Engineering aspect of emulsion polymerization

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Emulsion Short Course
Yonsei University

Contents

- Free radical polymerization kinetics
- Emulsion polymerization
- Reactor configuration
- Structured particles-Grafting process
- Process modeling

Free radical polymerization

Initiation

$$I - I \xrightarrow{k_d} 2\,I\bullet$$

$$I\bullet + M \xrightarrow{k_i} IM\bullet$$

Propagation

$$IM\bullet + nM \xrightarrow{k_p} IM_nM\bullet$$

Transfer

$$IM\bullet + RH \xrightarrow{k_{tr}} IMH + R\bullet \quad \text{(to CTA)}$$

$$IM\bullet + PH \xrightarrow{k_{tr}} IMH + P\bullet \quad \text{(to Polymer)}$$

Termination

$$2\,IM_n\bullet \xrightarrow{K_{t,c}} IM_{2n}I \quad \text{(Combination)}$$

$$2\,IM_n\bullet \xrightarrow{K_{t,d}} IM_nH + IM_n(\text{-}H) \quad \text{(Disproportion)}$$

Inhibitions of Polymerization

Oxygen

$$M\bullet + O_2 \xrightarrow{\text{fast}} MO\text{-}O\bullet$$

$$MOO\bullet + M \xrightarrow{\text{slow}} MOOM$$

Inhibitors

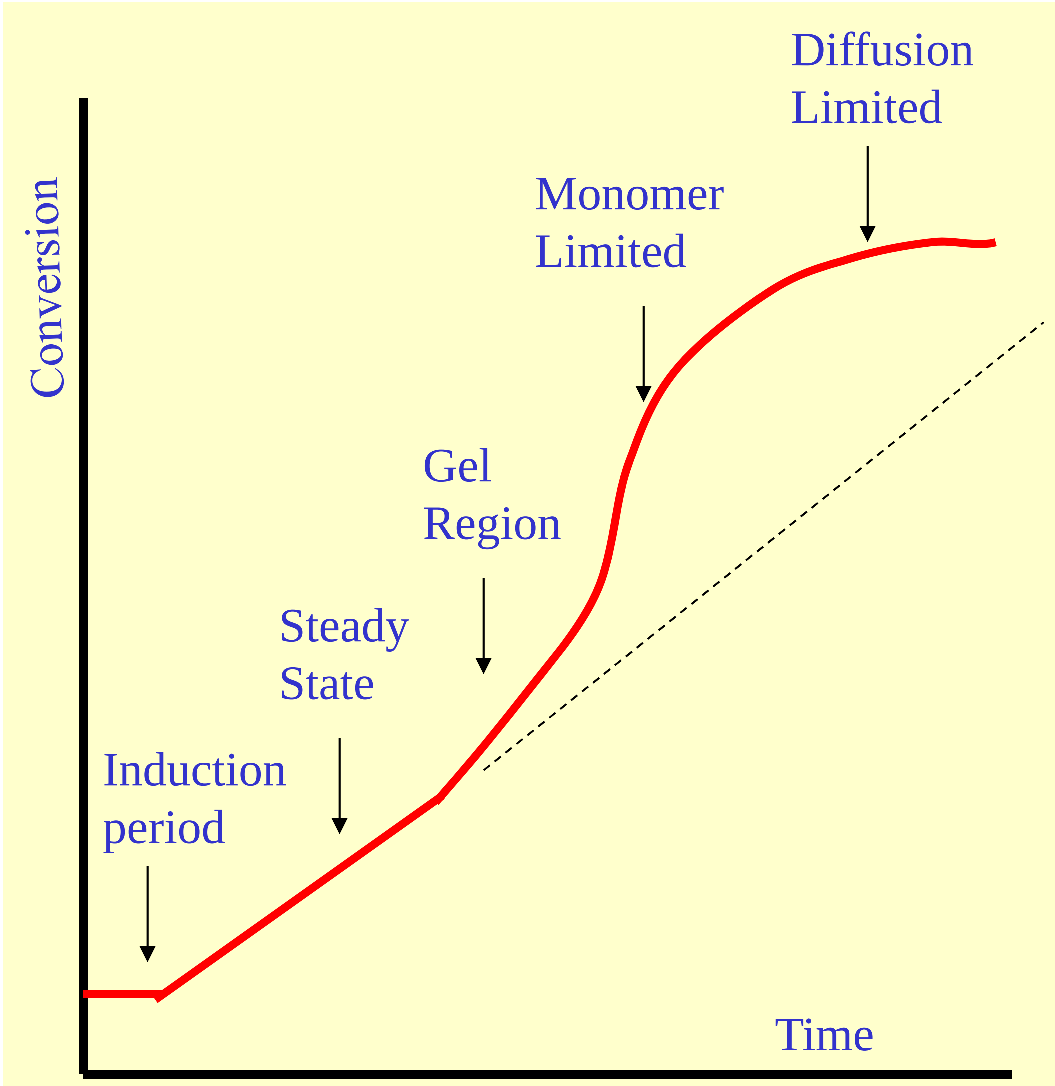
TBC:	t-butylpyrocatechol
MEHQ:	hydroquinone methylether
Benzoquinone:	oil soluble
Hydroquinone:	water soluble

Rate of Polymerization

Steady state process

(Ri = Rt; M • is constant)

$$R_p = k_p M \left(\frac{f\, k_d\, [I]}{k_t}\right)^{1/2}$$



Copolymerization

Copolymer composition; controlled by

Ratio of monomers in feed

Relative reactivity of monomers

Reactivity ratios

For monomers M_1 and M_2

$r_1 = k_{11}/k_{12}$

$r_2 = k_{22}/k_{21}$

$$\sim\sim M_1 \bullet + M_1 \xrightarrow{k_{11}} \sim\sim M_1 M_1 \bullet$$

$$\sim\sim M_1 \bullet + M_2 \xrightarrow{k_{12}} \sim\sim M_1 M_2 \bullet$$

$$\sim\sim M_2 \bullet + M_2 \xrightarrow{k_{22}} \sim\sim M_2 M_2 \bullet$$

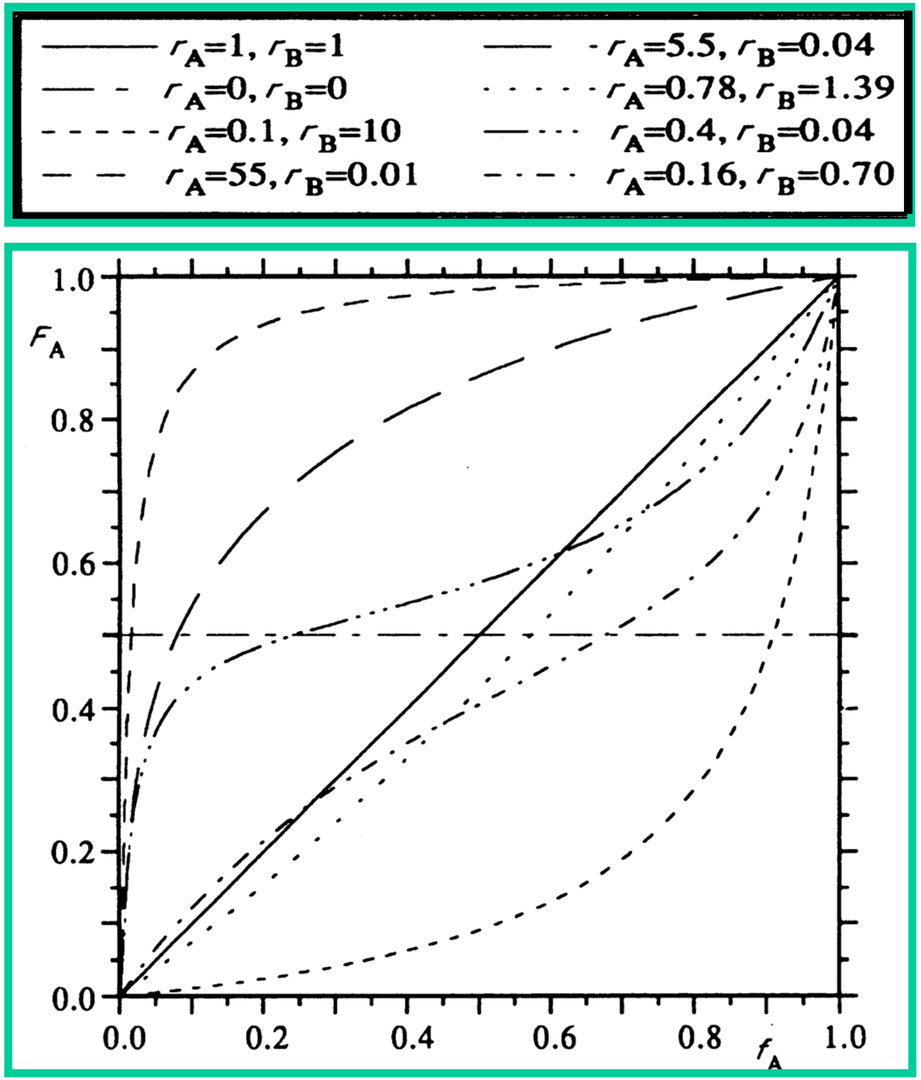
$$\sim\sim M_2 \bullet + M_1 \xrightarrow{k_{21}} \sim\sim M_2 M_1 \bullet$$

