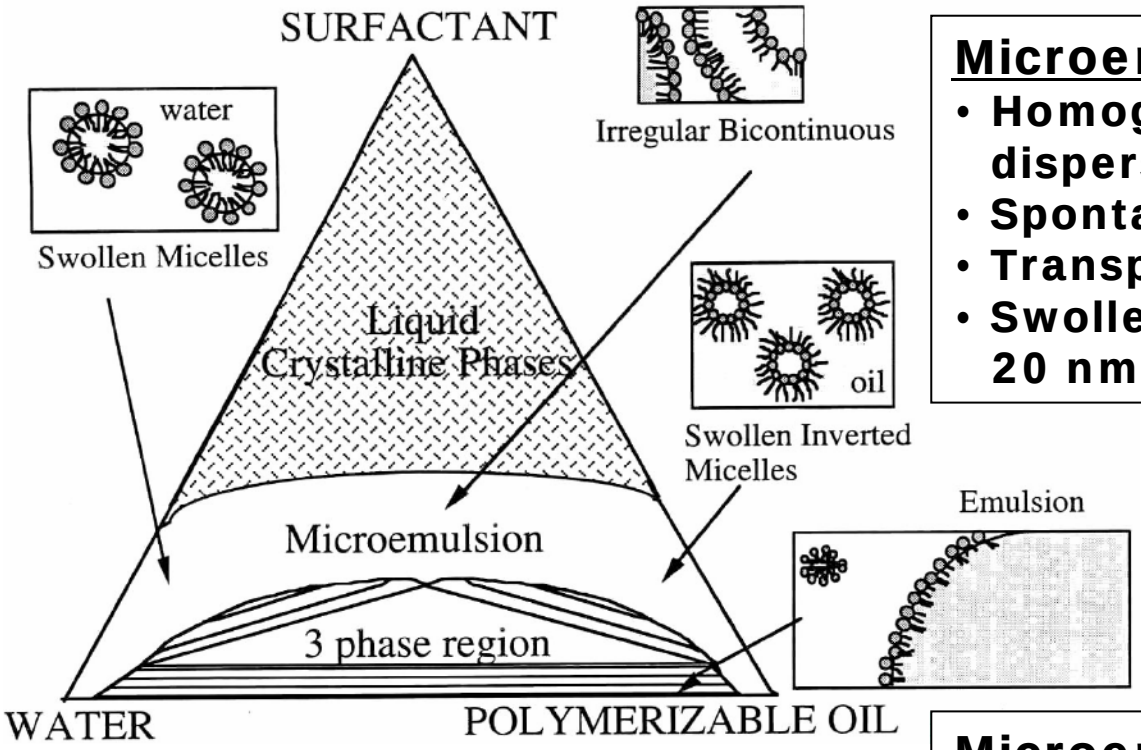


SiO_2@PS particles



TiO_2@PS particles

Microemulsion polymerization



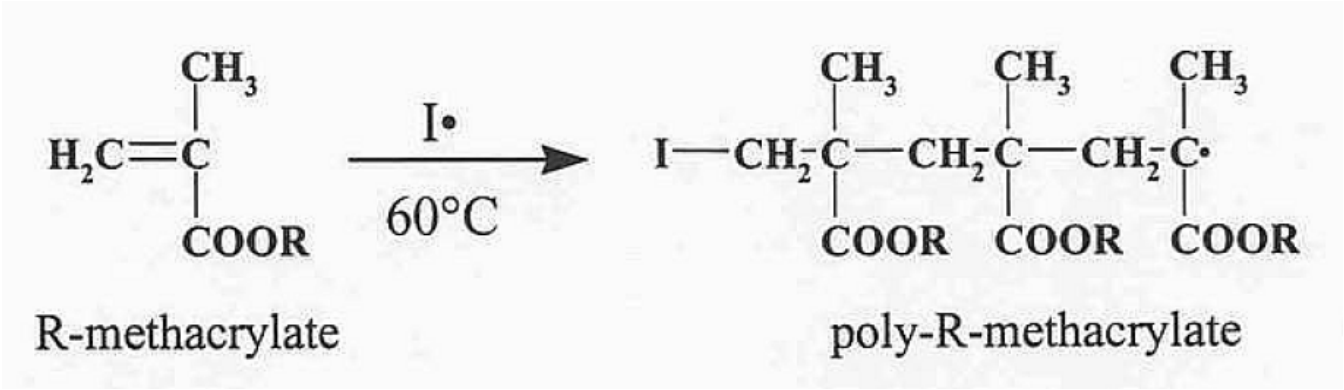
Microemulsion

- **Homogeneous; micelle dispersion**
- **Spontaneous**
- **Transparent**
- **Swollen micelles, less than 20 nm in diameter**

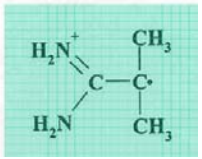
Microemulsion polymerization

- **Tacticity**
- **Knotting**
- **A high MW, more than 20 million Dalton**

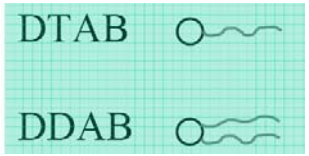
Polymerization



Water Soluble Initiators

KPS	Anionic	$SO_4^-\cdot$
V50	Cationic	

Cationic surfactants



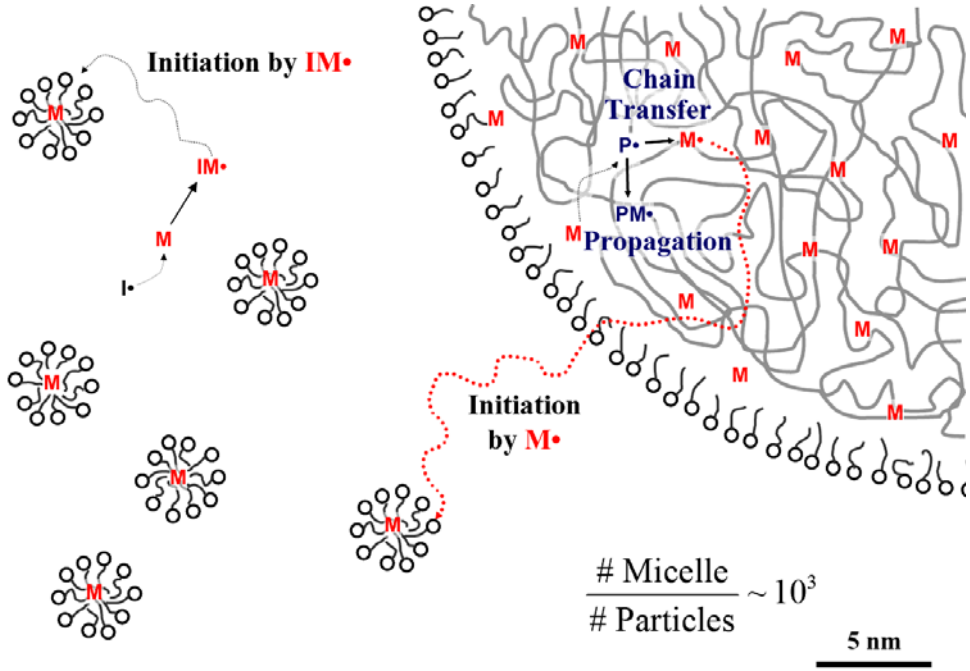
Initiation: $I\text{-}I \xrightarrow{k_d} 2I^{\bullet}$

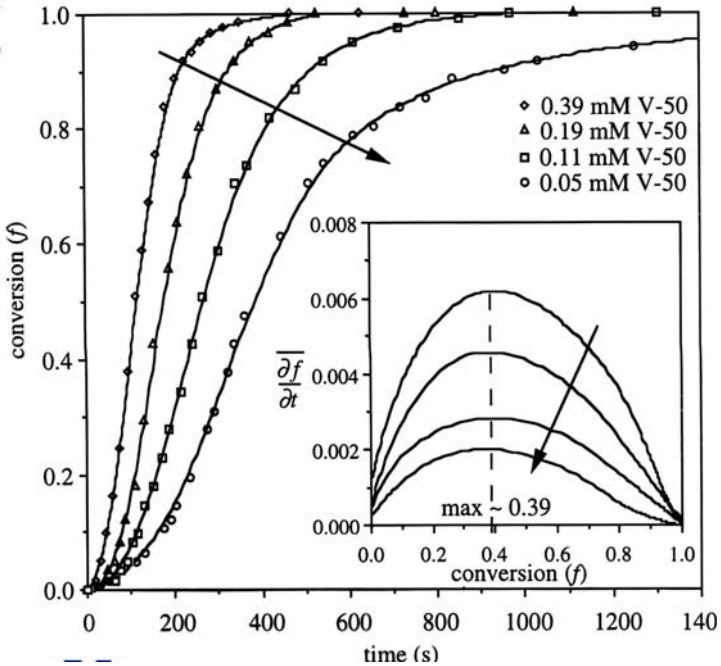
Propagation: $I^{\bullet} + M \longrightarrow IM^{\bullet} \xrightarrow{k_p} IM_n^{\bullet}$

Transfer: $IM_n^{\bullet} + M \xrightarrow{k_{tr}} IM_n + M^{\bullet}$

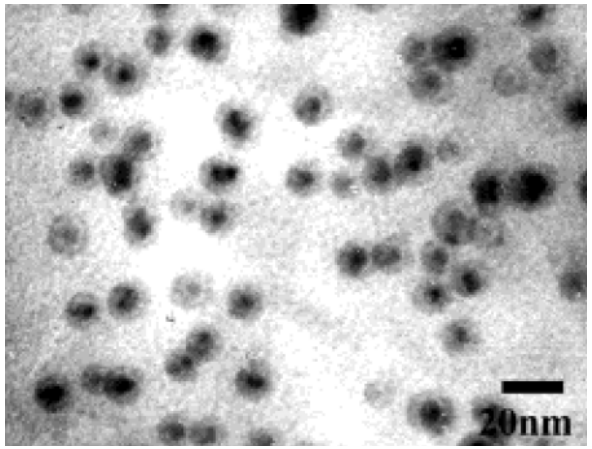
Combination: $IM_n^{\bullet} + IM_m^{\bullet} \xrightarrow{k_t} IM_{n+m}I$

Polymerization process



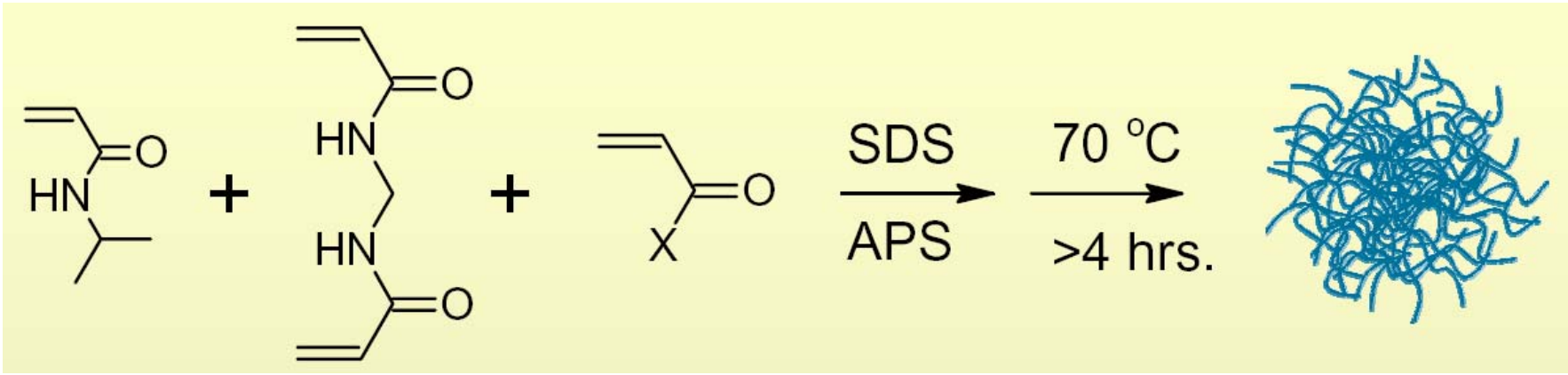


- **Rapid polymerization**
- **100% conversion**
- **Rate profile: parabolic**
- **Maximum rate ~40%**

