

# „Polymer-Dispersionen“

Klaus Tauer

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Definitions

Meaning & properties of polymer dispersions

Preparation of polymer dispersions

# Polymer Dispersions

## Polymer:

any of a class of natural or synthetic substances composed of very large molecules, called macromolecules, that are multiples of simpler chemical units called monomers. Polymers make up also many of the materials in living organisms, including, for example, proteins, cellulose, and nucleic acids.

## Dispersion:

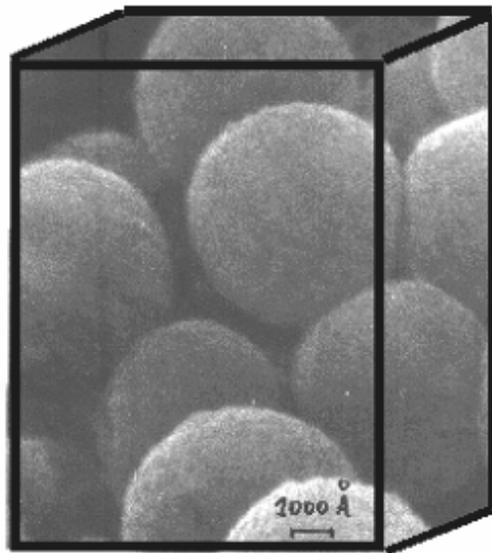
(physical chemistry) a special form of a colloid:

i.e. very fine particles (of a second phase) dispersed in a continuous medium

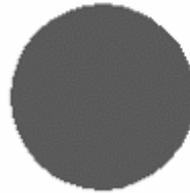
the most popular / famous / best-known case of a polymer dispersion is a LATEX

a latex is produced by heterophase polymerization, where the most important technique is emulsion polymerization

# What is a Polymer Dispersion?



macroscopic



1 g Polystyrene

$$V = 0.952 \text{ cm}^3$$

$$D = 1,22 \text{ cm}$$

$$N = 1$$

$$O = 4,767 \text{ cm}^2$$

$$0,002 \text{ DM}^*)$$

Dispersion



$$D = 50 \cdot 10^{-7} \text{ cm}$$

$$N = 1,455 \cdot 10^{16}$$

$$O = 1,143 \cdot 10^6 \text{ cm}^2$$

$$1,8 \cdot 10^3 \text{ DM}^*)$$

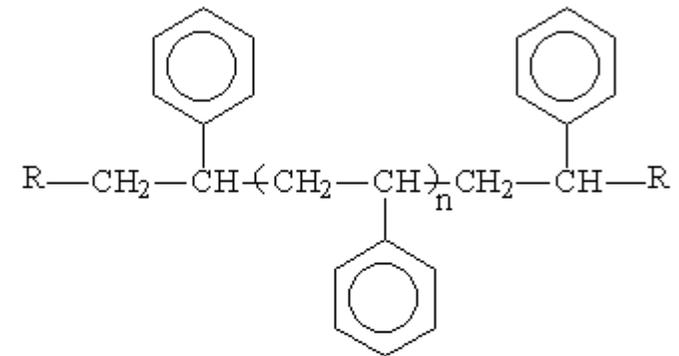
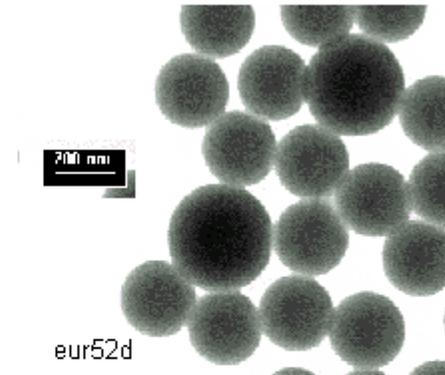
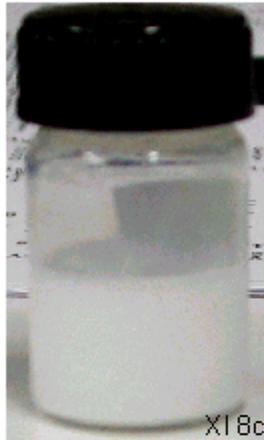
a) Polyscience, Inc. catalog 1995