Emulsion polymerization: *Partition coefficient*

Copolymer composition

$$F_A = \left(\frac{r_A f_A^2 + f_A f_B}{r_A f_A^2 + 2 f_A f_B + r_B f_B^2} \right)$$

$$F_B = \left(\frac{r_B f_B^2 + f_A f_B}{r_A f_A^2 + 2 f_A f_B + r_B f_B^2} \right)$$



Kinetic Chain Length

ν : Average number of monomer molecules polymerized

$$\nu = \frac{R_p}{R_i} = \frac{R_p}{R_i}$$

$$= \left(\frac{k_p^{\,2}}{2k_t}\right)\frac{[M]^2}{R_p} = \left(\frac{k_p}{2f\,k_d\,k_t}\right)\frac{[M]}{[I]^{1/2}}$$

Increased monomer feed rate → Increased MW

Increased initiator → Decreased MW

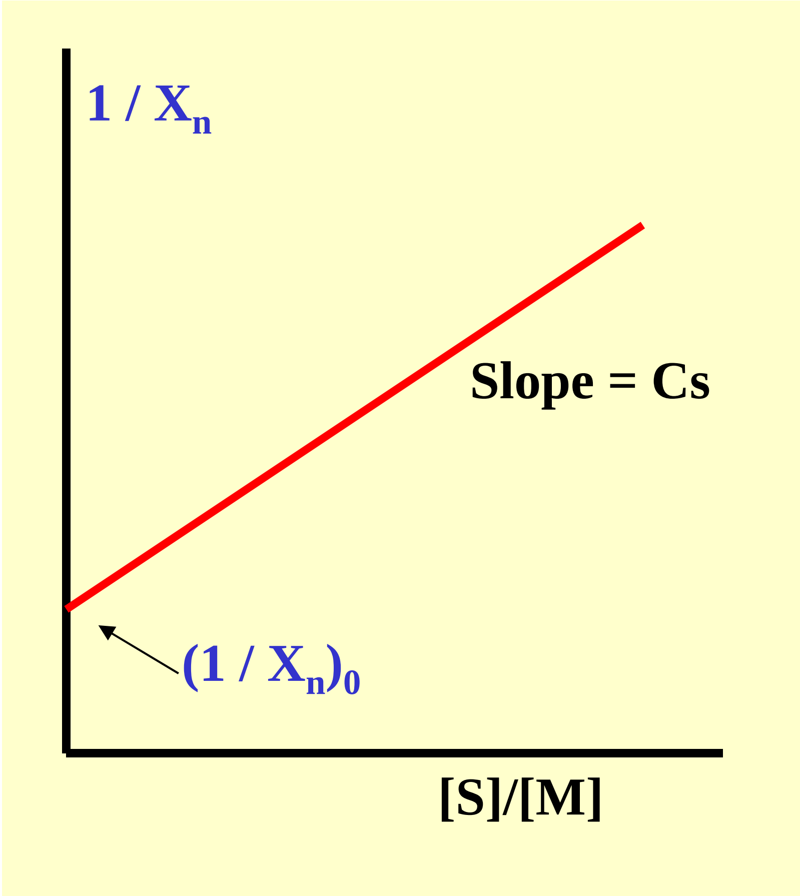
Increased temperature → Decreased MW

Chain transfer agent

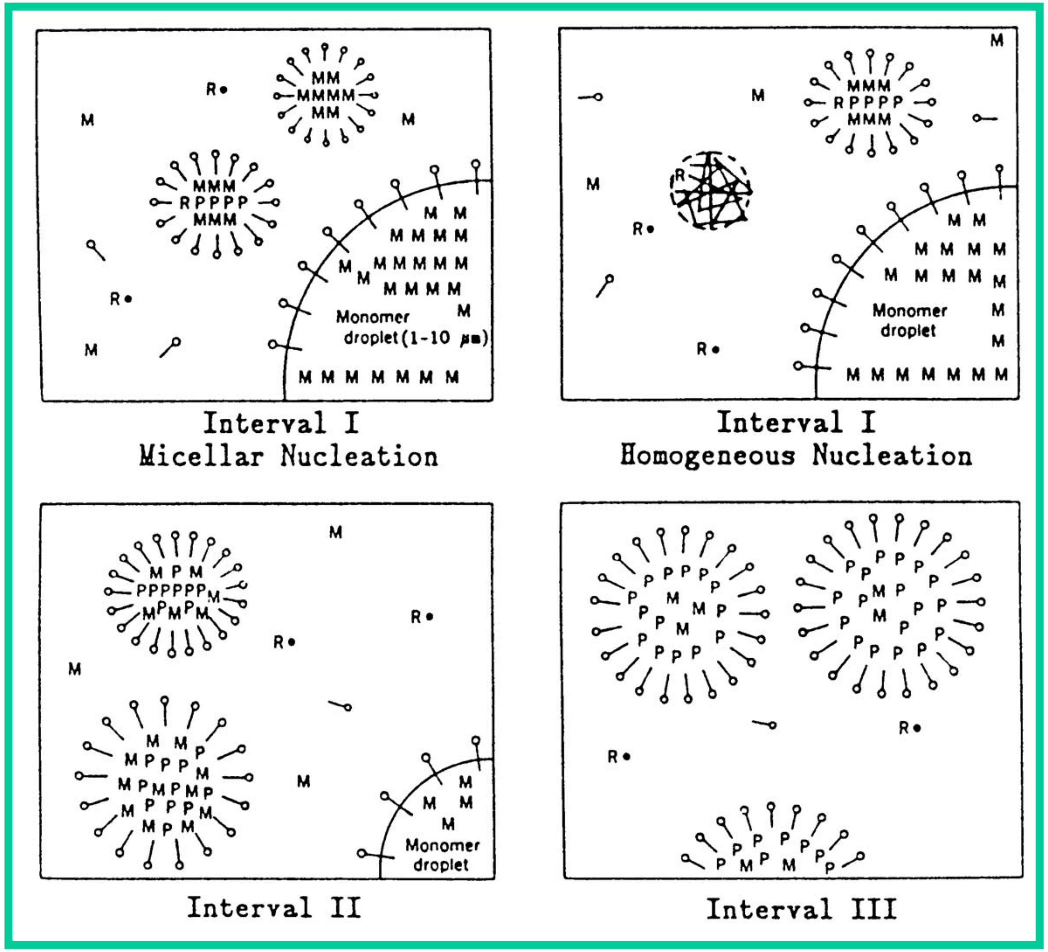
<u>Cs : Chain transfer constant</u>

$$X_n = \frac{R_p}{(R_t + R_{tr})}$$

$$1 / X_n = (1 / X_n)_0 + \mathbf{Cs}\,\frac{[S]}{[M]}$$



Batch Emulsion Polymerization Kinetics



D. Lee, Makromol. Chem., Makromol. Symp., 33, 117 (1990)

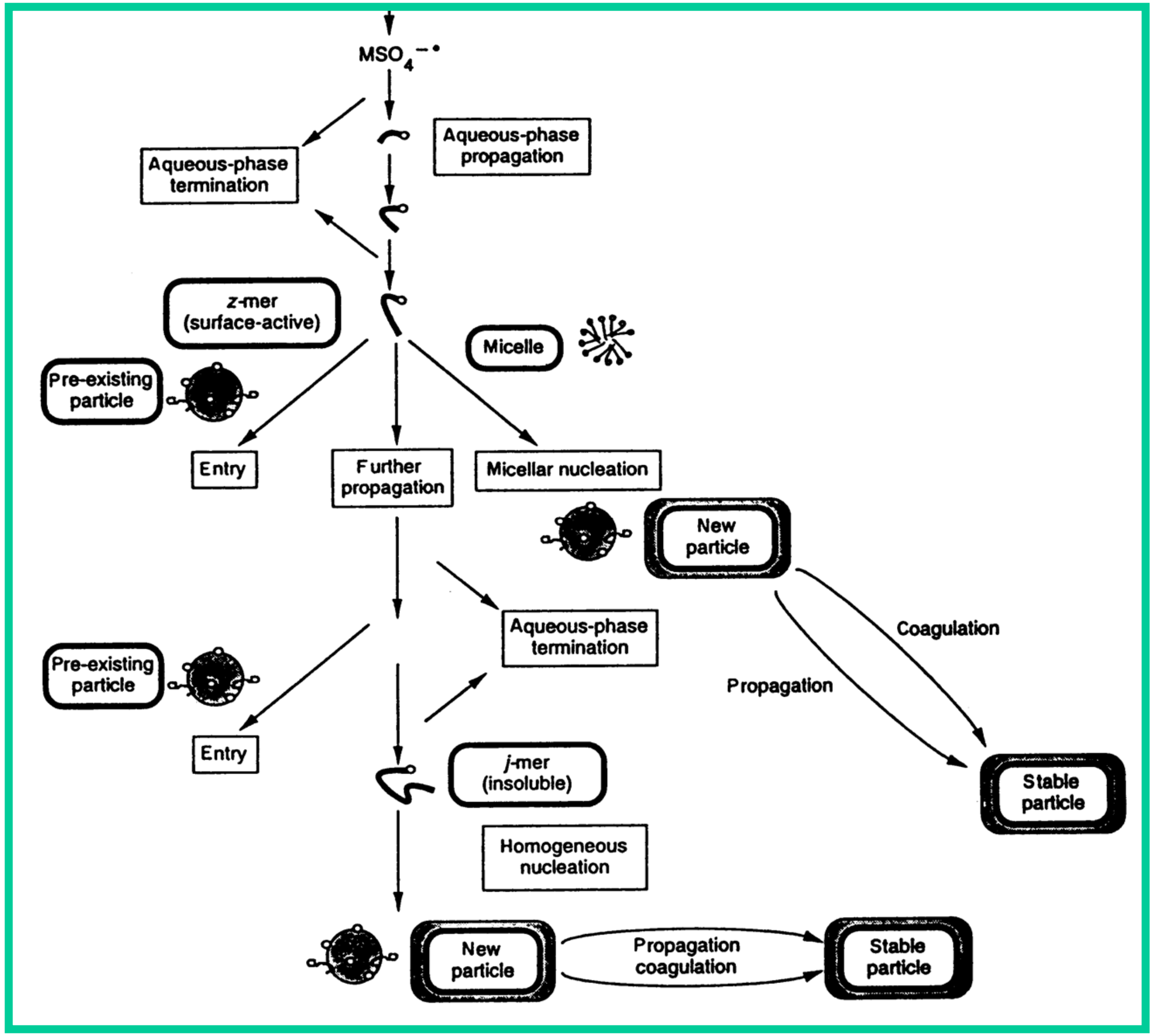
S-E Phase I

- Surfactant in form or micelles swollen with monomer
- Radicals form water soluble initiator captured by very small micelles, and polymerization begins by forming particles
- By end of phase 1, all particles are formed. There is no excess surfactant.

$$N \propto (C_s a_s)^{0.6} (\rho / \mu)^{0.4}$$

C_s :	Concentration of surfactant
a_s:	Area of surfactant molecule
ρ :	Rate of radical generation
μ:	rate of particle growth

Particle formation during interval I



R. Gilbert, in Emulsion polymerization and emulsion polymer edited by P. Lovel and M. El-Aasser, 1997

S-E Phase II

No new particles are formed.