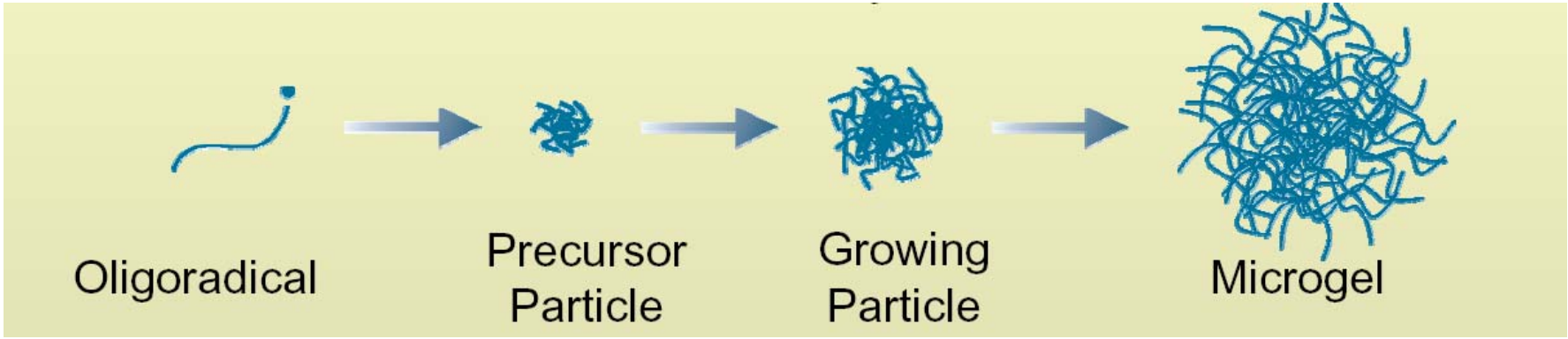


PMMA/PS nanoparticles

Precipitation polymerization

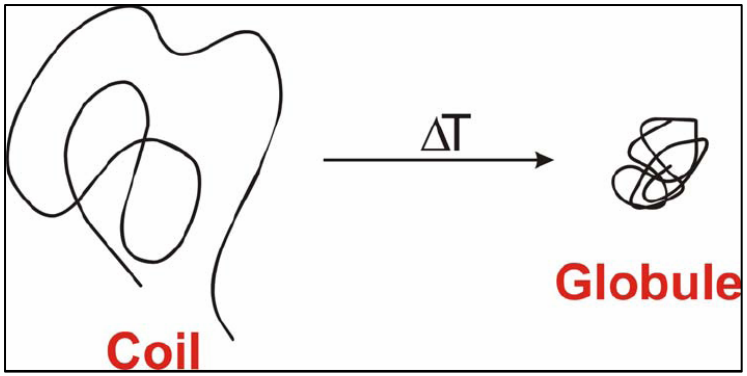


A basic composition



A nucleation and growth process

Properties of this technique



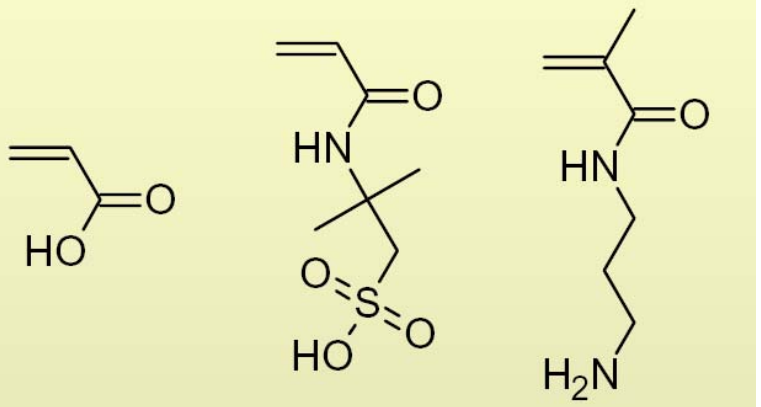
Fundamentals

- Homogeneous system
- Nucleation site is water
- A nucleation and growth
- Polymerization time: short (several hours)
- From hundreds of nanometers to 1 or 2 micrometers
- Very monodisperse
- Surfactant-free
- Crosslinking is possible

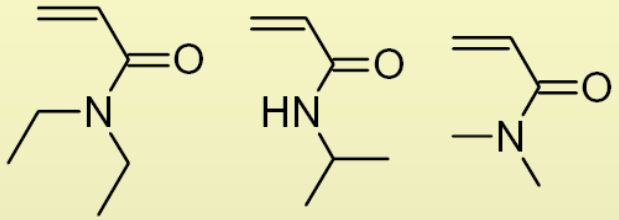
Components

- Monomers (water-soluble)
- Water
- Water-soluble initiator
- Surfactant (if need)