$N$  polymer particles with an average volume  $V_P$  dispersed in a liquid of volume  $V_W$

the liquid is called dispersion medium or continuous phase or serum or homogeneous phase

\*) 1 DM = 1.95583 €

# Molecular Composition of a Latex



solids: 50 %,  $D = 200 \text{ nm}$ ,  
 $M_N = 6 \cdot 10^5 \text{ g mol}^{-1}$ , styrene

$$N \sim 2.3 \cdot 10^{14} \text{ cm}^{-3}$$

4400 macromolecules  
per particle

$$n \sim 6000$$

General:

$$N \sim 10^5 - 10^{15} \text{ cm}^{-3}$$

$1 - 10^{12}$  macromolecules  
per particle

$$n \sim 1 - 10^6$$

polymer dispersionen:

high concentration of polymer with low viscosity



thickener (BASF AG, Ludwigshafen)

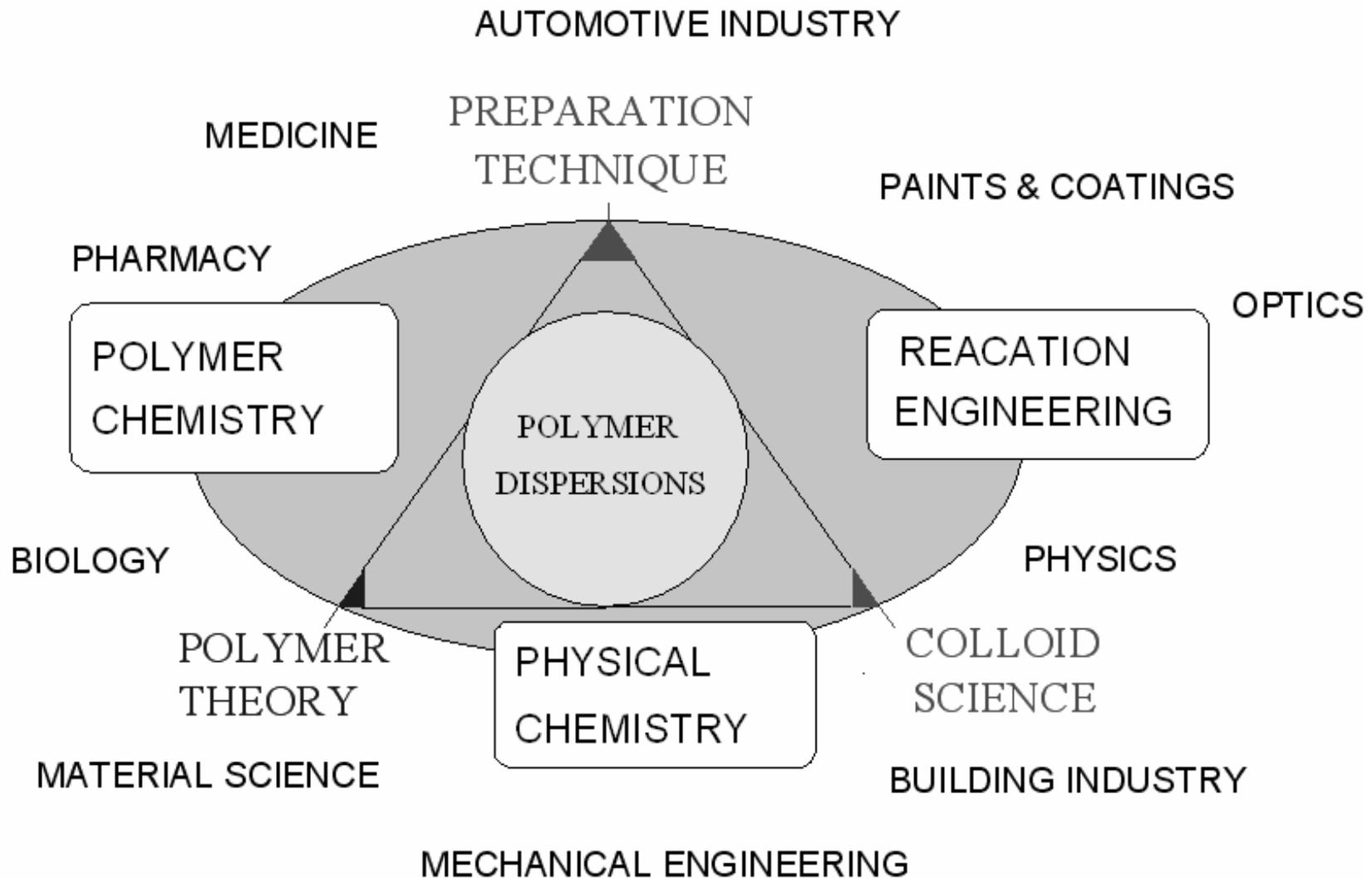
## **Virtual EASE 2003/1 „Thickening agent“**