- Each particle contains 0 or 1 radical due to fast termination in a small particle.
- As particles grow, the amount of emulsifier available to stabilize the particle surface area is reducing.

$$R_p = k_p \, (N/2) \, [M]$$

R_p :	Rate of polymerization per ml of water
k_p :	propagation constant
N:	Number of particle per ml of water
M:	Concentration of monomer in particles

S-E Phase II

$$M_n \propto \frac{\text{Rate of polymerization}}{\text{Rate of radical capture}} = \frac{k_p [M]}{(\rho \; / N)} = k_p N [M] / \rho$$

- Added soap must not exceed surface coverage, or new particles will form.
- The smaller particles have greater surface area and compete at the expense of larger particles.
- [M] is controlled by:

  Monomer add rate and limited swelling of particles

Rate of polymerization vs Molecular weight

R_p depends on N and M, but not on the rate of radical generation during the steady-state period.

$$R_p = k_p \,(N/2)\, [M]$$

$$M_n = 2\, R_p / \rho$$

High molecular weight polymers can be obtained without hurting reaction rate by the combination of *large N and small* ρ.

S-E Phase III

- During Phase III, the batch is finished off.
- Crosslinking increases dramatically during final conversion

$$\text{Rate of crosslinking} \propto \frac{\text{Rate of generation of branches}}{\text{Rate of generation of polymers}}$$

$$\propto \frac{\text{Concentration of polymer}}{\text{Concentration of monomer}} = \frac{\text{Conversion}}{\text{1-Conversion}}$$

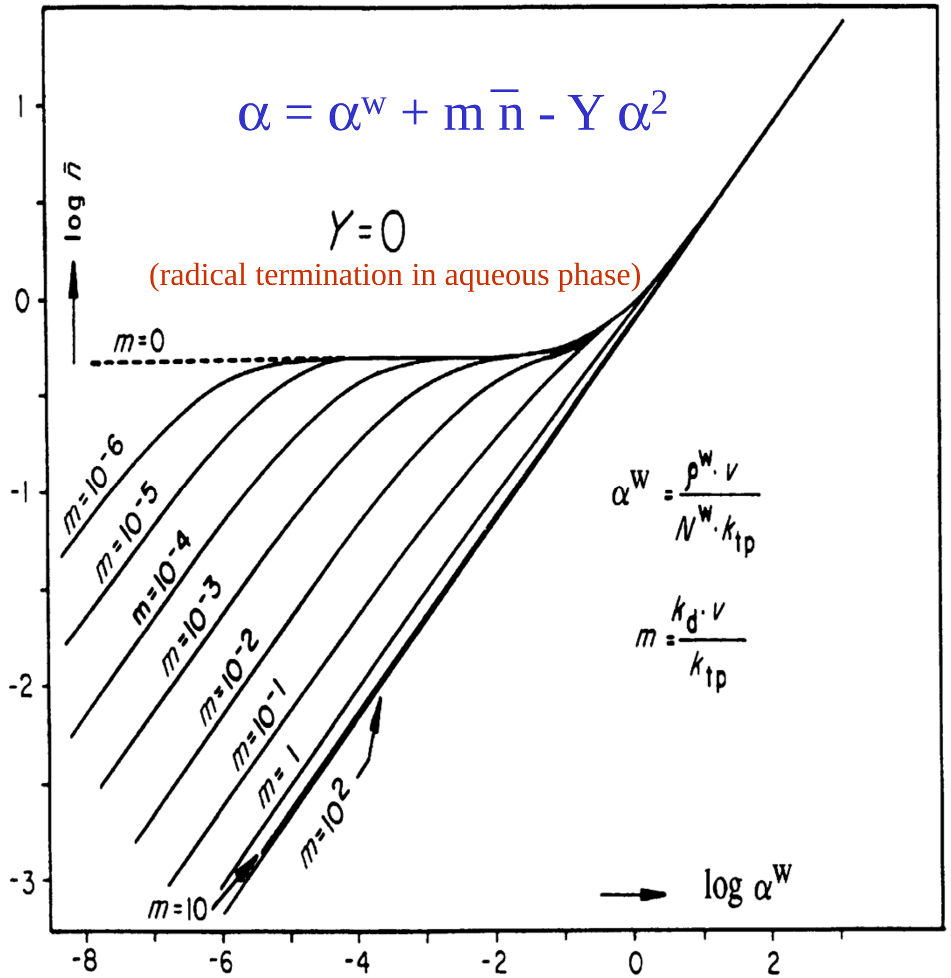
$\bar{n}$ calculation

- Calculation of live radicals in particle phase
- Stationary state distribution of radicals