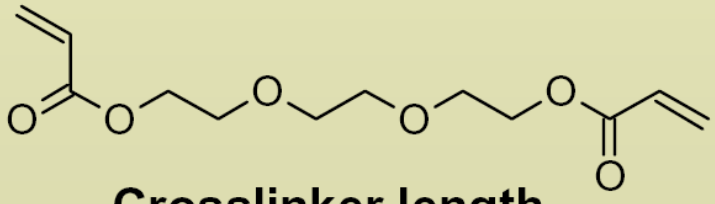
Designing microgel particles



pH sensitive/polyelectrolytes



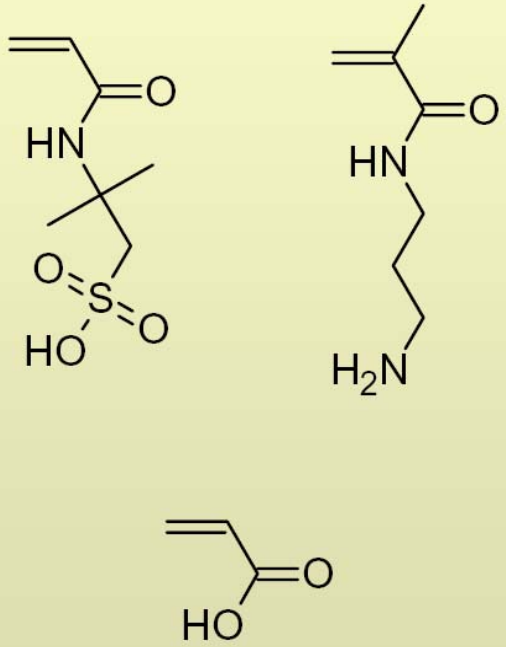
thermosensitive



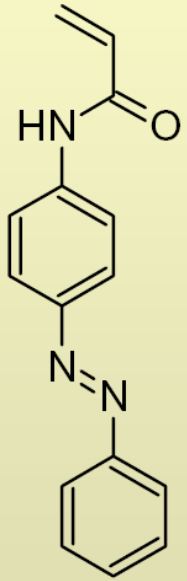
Crosslinker length

Responsivity and sensitivity

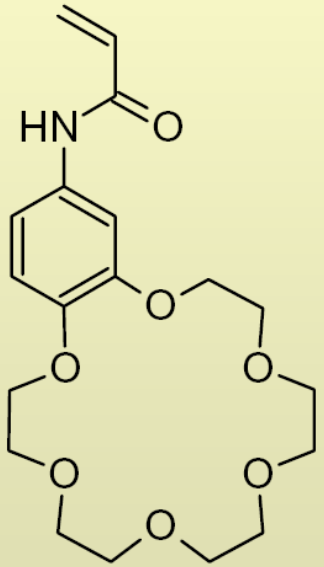
Electric Field



Light

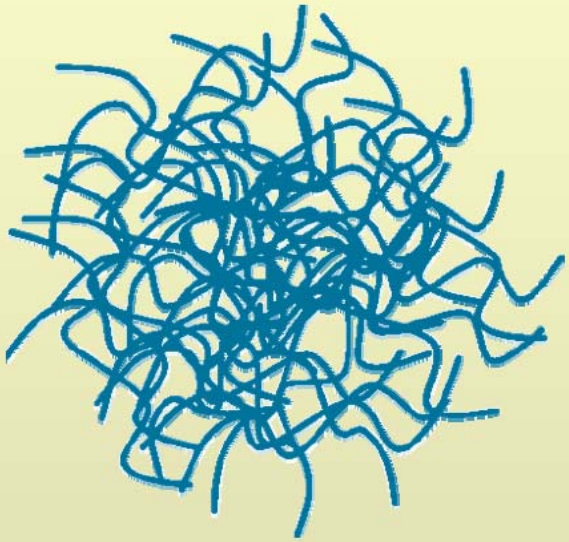


Metal Ions

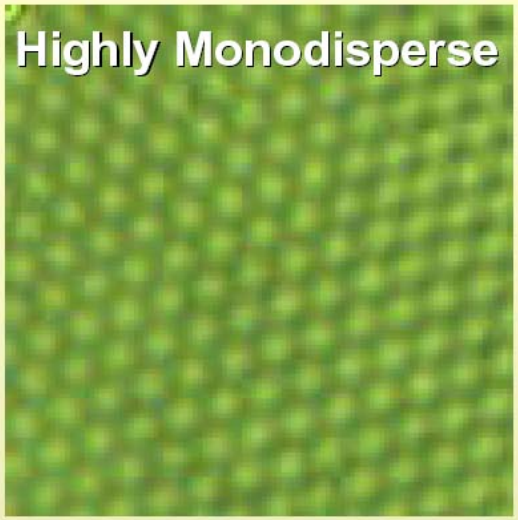


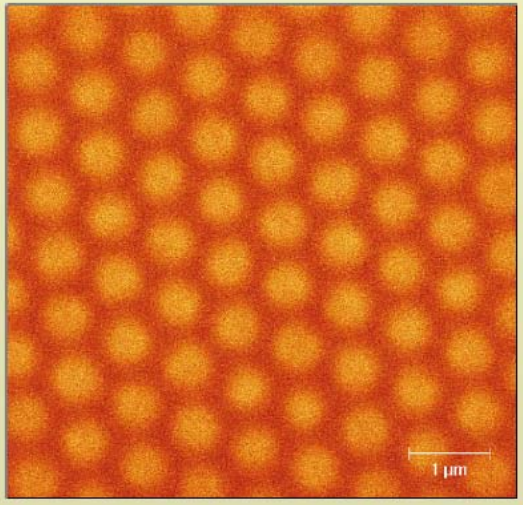
Microgel characterization

Infinite Spherical Network

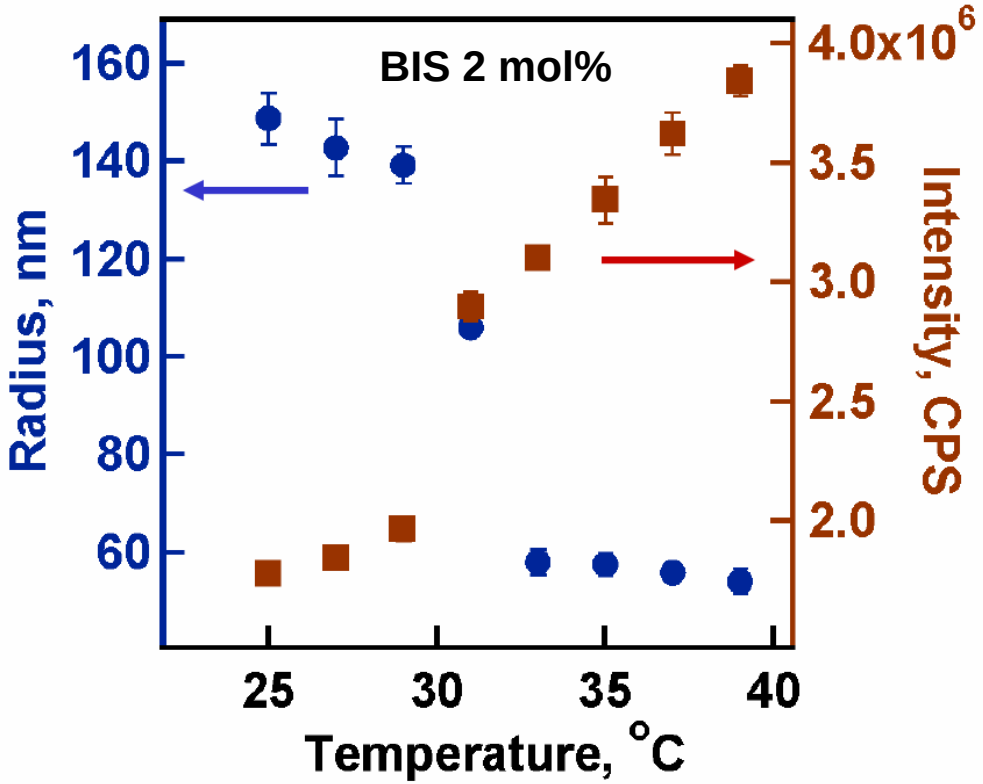


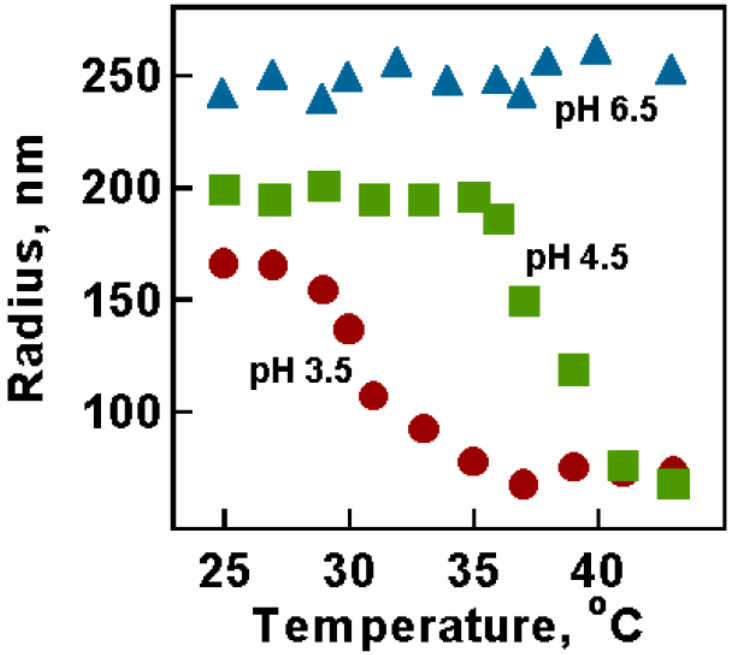
High water content (90-99% v/v)
a microgel is effectively *all surface area*

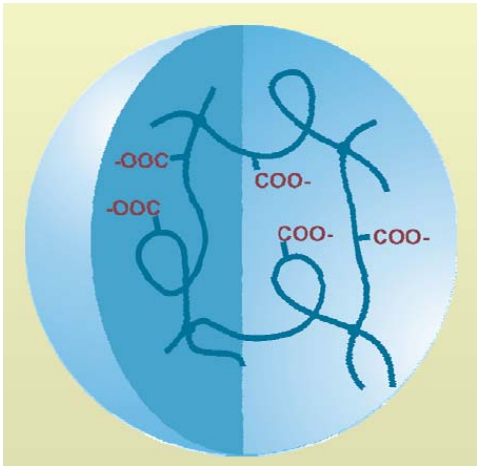




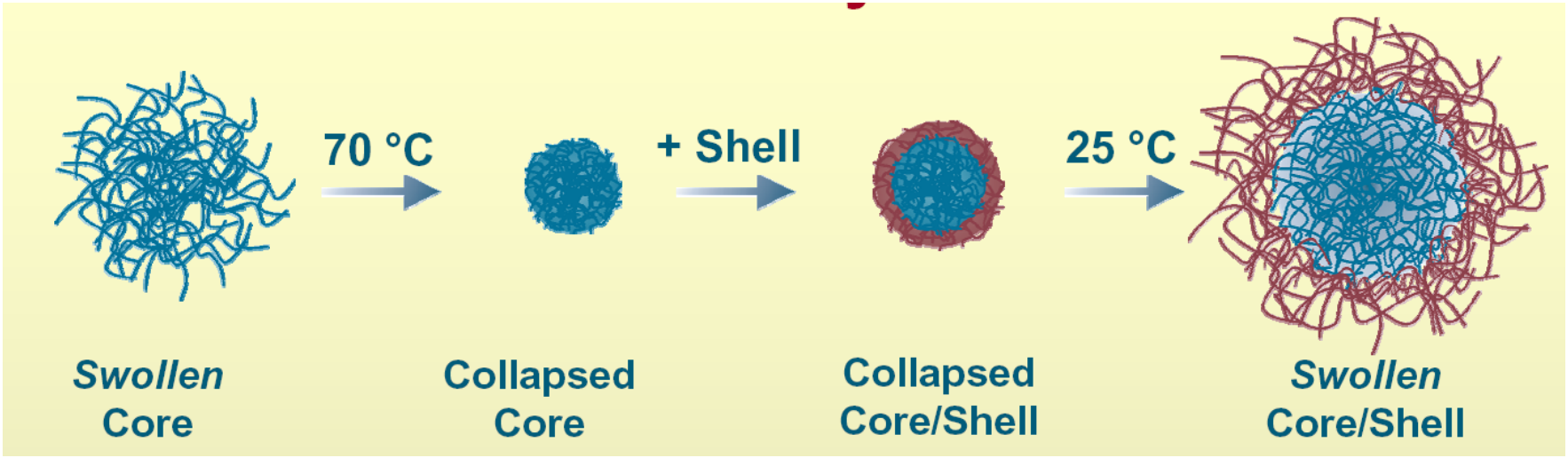
Phase transitions

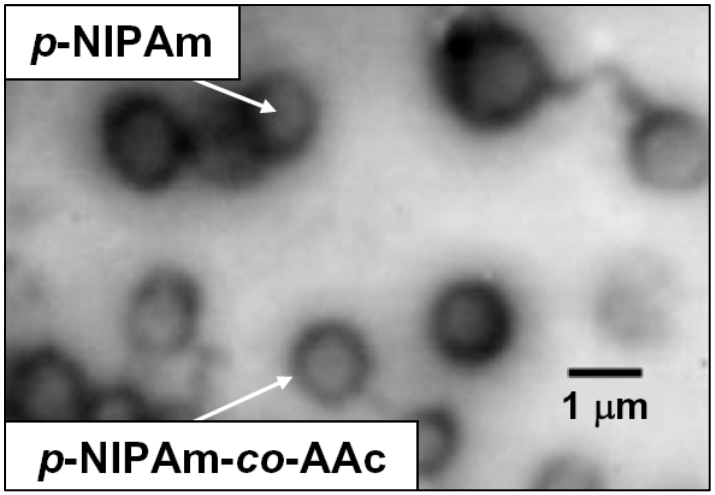




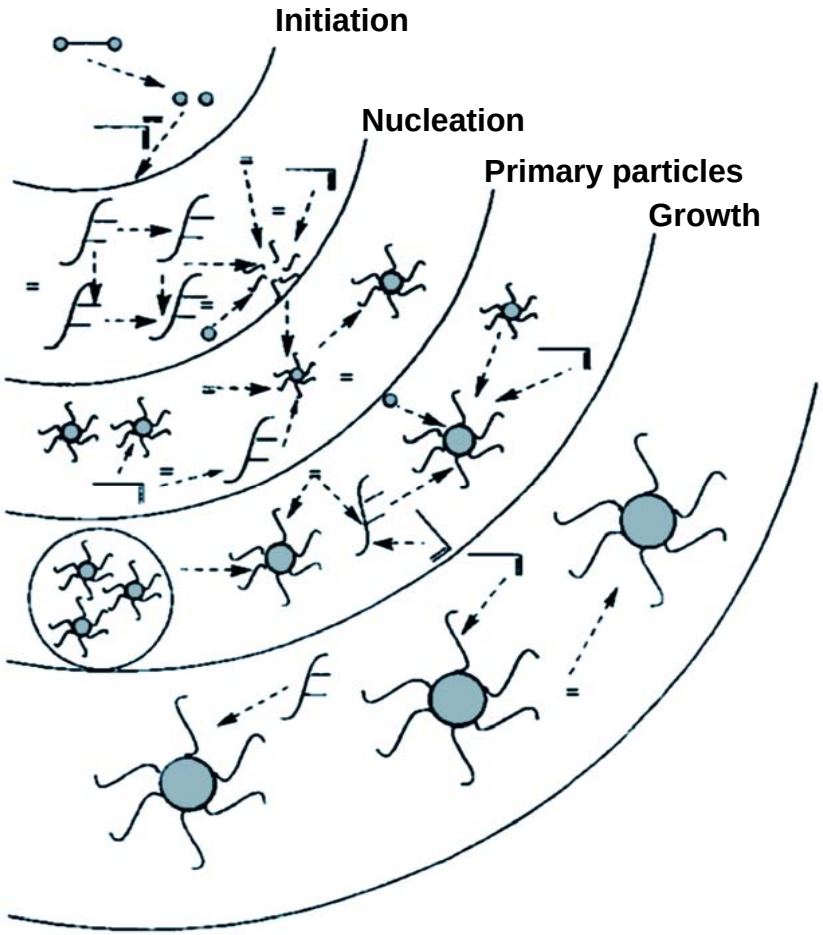


Core-shell microgel particles





Dispersion polymerization



A dispersion polymerization process

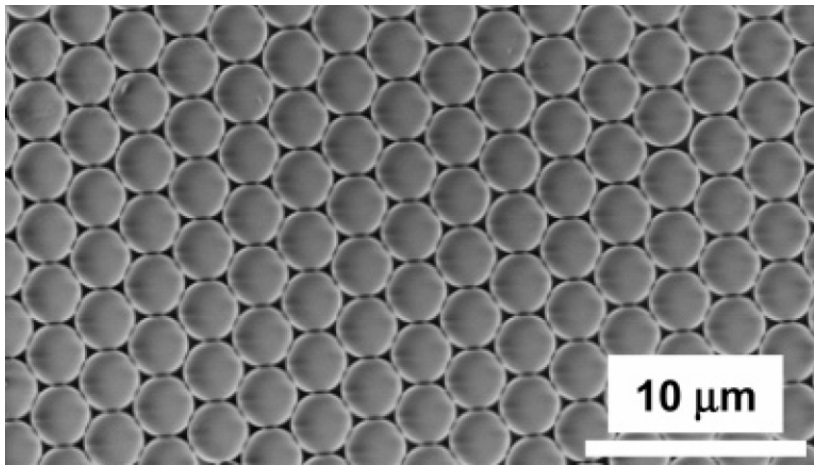
Fundamentals

- Homogeneous system
- Nucleation site is media
- A nucleation and growth
- Polymerization time: long (more than 24 hours)
- From a micromerter to 15 micrometers
- Very monodisperse
- Stabilizer is needed
- Crosslinking is impossible

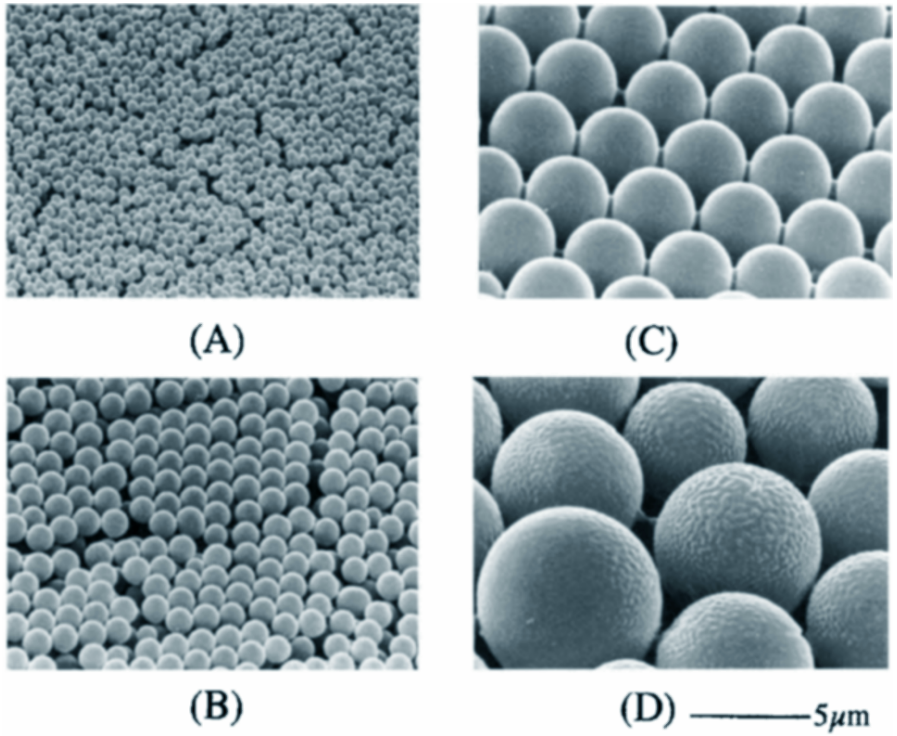
Components

- Monomers (medium-soluble)
- Alcohol
- Water-insoluble initiator
- Stabilizer; polymer (PVP, PAAc....)