Sterocoll is an acidic aqueous polymer dispersion containing polymer particles rich in carboxylic acid groups. It is used as thickening agent.

First the polymer dispersion is diluted with water to lower the polymer content from 30 % to 5 %. It is still a white liquid having low viscosity.

By addition of a small amount of an aqueous sodium hydroxide solution the pH is increased and the carboxylic acid groups are negatively charged. This makes the polymer particles soluble in water and a polymer solution is formed. At the same time the viscosity strongly increases due to the unfolding of the polymer molecules. At the end a clear gel is obtained.

# The Meaning of Polymer Dispersions



→ each application needs a polymer dispersion with special properties

important application properties:

*viscosity*



viscosity-psd

dilatancy (BASF AG, Ludwigshafen)

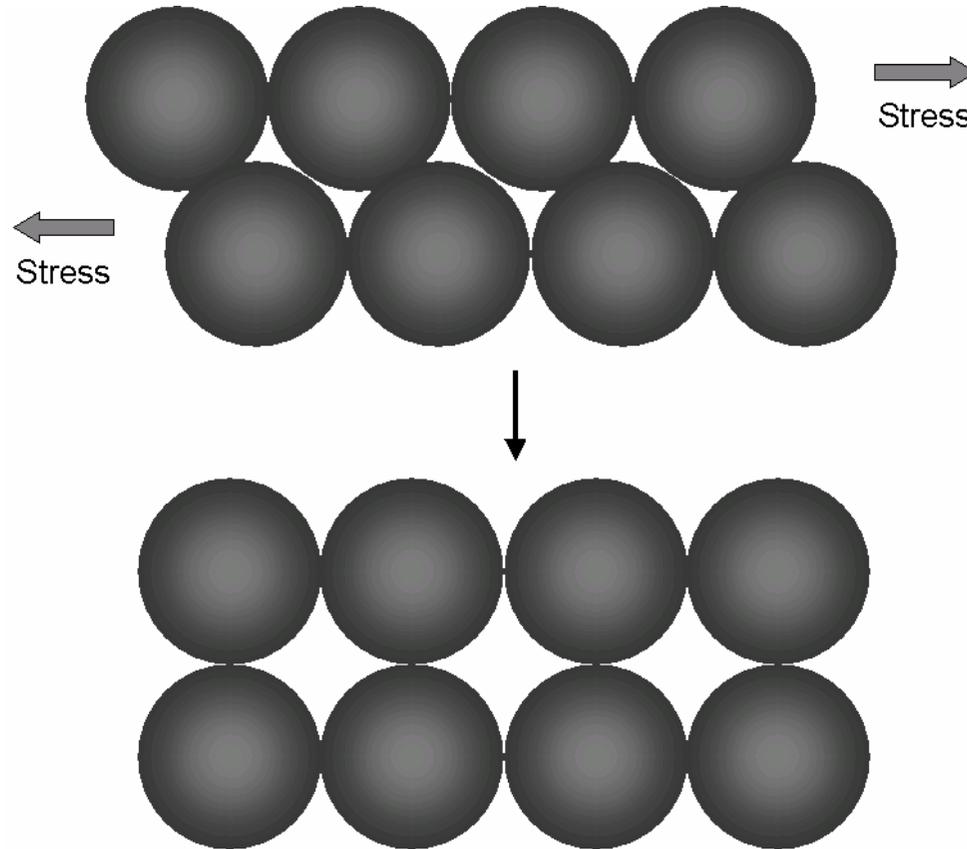
## „Dilatancy“

Dilatancy is a rheological phenomenon. A dilatant liquid shows viscosity raise as the shear rate is increased. Or in other words when a rod or a stirrer is moved at higher velocity in the liquid it thickens.