  absorption

  = initiator decomposition

  + desorption - termination



J. Ugelstadt et al., J. Polym Sci., 5, 2281 (1967)

Reactor classifications

- Batch process
  - Adding all ingredients to the reactor
  - Batch to batch variability during interval I
    - Seeded polymerization
  - Composition drift
  - Monomer partitioning (solubility difference)
  - Heat transfer requirement
- Semi-continuous process
  - Controlled introduction of monomers
  - Optimum monomer addition profile for composition control
- Continuous process
  - CSTR vs Tubular reactor
  - Single vs multiple reactors

Advantages: Semi continuous process

- Reaction temperature
  - Controlled by monomer feed rate
- Copolymer composition
  - Monomer feed control
- Particle concentration
  - Seed latex
  - Controlled feeding of emulsifiers, initiators, and monomers
- Particle size distribution
  - Controlled feeding of emulsifiers and monomers
- Structured particle
  - Easier to control morphology

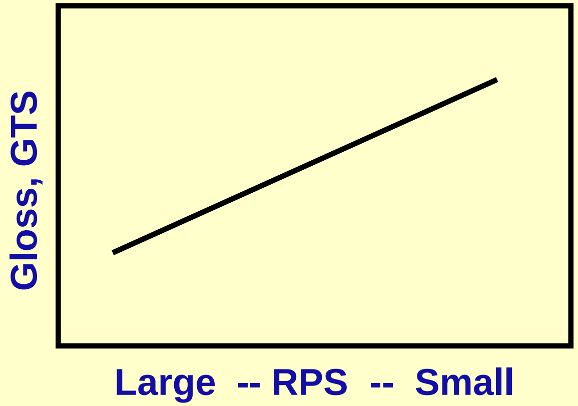
Structured latex particles - Grafting

Tailored structure for desired final physical properties

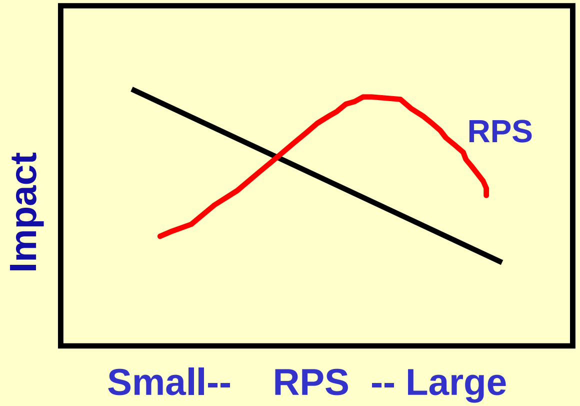
Thermodynamic and kinetic process parameters

- polymer/water interfacial tension
- core polymer particle size and size distribution
- particle surface polarity
- surfactant type and level
- initiator type and level
- chain transfer agent
- monomer to polymer ratio
- reaction temperature
- crosslinking

Parameter - Structure - Property



L --	Graft Level	-- H
L --	Rubber Gel	-- H
H/S --	Morphol	-- C/S
H ---	Metering Rate	-- L
L --	Initiator Level	-- H
L --	Rxn Temp	-- H
H --	CTA	-- L



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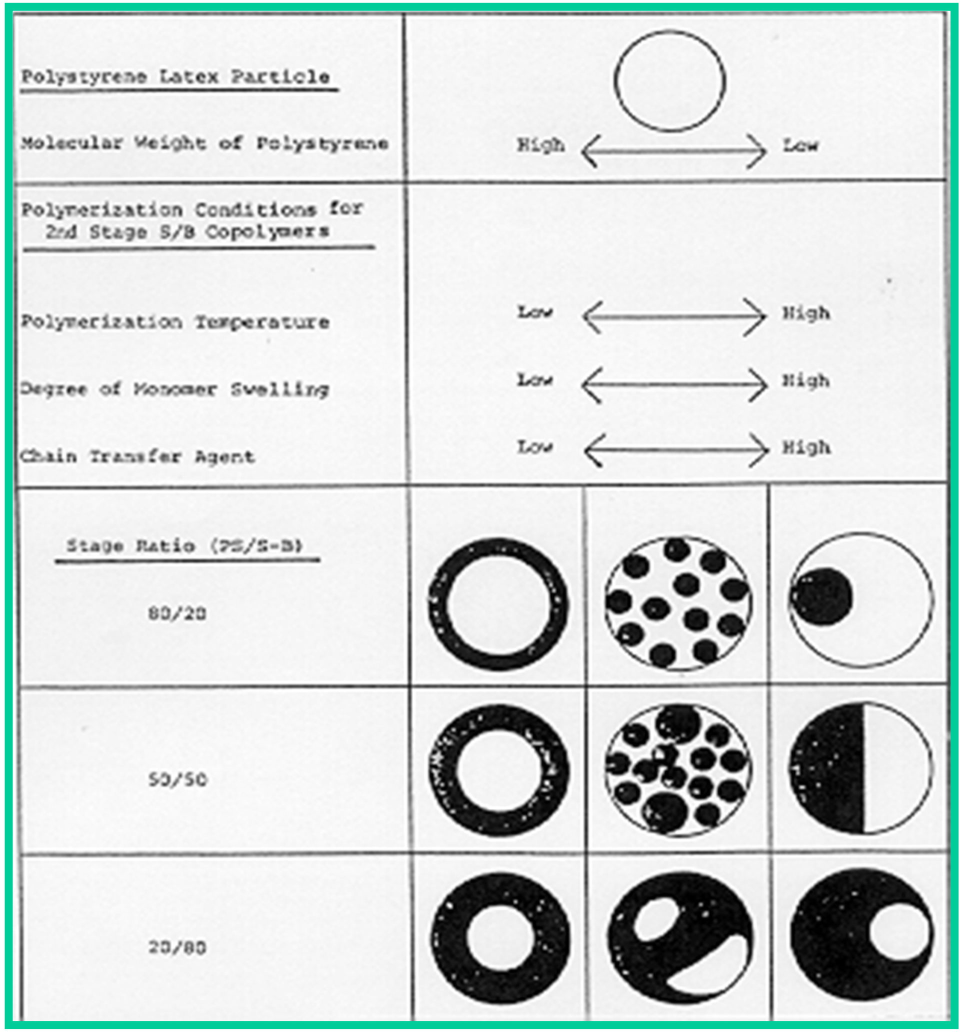
H ---	Metering Rate	-- L
L --	Initiator Level	-- H
L --	Rxn Temp	-- H
H --	CTA	-- L

Kinetic Parameter Controls



D.I. Lee, ACS Symp. Ser., 165, 405 (1981)

Defining grafting parameters

Formulation Parameters	Process parameters
Seed latex particle size	Reaction temperature
Monomer level	Batch or Semi continuous
Initiator type and level	Feed rates
CTA level	
Additional surfactant	

Experimental design:

Plackett-Burman screening design

(n+1 experiments for n variables)