Monodisperse polymer microparticles

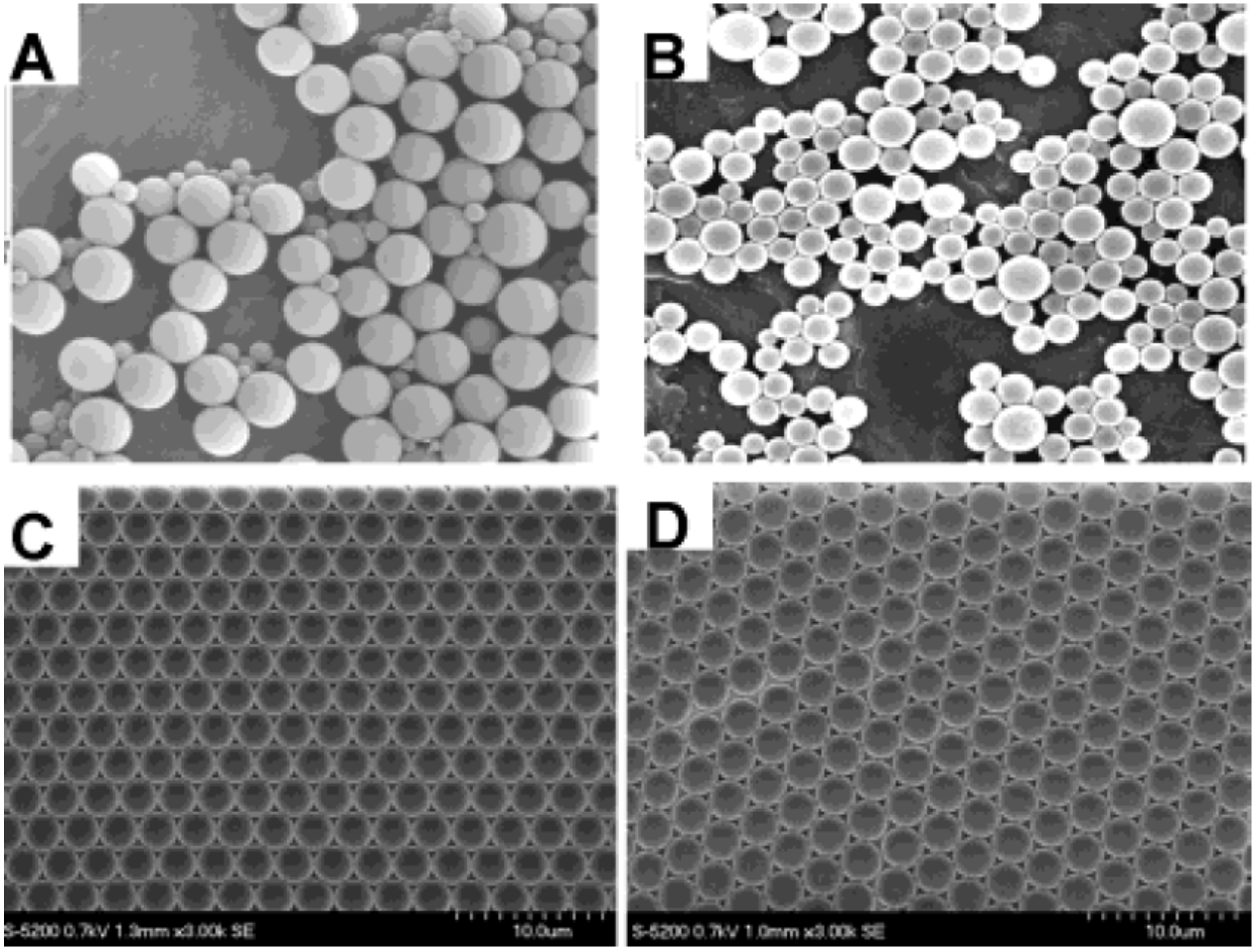


Monodisperse PS particles
- **PVP**
- **Ethanol medium**



Poly (HEMA) microparticles
- **Poly (St-b-BD) stabilizer**
- **2-butanol/toluene media**

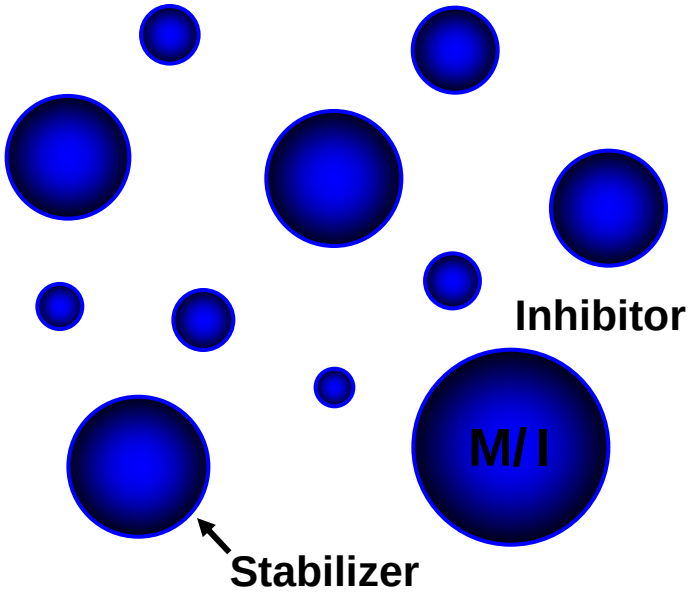
Crosslinking in dispersion polymerization



Conventional method;
(a) 1% dye; (b) 0.35% DVB

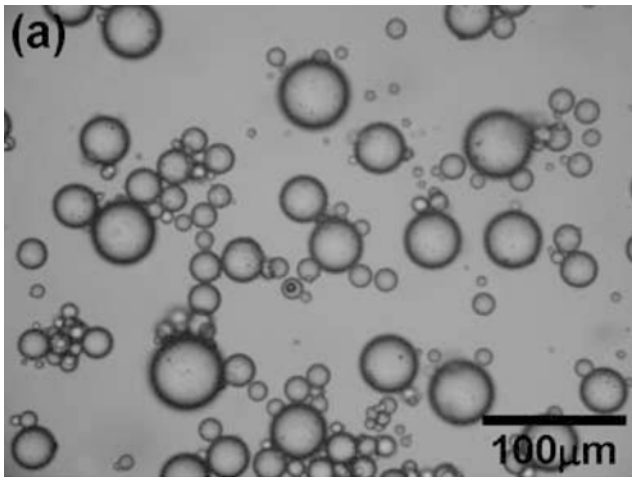
Two-staged method;
(c) 1% DVB; (d) 1% EGDMA

Suspension polymerization



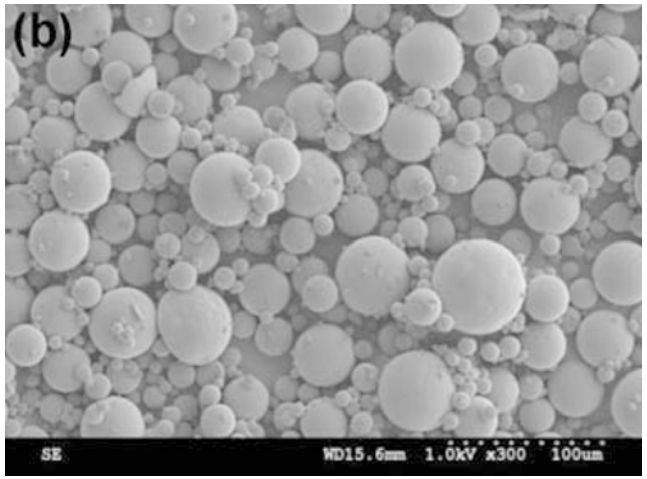
Fundamentals

- A heterogeneous system
- Nucleation site is monomer phase (droplet)
- Polymerization time: long (more than 10 h)
- From 1 micrometer to thousands of micrometers
- Very polydisperse