With the polymer emulsion shown in the experiment the effect has been driven to an extreme. The emulsion consists of small polymer particles of ca. 300 nm. As long as the shear rate is low e.g. during pouring or slow stirring it stays thin. The particles order themselves into rows or planes that can pass each other with only little friction.

The liquid flows easily. As the rod is rapidly pulled out the applied shear rate increases, the order of the particles is completely destroyed. They interlock and can not move independently any more. The whole system is converted into a solid like state. It now can transmit forces that the beaker can be lifted.

## “stress makes tough”



- stress shifts the particle layers in highly concentrated emulsions so that the space between the particles increases
- water cannot redistribute quickly enough
- subsequently the latex solidifies (walking on the beach)

important application properties:

*viscosity*



viscosity-psd (BASF AG, Ludwigshafen)



dilatancy

## **„Diversity matters“**

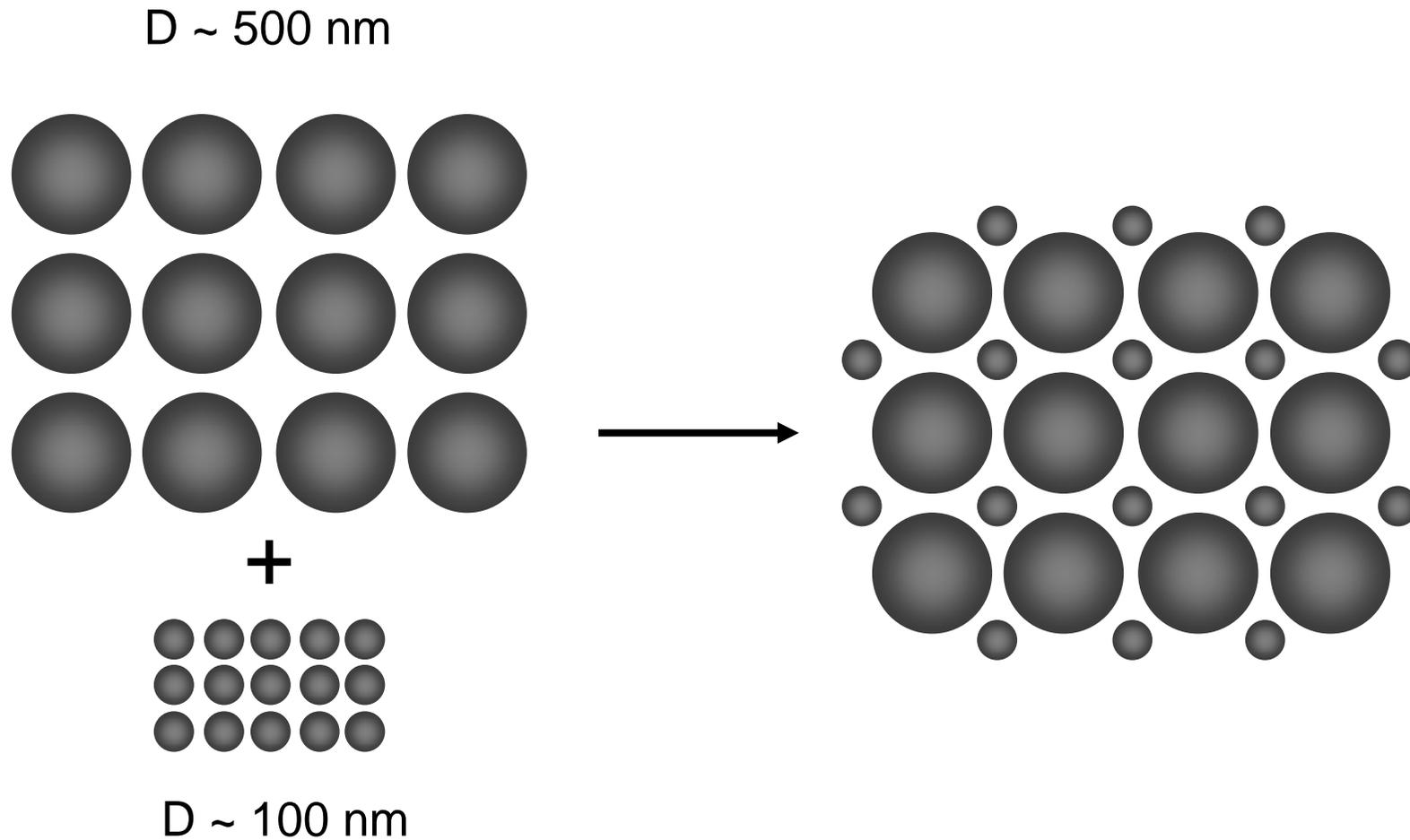
This experiment shows that the viscosity of a polymer colloid strongly depends on particle size distribution.