Factorial or partial factorial design

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Grafting

Molecular weight of Graft chain

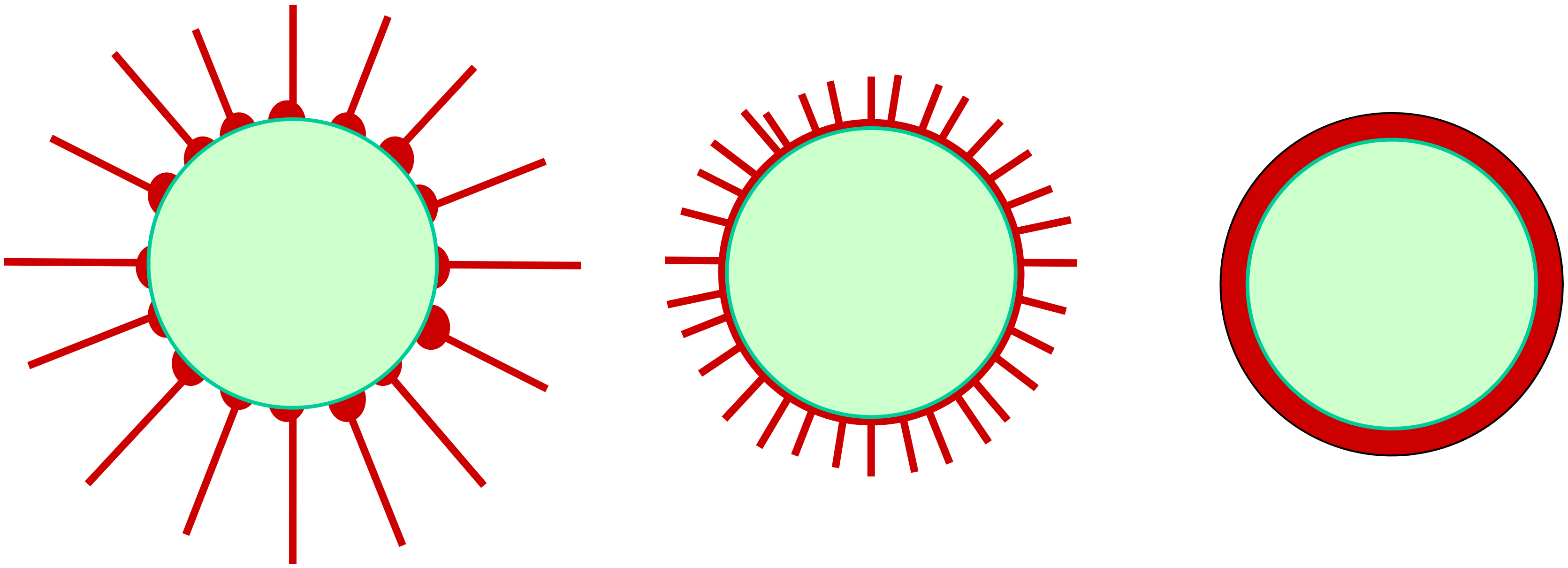
Seed latex particle size ↑	MW ↓
CTA level ↑	MW ↓
Monomer add rate ↑	MW ↑
Initiator level & add rate ↑	MW ↓
Reaction temperature ↑	MW ↓

Graft efficiency = Wt of grafted polymer/Wt of total polymer formed

Seed latex particle size ↑	GL ↑
CTA level ↑	GL ↓
Monomer level ↑	GL ↓
Initiator level ↑	GL ↑
Reaction temperature ↑	GL ↑