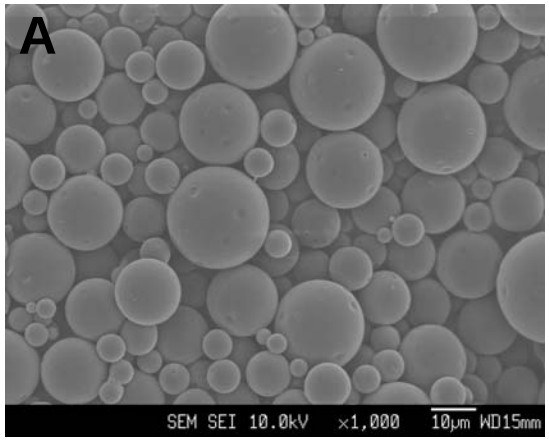
MMA droplets

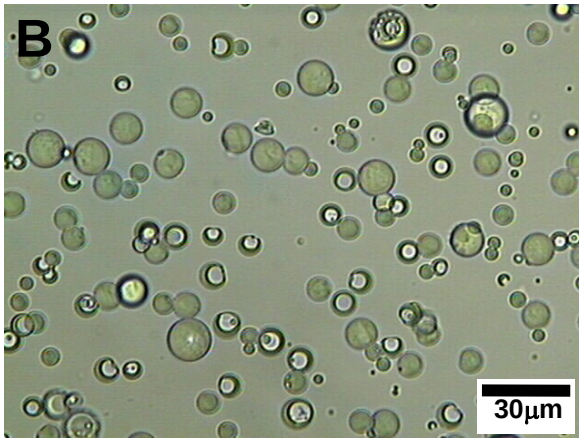
△

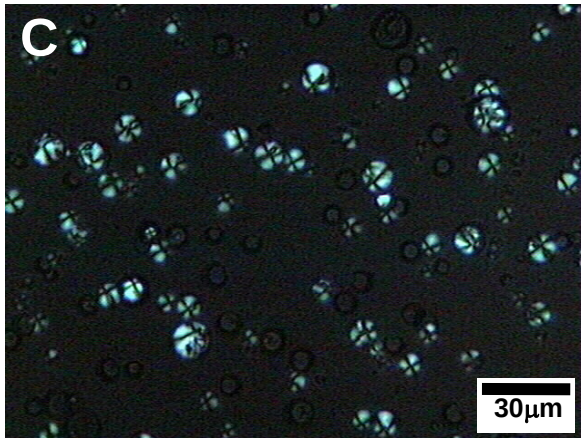


PMMA particles

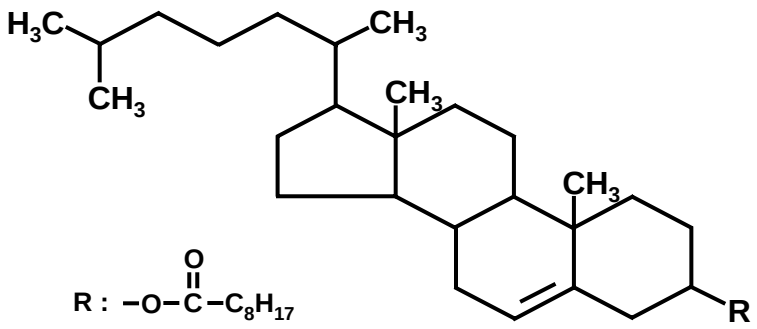
Wax/polymer composite particles





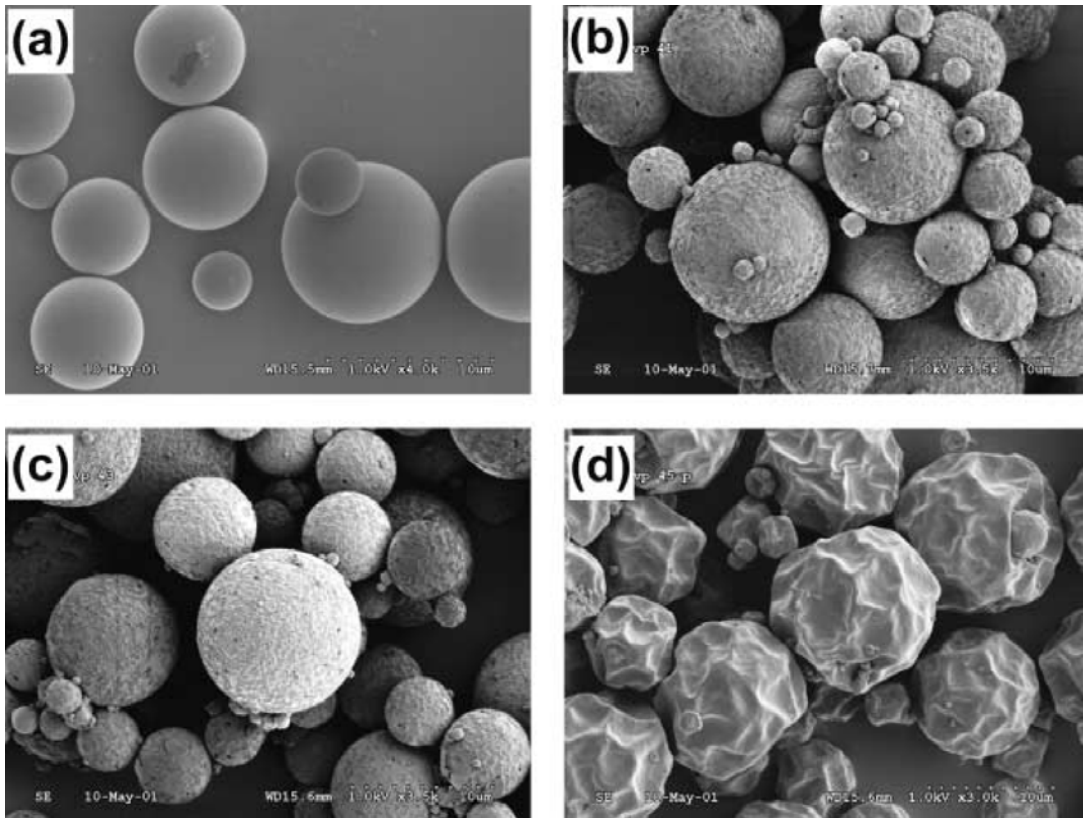


CN@PMMA microcapsules

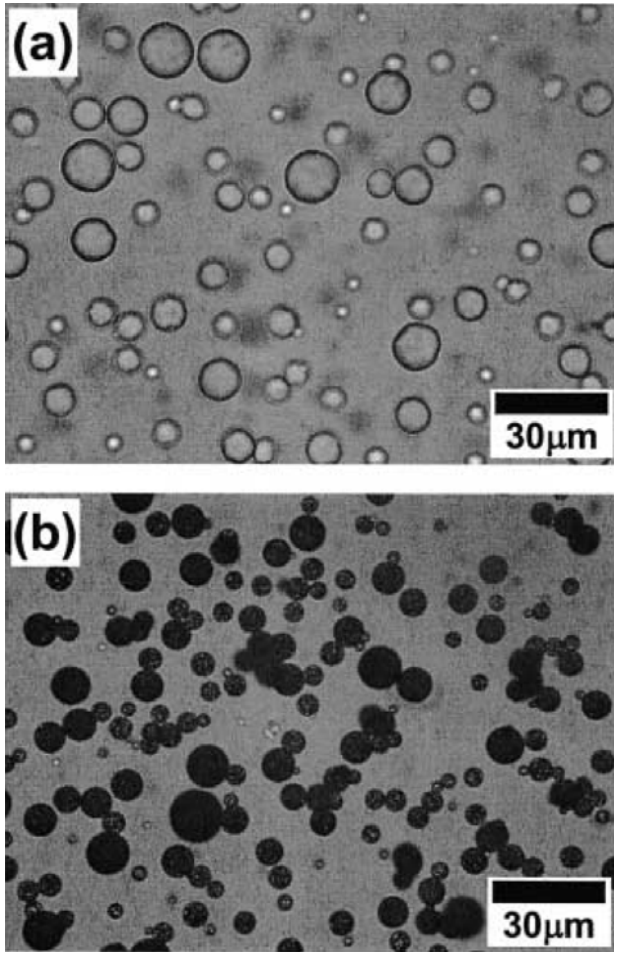


Cholesteryl nonanoate (CN)

Inorganic/polymer composite particles

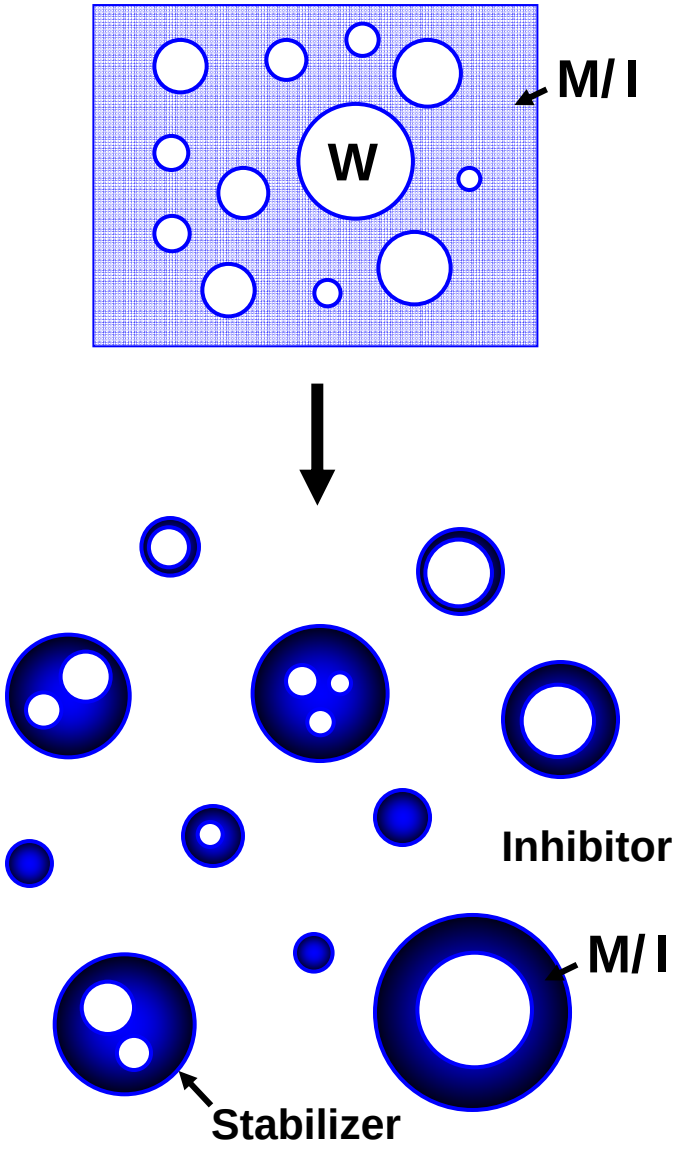


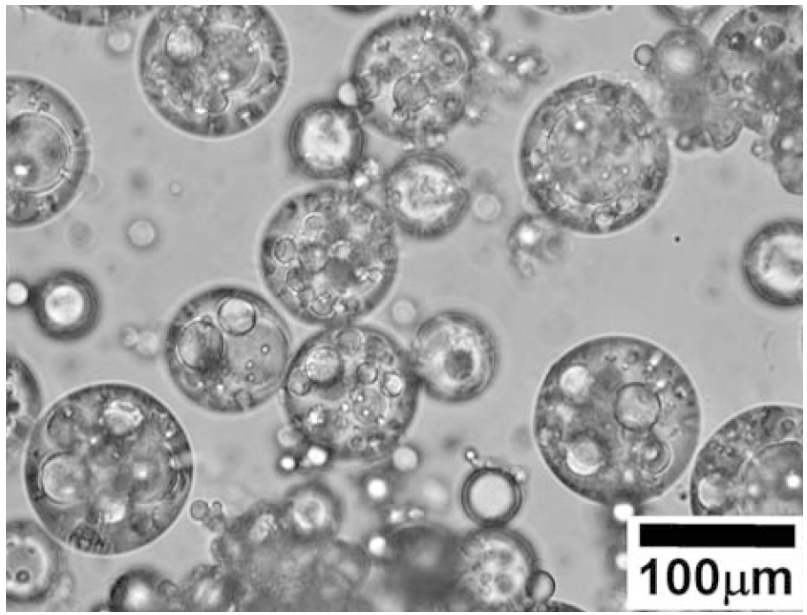
TiO_2/PMMA composite particles
(30 nm TiO_2)



Light blocking

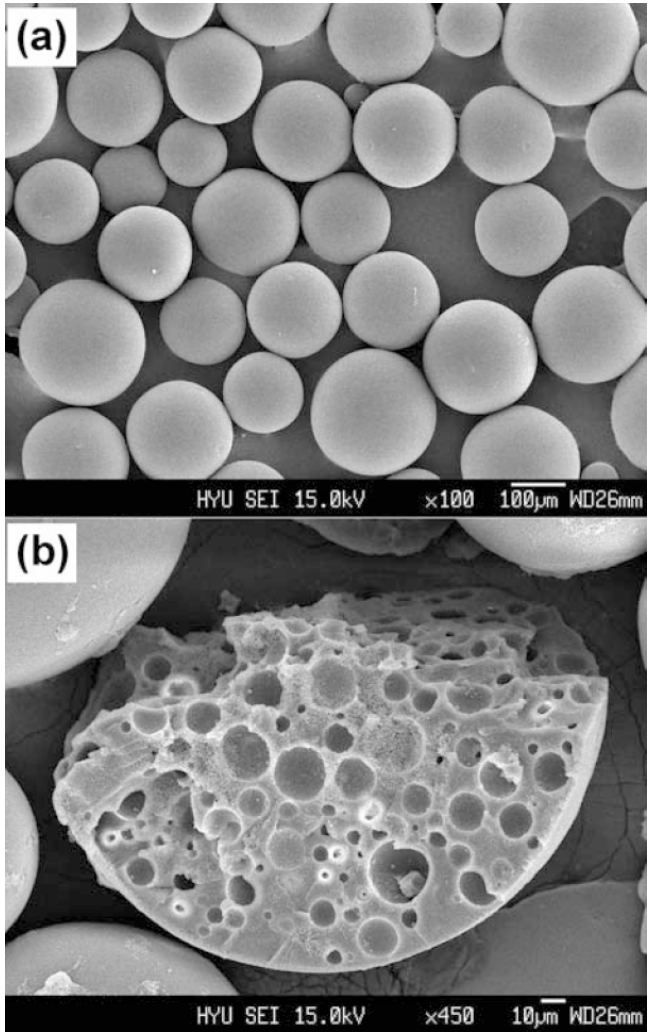
W / O / W double emulsion polymerization



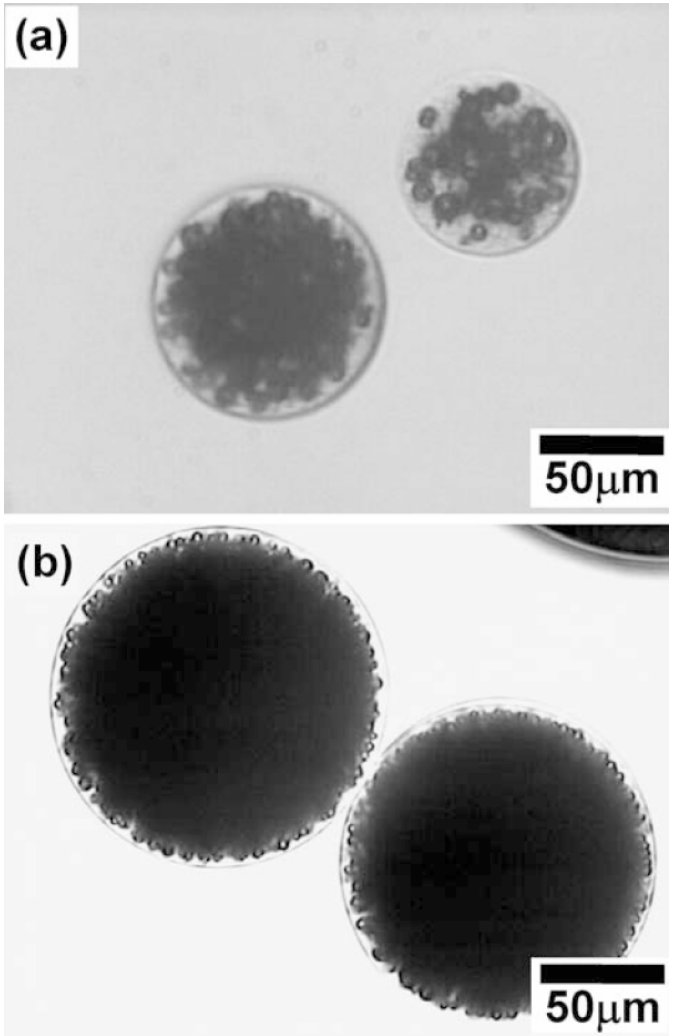


W/O/W double emulsions
(Oil is the mixture of MMA and AIBN)