The first polymer colloid contains small polymer particles with a diameter below 100 nm. The second consists of particles with a diameter of bigger than 500 nm. Both polymer colloids are pasty, their viscosities are high.

After mixing the resulting dispersion has a bimodal particle size distribution and the viscosity is much lower than either one before.

The small particles fill up the space between the big ones and the more diverse mixture is flowing more freely.

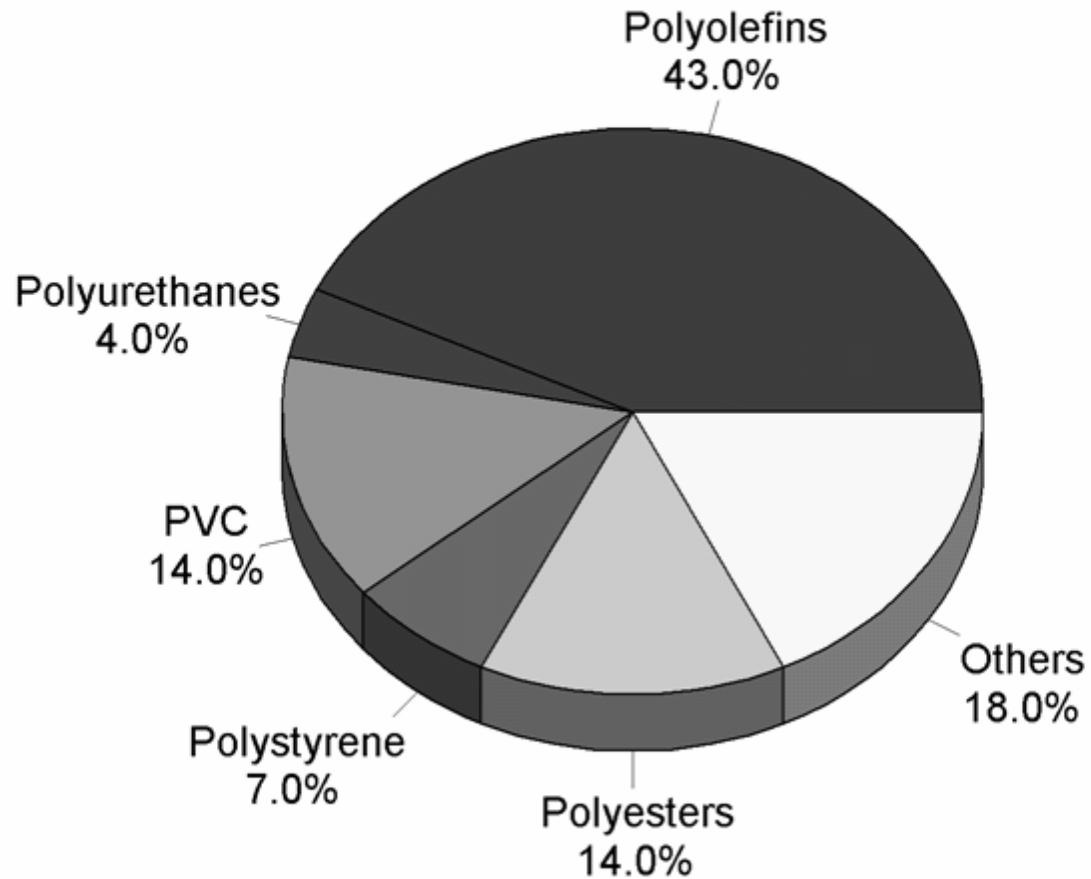
“thick + thick = thinner”