Graft MW vs Graft sites

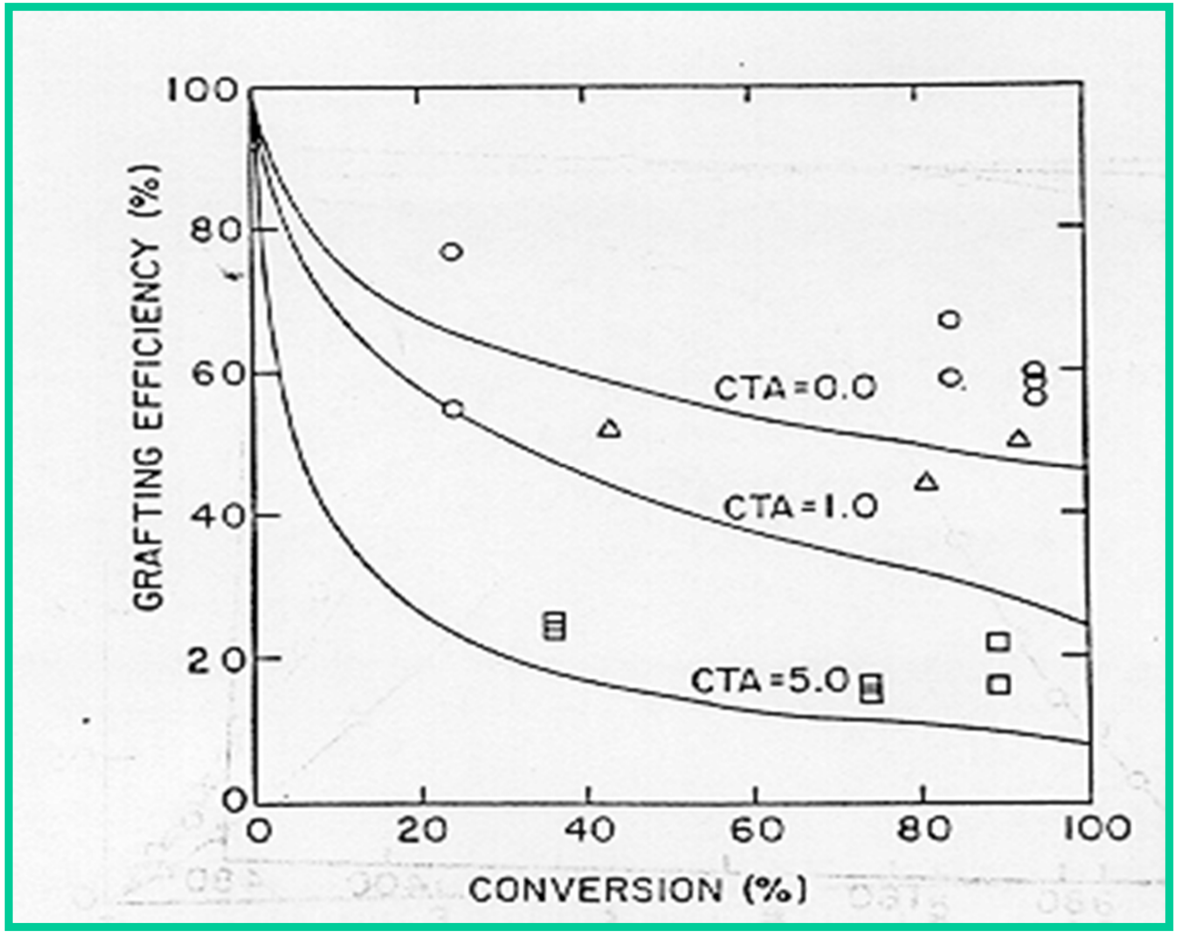
At the same Graft level



High MW, Less graft sites
High toughness, low gloss

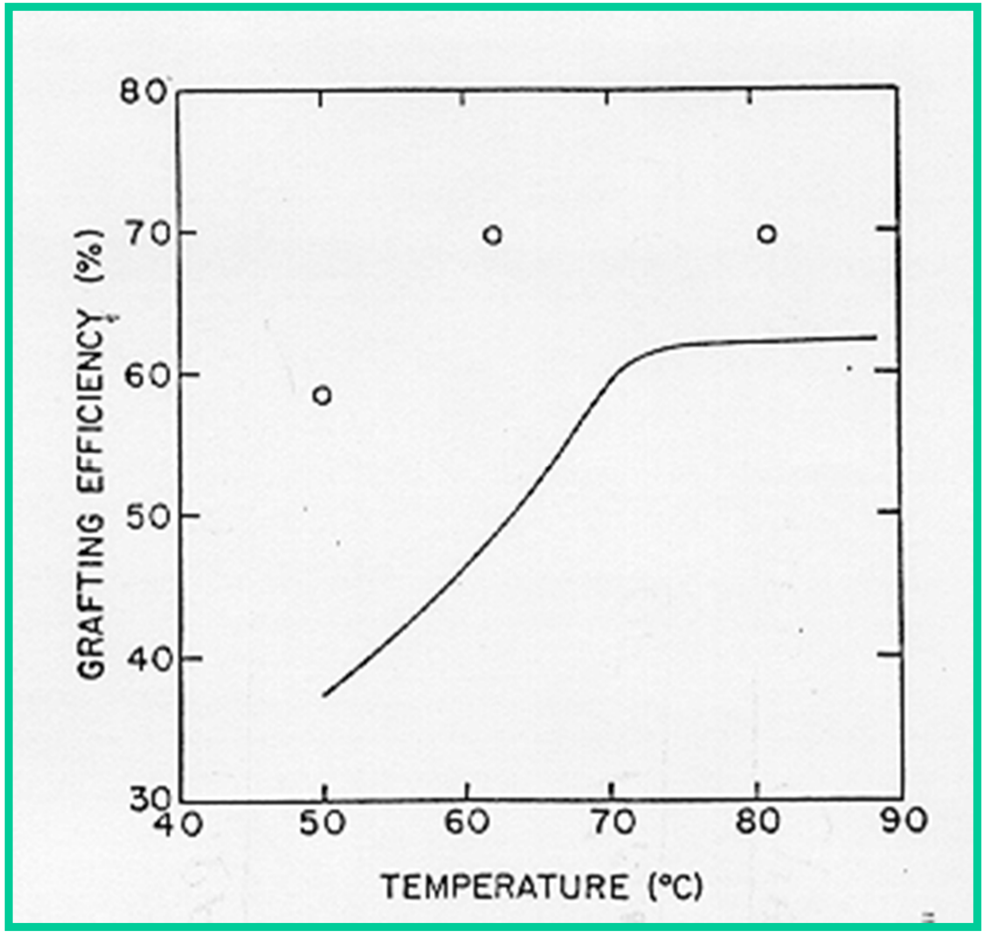
Low MW,Many graft sites
Low toughness, High gloss

Effect of Chain Transfer Agent on Grafting



D. Sundberg, Annual EPI Short Course, Lehigh Univ., (1986)

Effect of Reaction Temp on Grafting

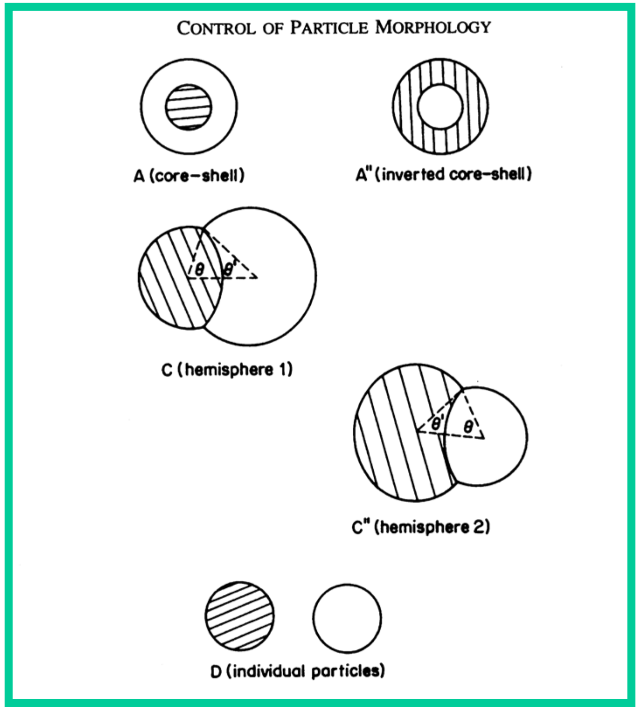


D.C. Sundberg, Annual EPI Short
Course, Lehigh Univ., (1986)

Structure - Thermodynamic consideration

Free energy change

$$\Delta G = \Sigma\, \chi_{ij} A_{ij} - \chi_{iw} A^{1}_{0}$$



Y. Chen, Macromolecules, 24, 3779 (1991)

Case	$\Delta\psi$ (surface energy per unit area)
A (core-shell)	$F[\gamma_{12}(V_r+1)^{-2/3}+\gamma_{2w}]-\gamma_{1w}Y$
A″ (inverted core-shell)	$F[\gamma_{12}(V_r^{-1}+1)^{-2/3}+\gamma_{1w}]-\gamma_{1w}Y$
C(hemisphere 1)	$(F/2)\{(V_r+1)^{-2/3}\gamma_{1w}(1+\cos\theta)+(V_r+1)^{-2/3}$ $(1-\cos\theta)\gamma_{12}+(R_2/R)^2(1+\cos\theta)\gamma_{2w}\}-\gamma_{1w}Y$ $(R_2/R)^3=\{1-(V_r+1)^{-1}\{1-(\frac{1}{8})(1-\cos\theta)$ $[3\sin^2\theta+(1-\cos\theta)^2]\}\}/\{1-(\frac{1}{8})(1-\cos\theta)$ $[3\sin^2\theta+(1-\cos\theta)^2]\}$ $(R_2/R)=(V_r+1)^{-1/3}\sin\theta/\sin\theta$
C″ (hemisphere 2)	$(F/2)\{(R_1/R)^2(1+\cos\theta)\gamma_{1w}+\gamma_{12}(1-\cos\theta)(V_r^{-1}+1)^{-2/3}+$ $(V_r^{-1}+1)^{-2/3}(1+\cos\theta)\gamma_{2w}\}-\gamma_{1w}Y$ $(R_1/R)^3=\{1-(V_r^{-1}+1)\{1-(\frac{1}{8})(1-\cos\theta)$ $[3\sin^2\theta+(1-\cos\theta)^2]\}\}/\{1-(\frac{1}{8})(1-\cos\theta)$ $[3\sin^2\theta+(1-\cos\theta)^2]\}$ $R_1/R=(V_r^{-1}+1)^{-1/3}\sin\theta/\sin\theta$
D (individual particles)	$F(\gamma_{1w}+\gamma_{2w}V_r^{2/3})(V_r+1)^{-2/3}-\gamma_{1w}Y$

[a]Where $Y = K(V_f+1)^{-2/3}$, $K=(1+W_r\rho_1/\rho_{2m})^{2/3}$, $V_f = W_r\rho_1/\rho_2$, and $F=[Y^{3/2}+(1-\rho_2/\rho_{2m})X/(1+1/V_f)]^{2/3}$. Here ρ, ρ_2, and ρ_{2m} are the densities of polymer 1, polymer 2, and monomer 2, respectively; W_r is the weight ratio of total monomer 2 to polymer 1; X is the polymerization conversion, R_1, R_2, and R are the radii of polymer phase-1, polymer phase-2, and the overall composite particles, respectively; θ and θ' (see Figure 9.2) are the angles between the line that connects the two centres of the hemispheres and the line that connects the centres and the three-phase point; γ_{12}, γ_{1w}, γ_{2w} are the interfacial tensions between the two polymer phases, polymer phase-1 and water (containing surfactant, if present), and polymer phase-2 and water (containing surfactant, if present) respectively. A polymer phase is defined as polymer 1 or polymer 2 dissolved in MMA monomer; V_r is the volume ratio of polymer phase-2 to polymer phase-1 (from ref. 39)