Hollow polymer particles

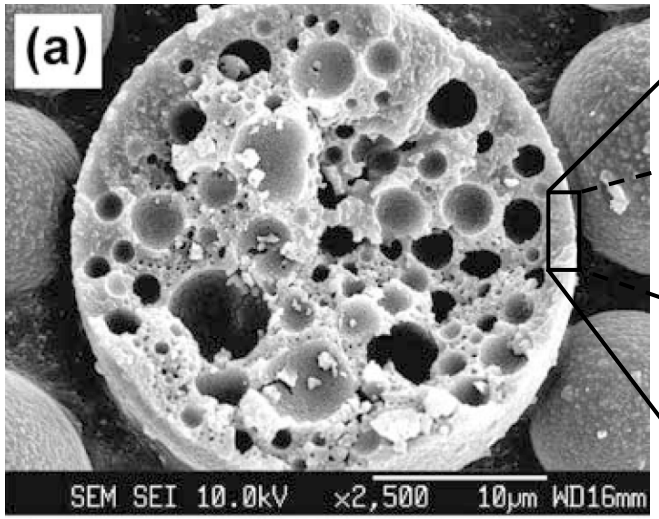


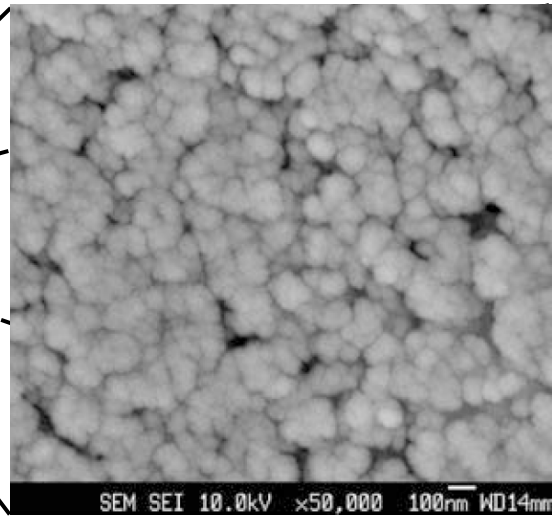
PMMA hollow particles

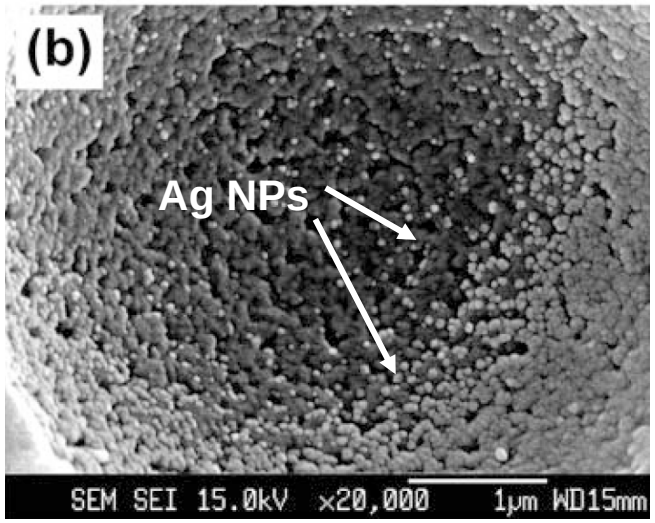


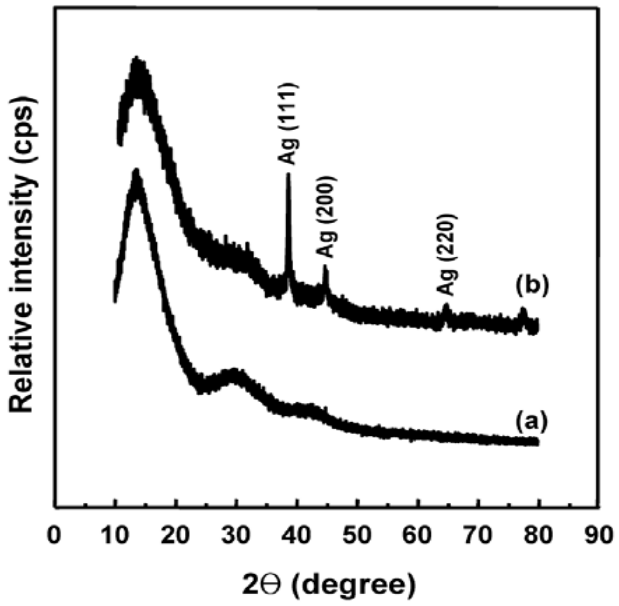
Dark pores in toluene

Ag NP in pores

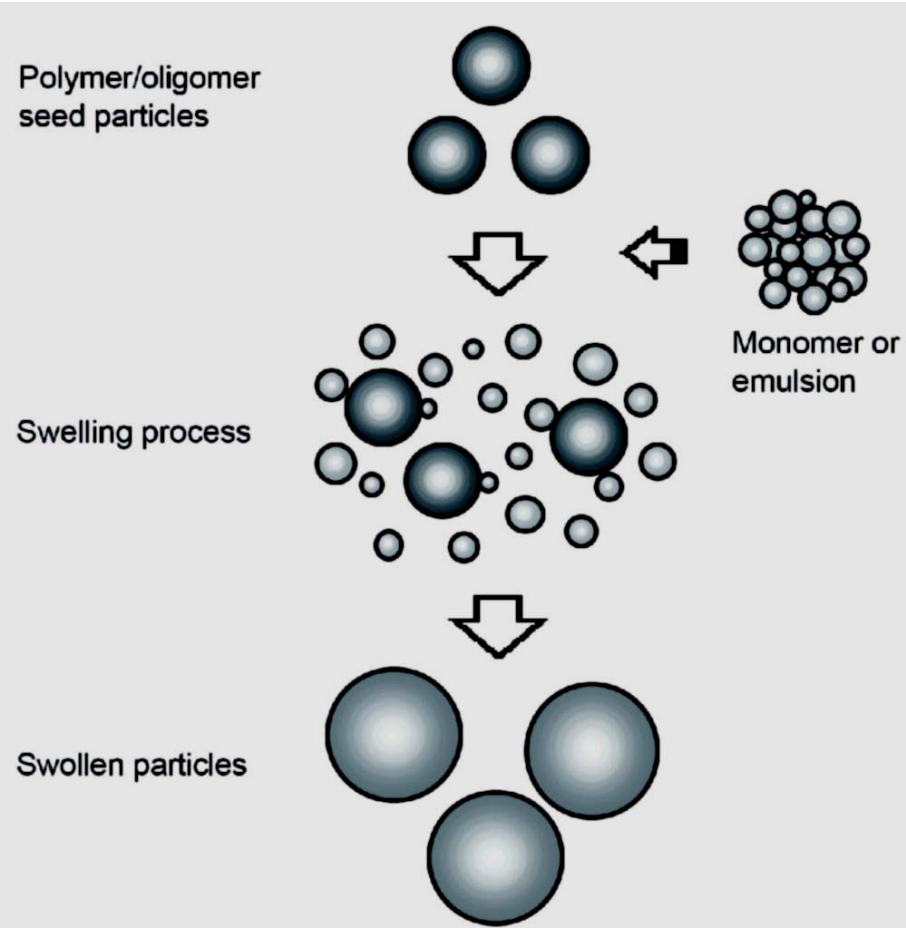








Seeded swelling & polymerization



Fundamentals

- A heterogeneous system
- Nucleation site is monomer phase (droplet)
- A swelling and polymerization
- Polymerization time: long (more than 10 h)
- From tens of nanometers to thousands of micrometers
- Very monodisperse
- Stabilizer: PVA, PAAc…
- Crosslinking is possible

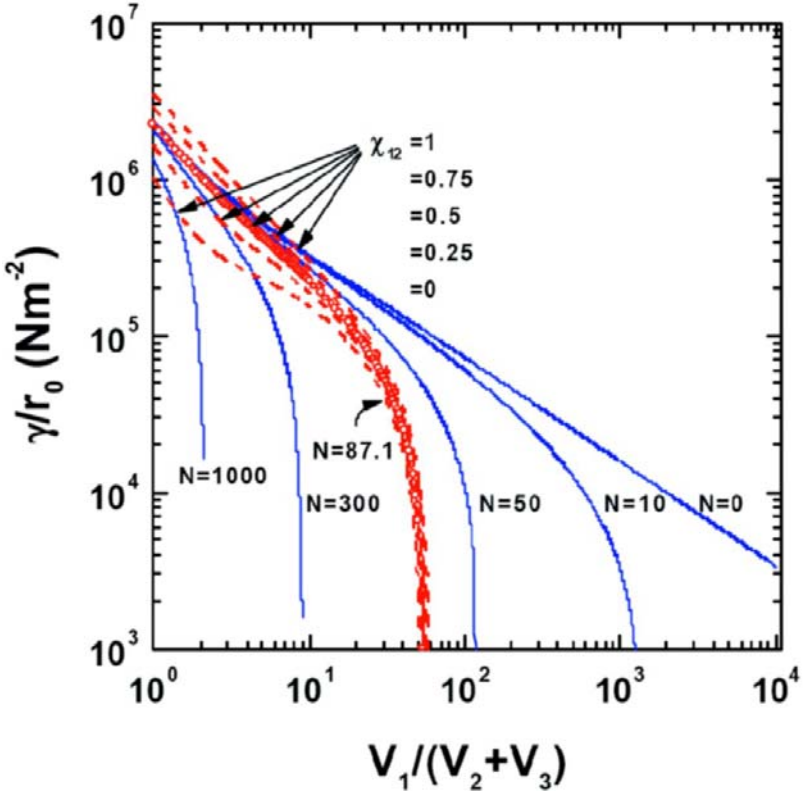
Components

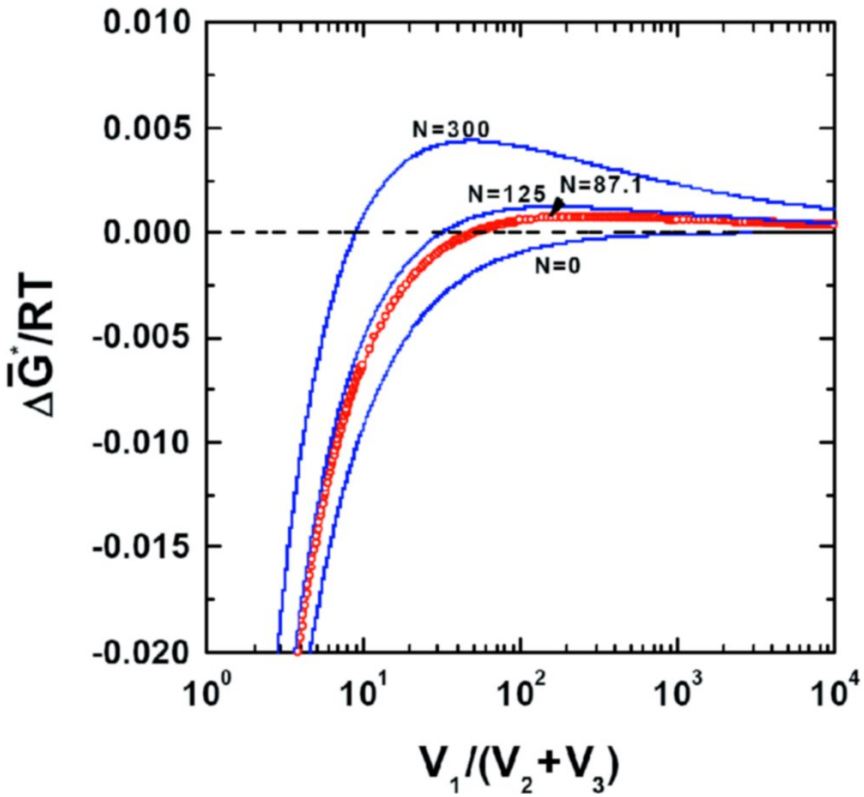
- Seed particles
- Water
- Monomers (with initiator)
- Stabilizer