- the smaller particles distribute evenly between the larger particles
- subsequently water is “released” and the dispersion diluted

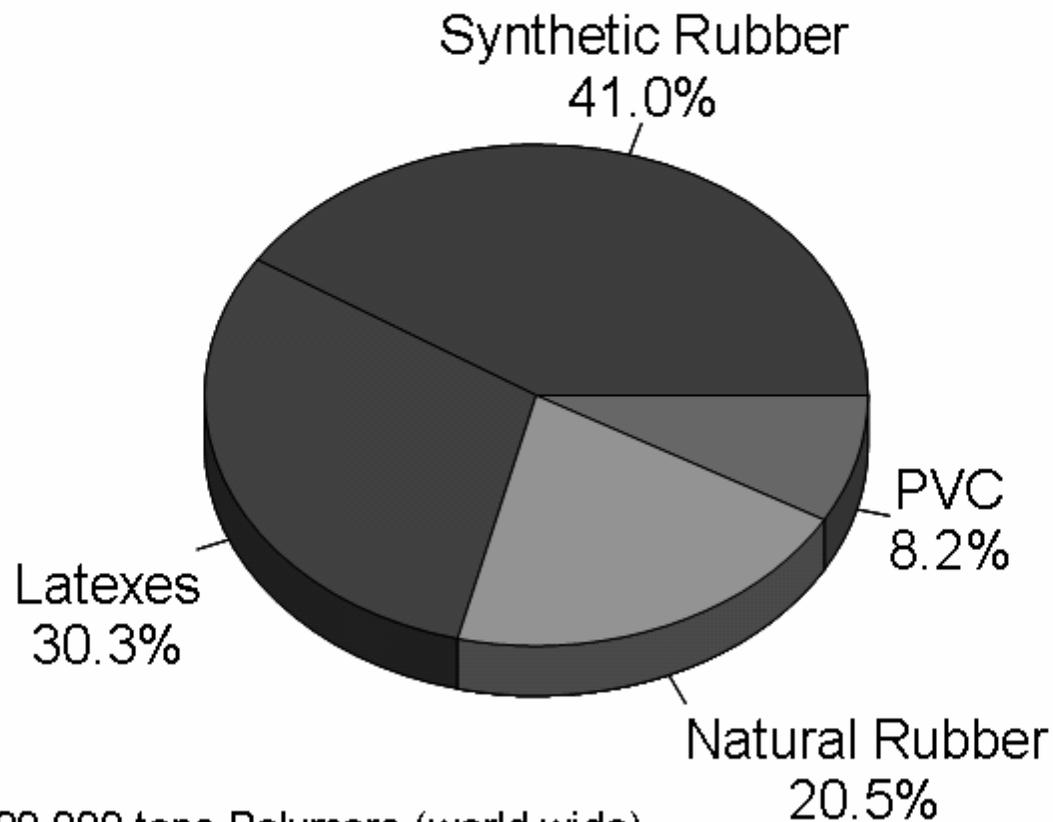