Structure - Thermodynamic consideration

Core shell morphology

Increase seed particle size
Decrease χ_{sw}
Increase cross-link density

$$\frac{\chi_{cw} - \chi_{cs}}{\chi_{sw}} \geq \frac{1 - V_s^{1/2}}{V_c^{1/2}}$$

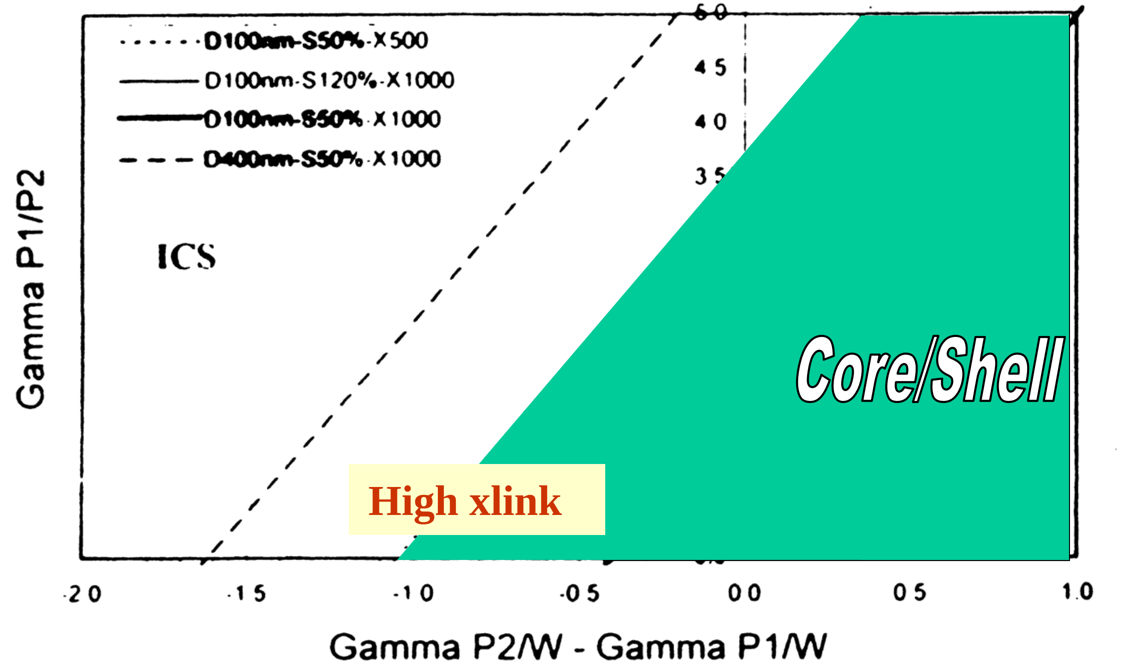


Figure 8. Morphology domain map of the effect of the interfacial tensions. By selecting a set of interfacial tensions ($\gamma_{P_2/W} - \gamma_{P_1/W}$) and γ_{P_1/P_2} and selecting the line relevant to the seed particle diameter (D), the stage ratio (S), and the cross-linking density ($X = M_c/M$), one can determine the most stable morphology of such a system.

D. Sundberg, Macromolecules, 29, 8466 (1996)

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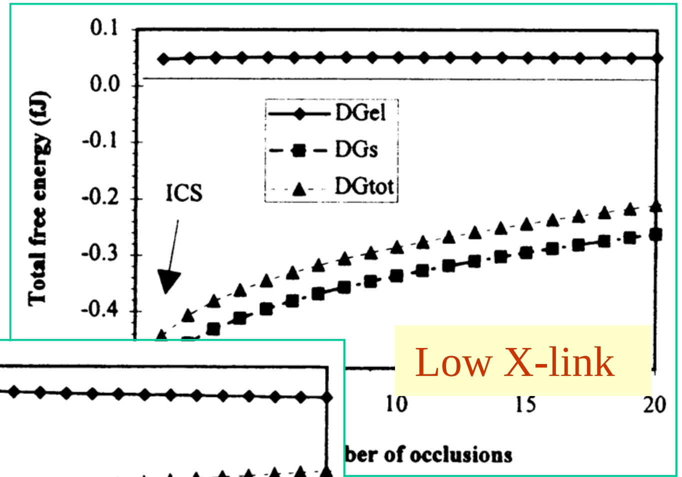
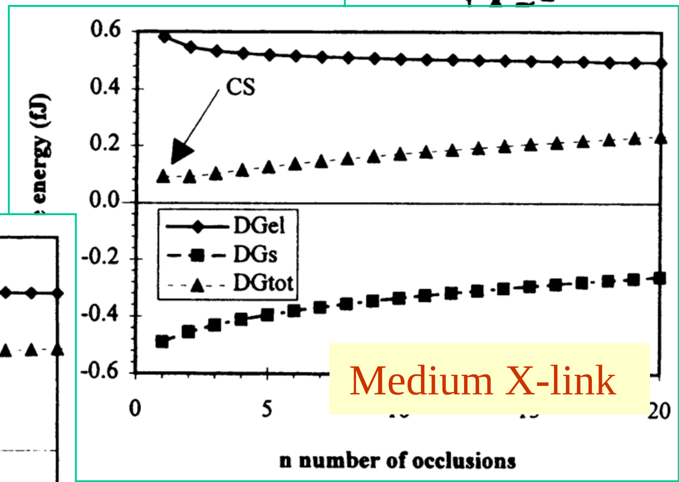
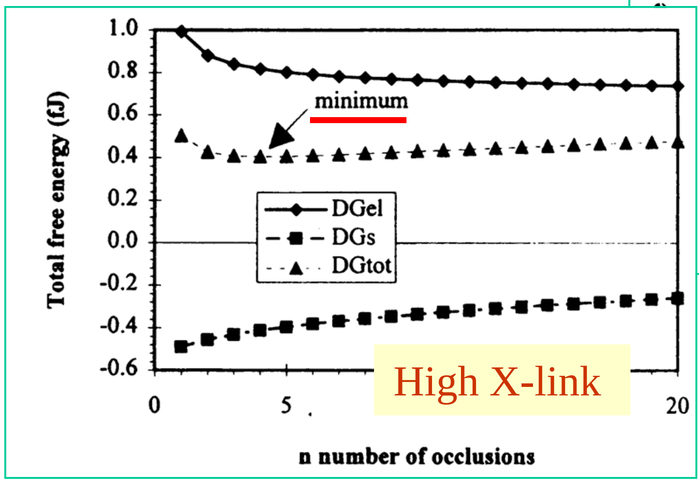
Structure - Kinetic consideration

No of Internal Occlusions and
Minimum Cross-link density
for core shell structure