Swelling process

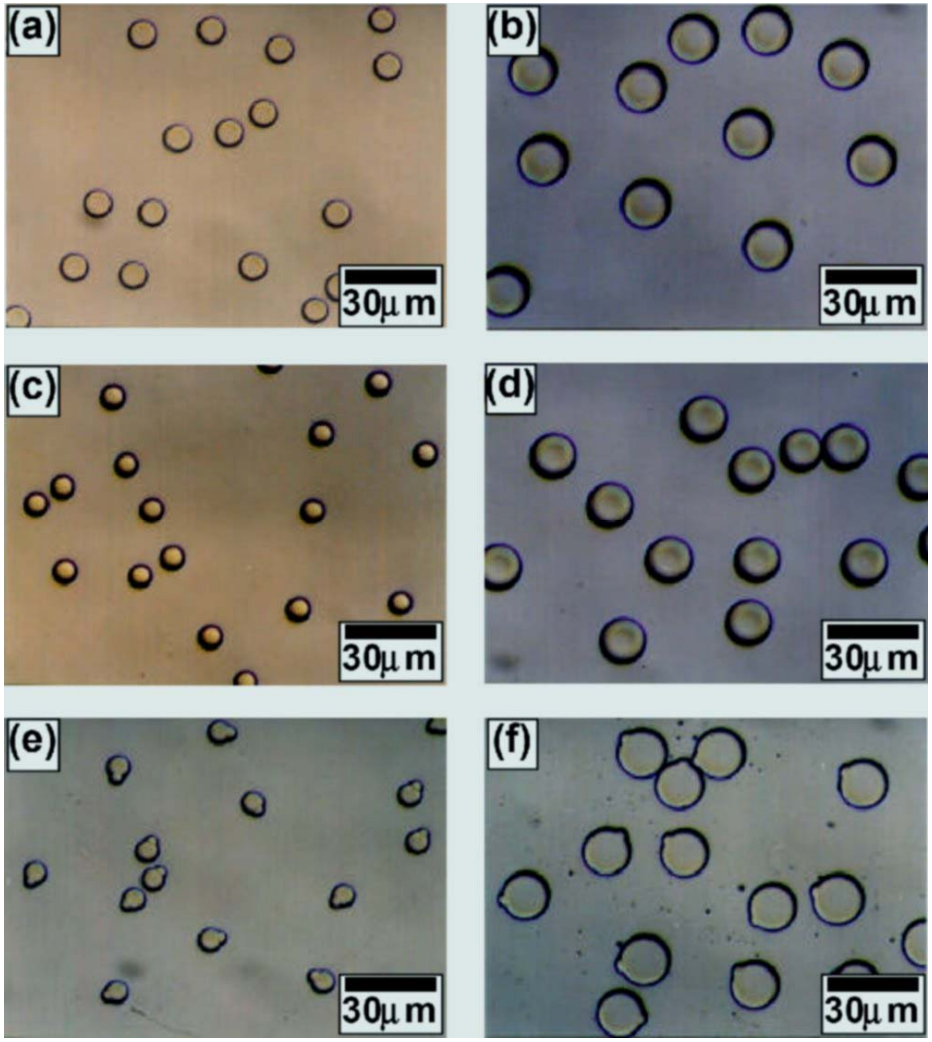
$$\Delta\bar{G} = \mathrm{R}T\left[\ln\phi_1 + \left(1 - \frac{1}{j}\right)\phi_2 + \phi_2^2\chi + \frac{2\bar{V}_1\gamma}{r\mathrm{R}T}\right]$$

$$\Delta\bar{G}^* = \mathrm{R}T\left[\ln\phi_1 + \left(1 - \frac{1}{j_2}\right)\phi_2 + \phi_3 + \phi_2^2\chi_{12} + \phi_3^2\chi_{13} + \phi_2\phi_3\left(\chi_{12} + \chi_{13} - \frac{\chi_{23}}{j_2}\right) + \frac{2\bar{V}_1\gamma}{r\mathrm{R}T} + N\bar{V}_1\left(\phi_3^{1/3} - \frac{\phi_3}{2}\right)\right]$$

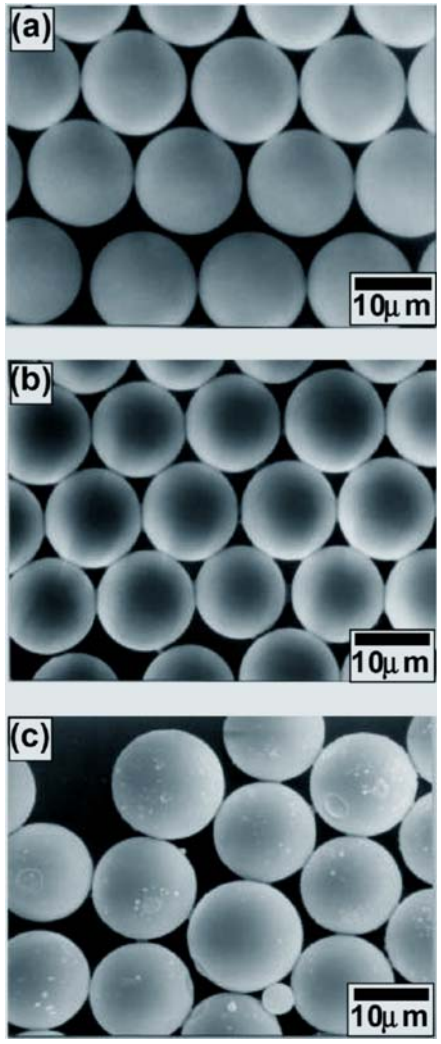




Swelling and polymerization

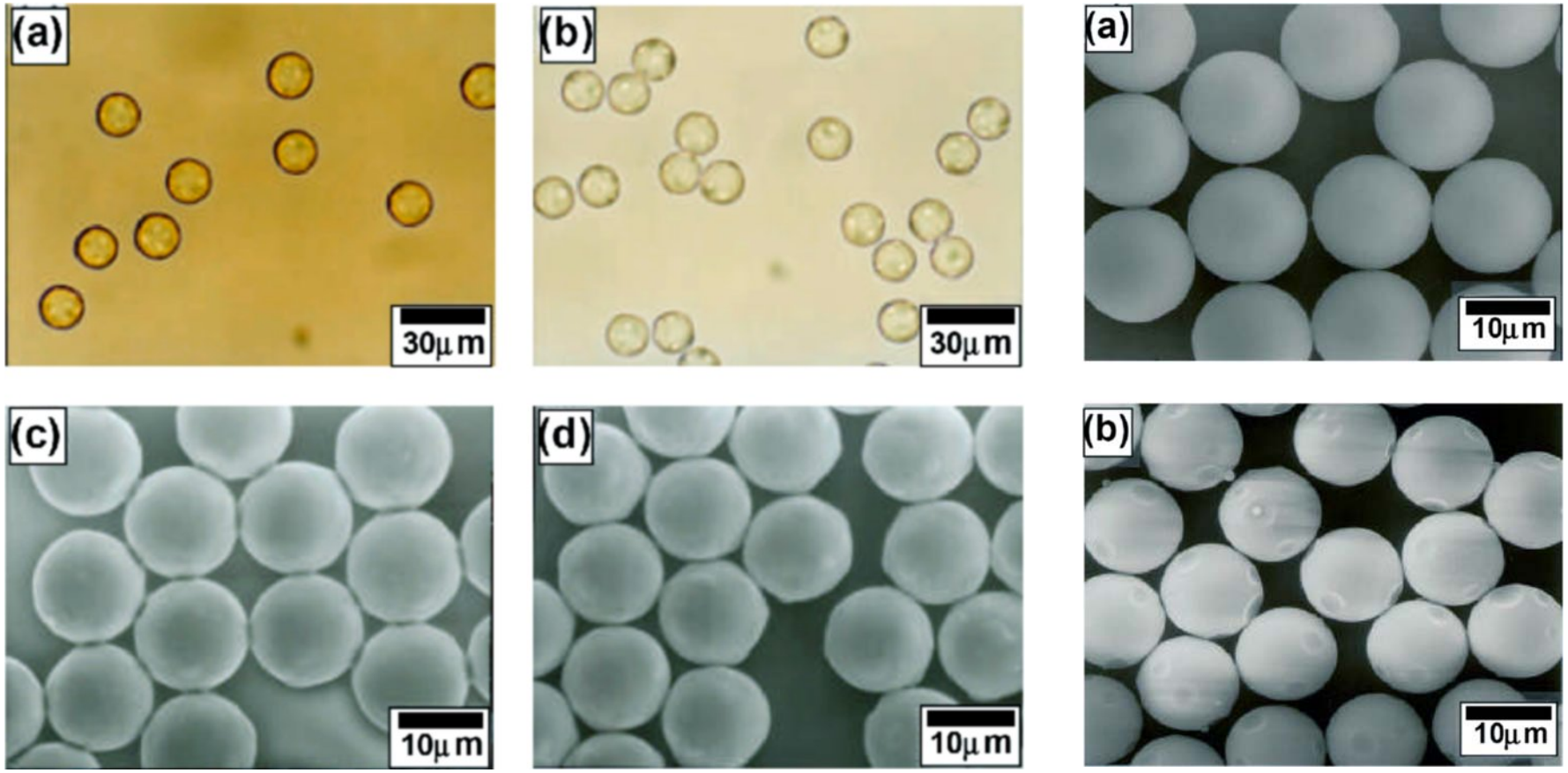


Monomer swellings
(after 30 sec and 2h)