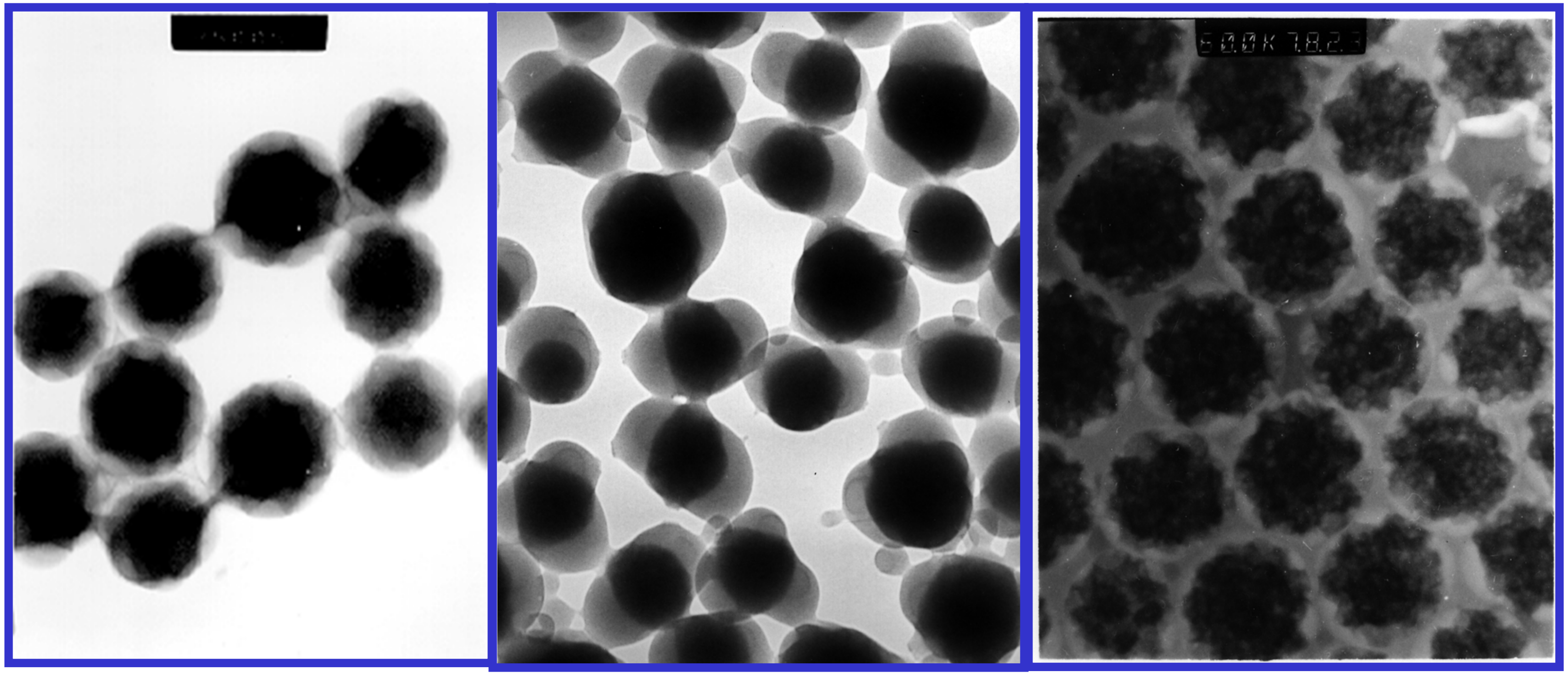






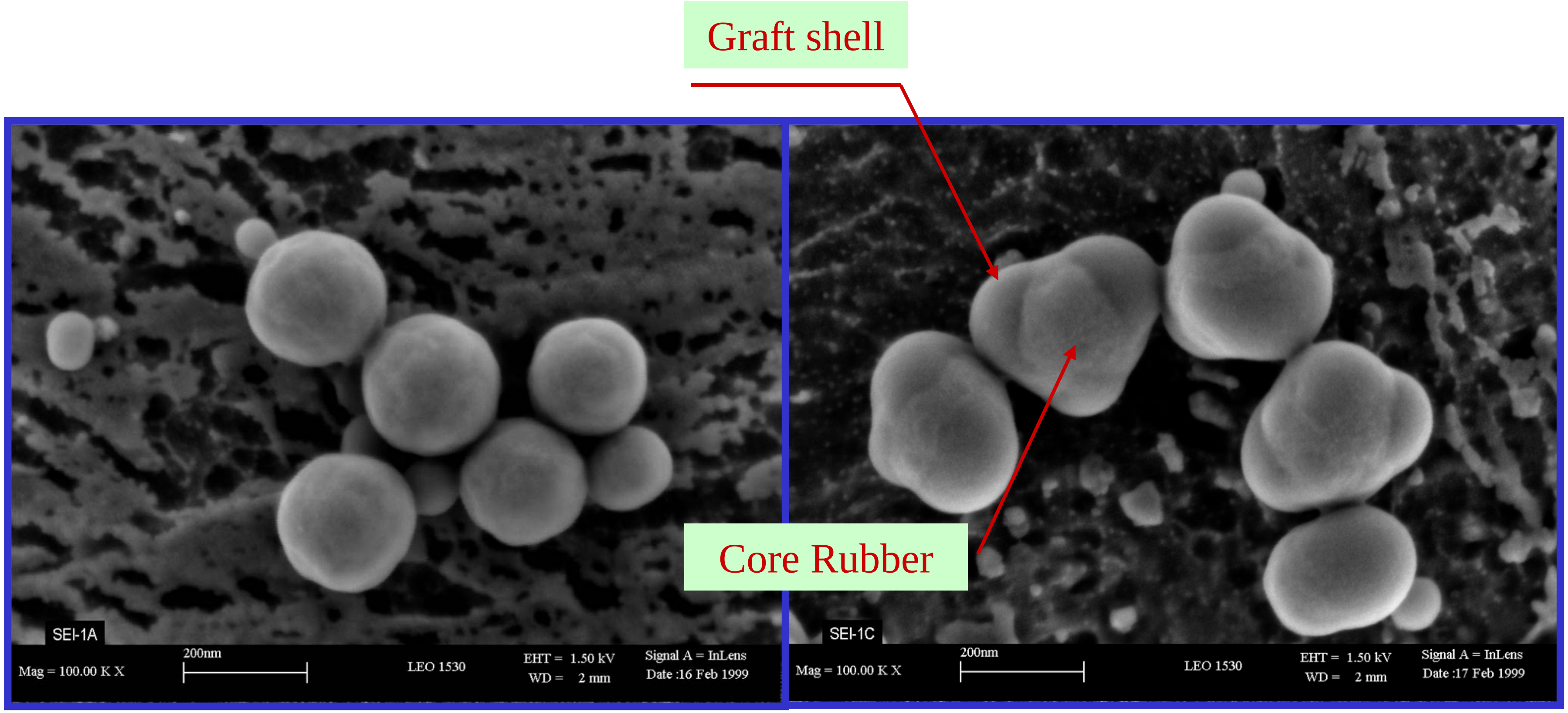
D. Sundberg, Macromolecules, 29, 8466 (1996)

TEM pictures of the graft latexes



Core/shell | Hemisphere | Occlusions

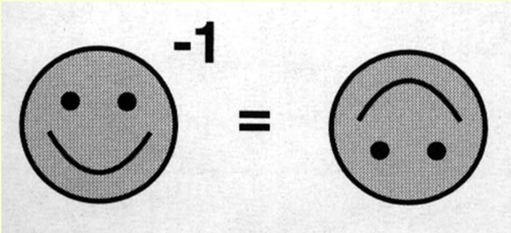
SEM pictures of the graft latexes

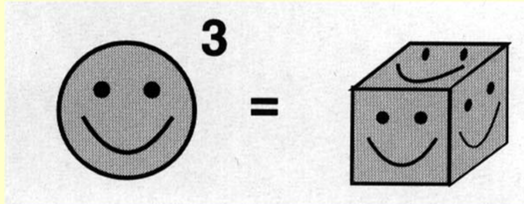


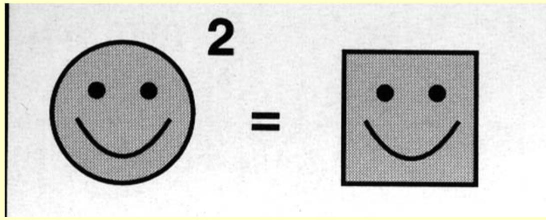
Process Modeling

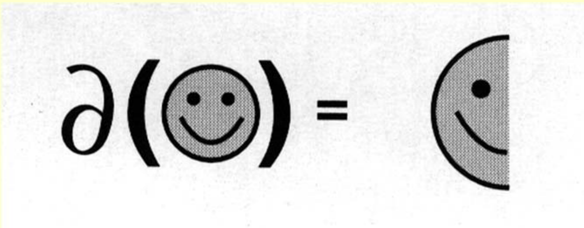
- Polyred / Hysis - Wisconsin
- *Polymer plus - Aspen*
- In house programs

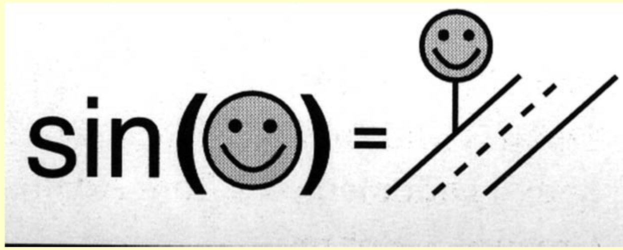
Mathematics

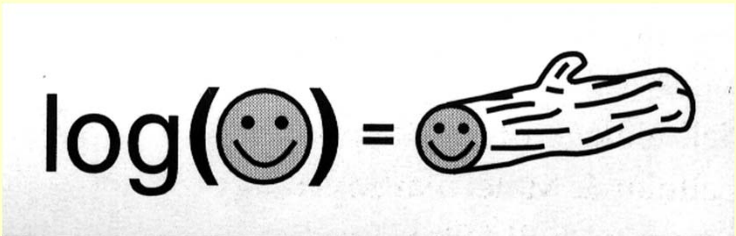












Objectives

- Calculation of kinetics and molecular properties from the recipe without doing experiments
  - Conversion curve
  - Particle nucleation and growth
  - Particle size and size distribution
  - Polymer composition profile
  - Heat generation
  - Molecular weight, means, and distribution

What's good for?

- Simulation doesn't cost much.
  - Better understanding of polymerization by elucidation of mechanisms
  - Better planning and analysis of experiments
  - Straight forward and a easy way to adjust molecular properties
  - Can predict the properties by changing the recipes