PS particles

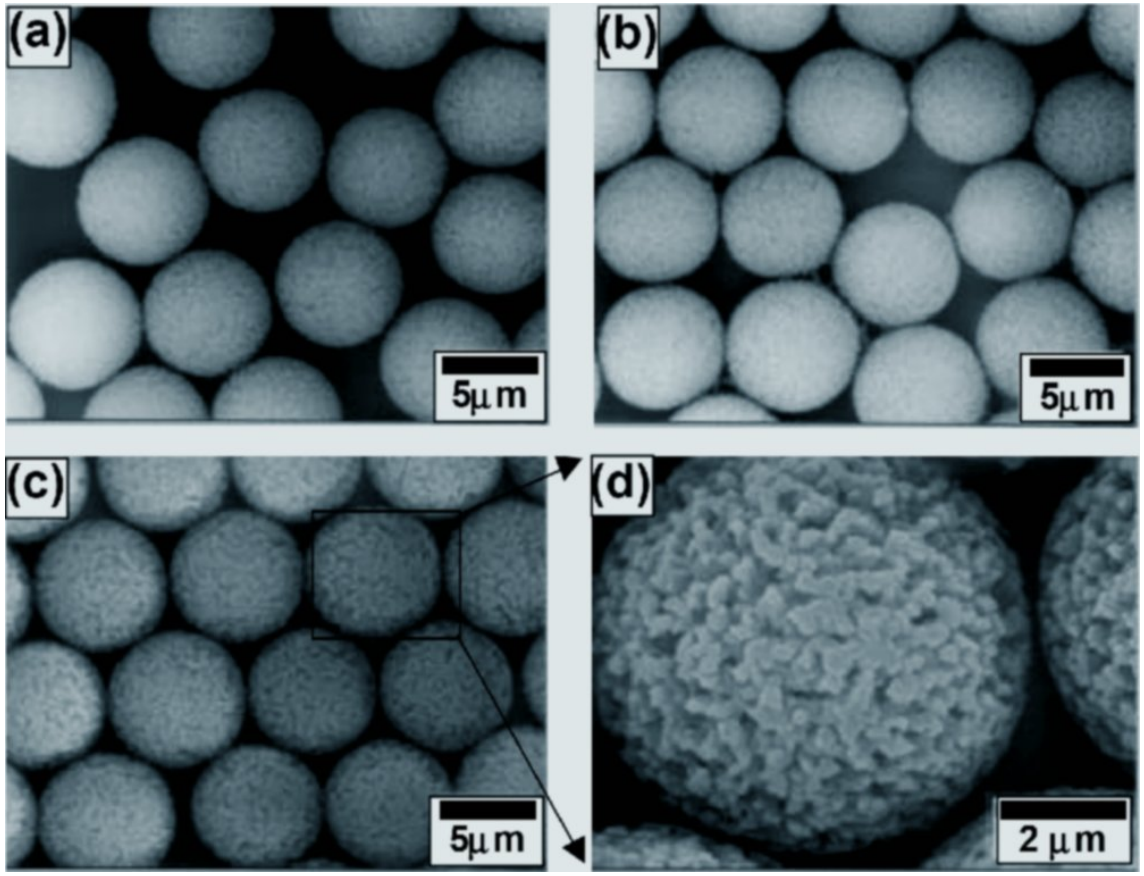
Composite particles



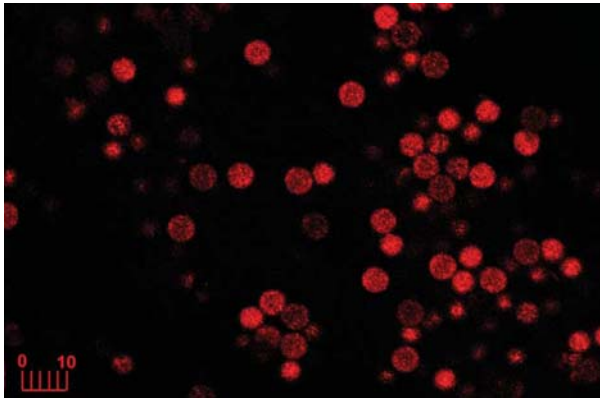
PS/PGMA composite particles

PS/PCMS composite particles

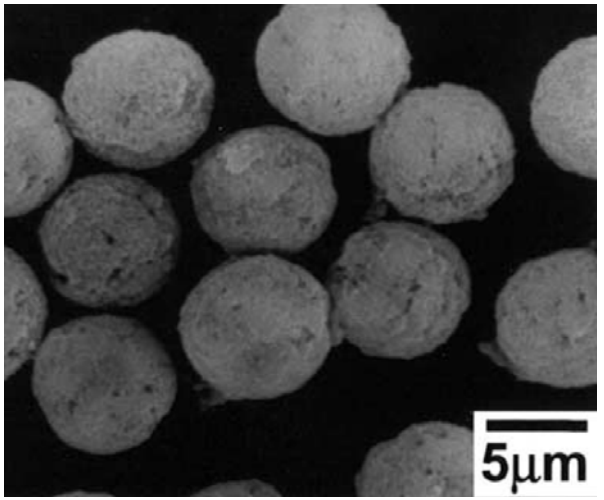
Porous particles



Porous PS particles

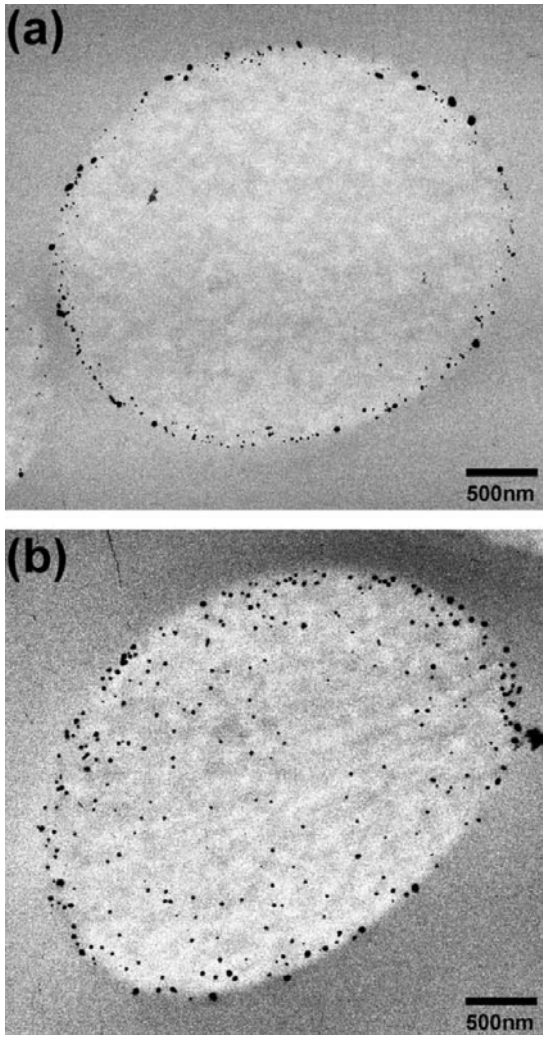


Resveratrol loaded particles

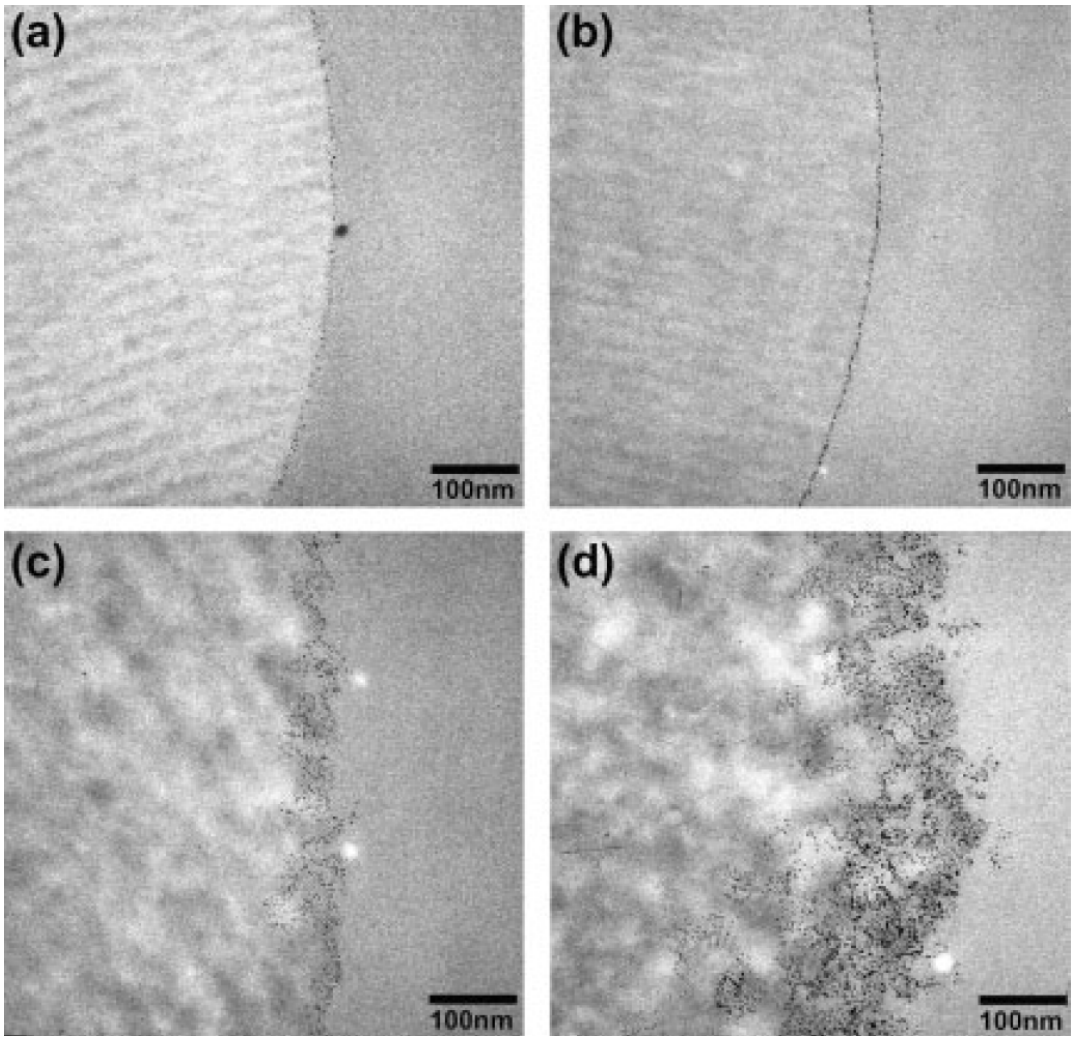


Conducting particles
(PS/polyaniline)

Metal/polymer composite particles

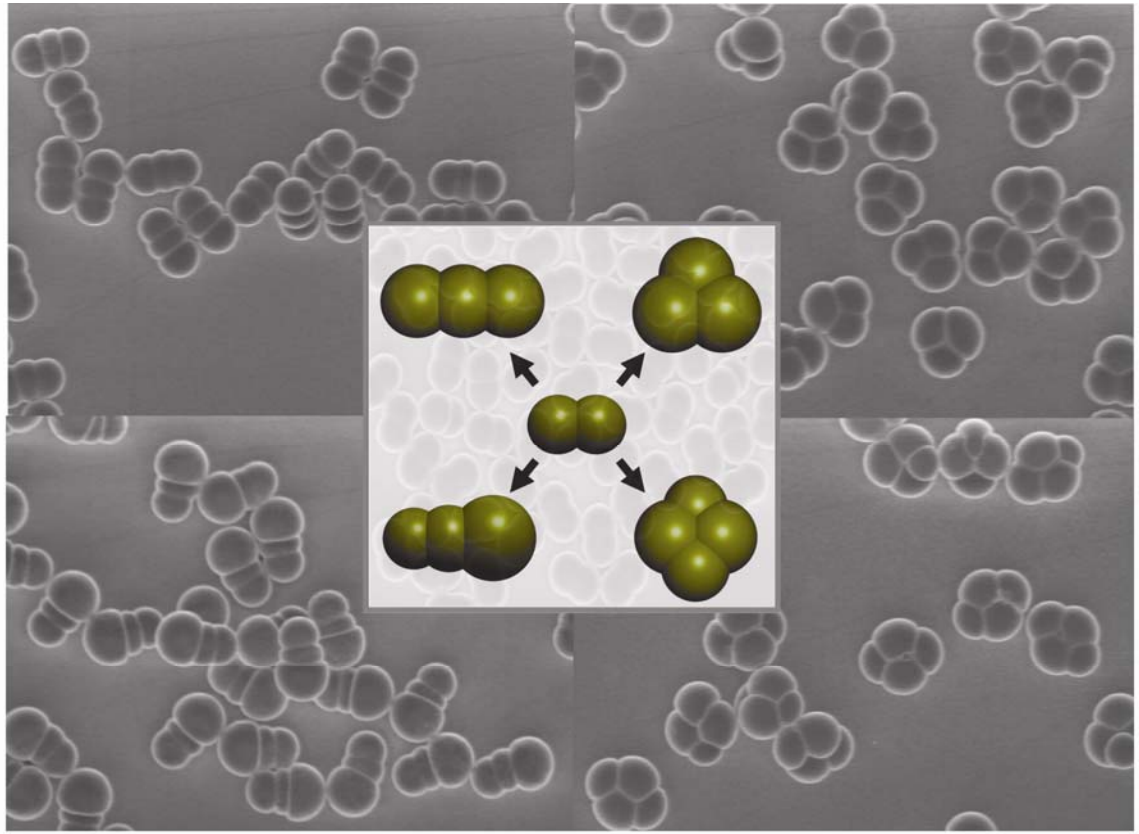


Ag/poly(EGDMA) particles

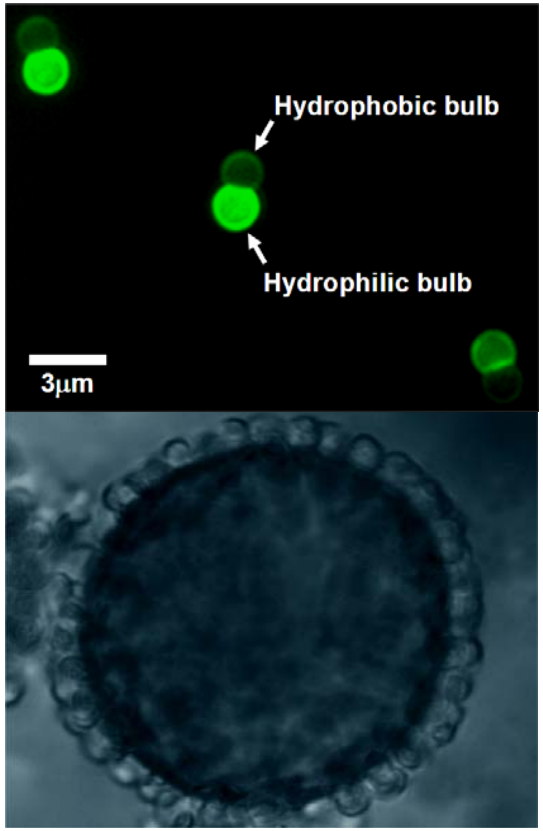


Au/poly(EGDMA) particles

Non-spherical particles



Controlling shape anisotropy



Controlling chemical anisotropy

“Combination of dispersion polymerization and seeded polymerization”