# World Production of Polymers

Yearly production:  $\sim 190 \cdot 10^6$  tons



# Emulsion Polymerization Products

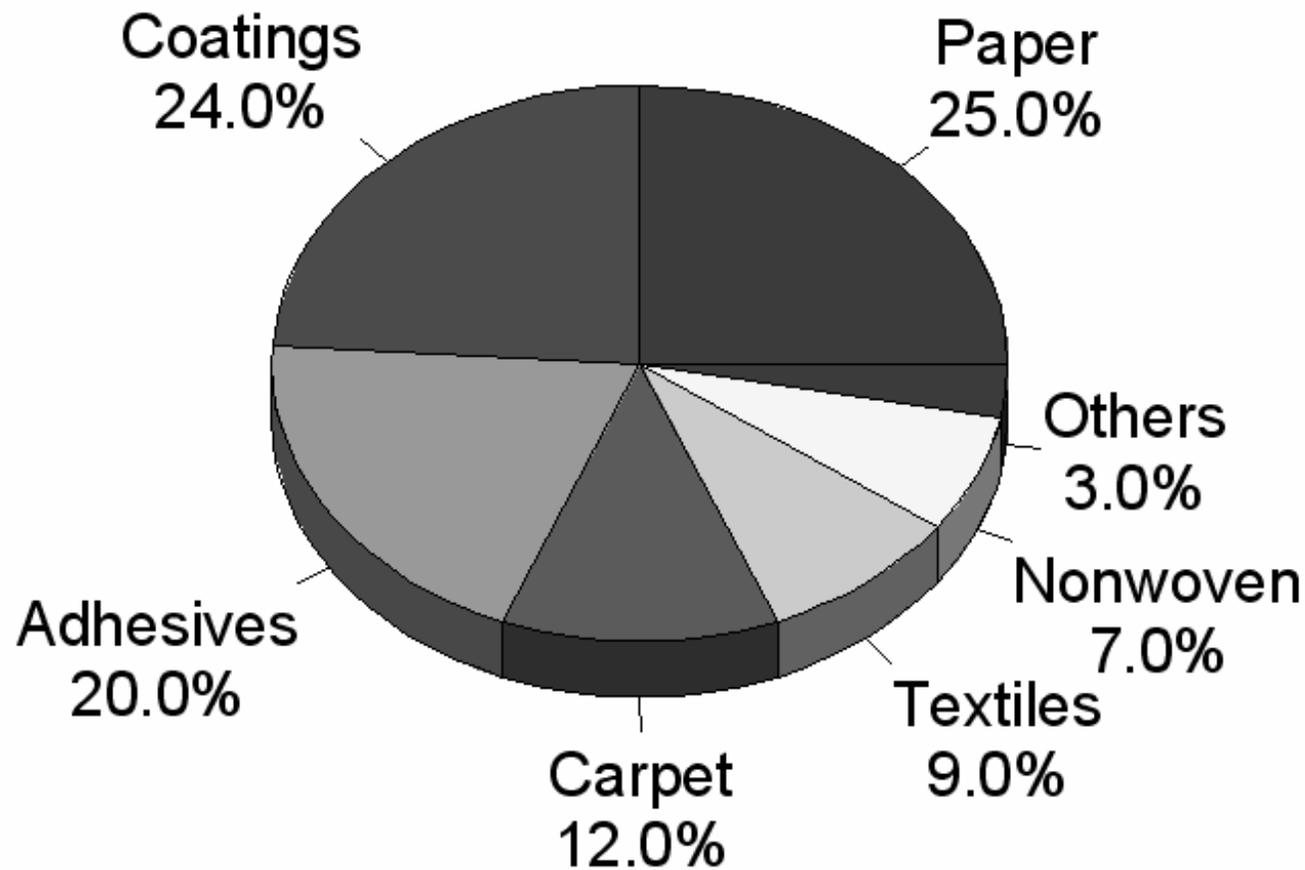
Total Amount ca. 25.000.000 tons (world wide)



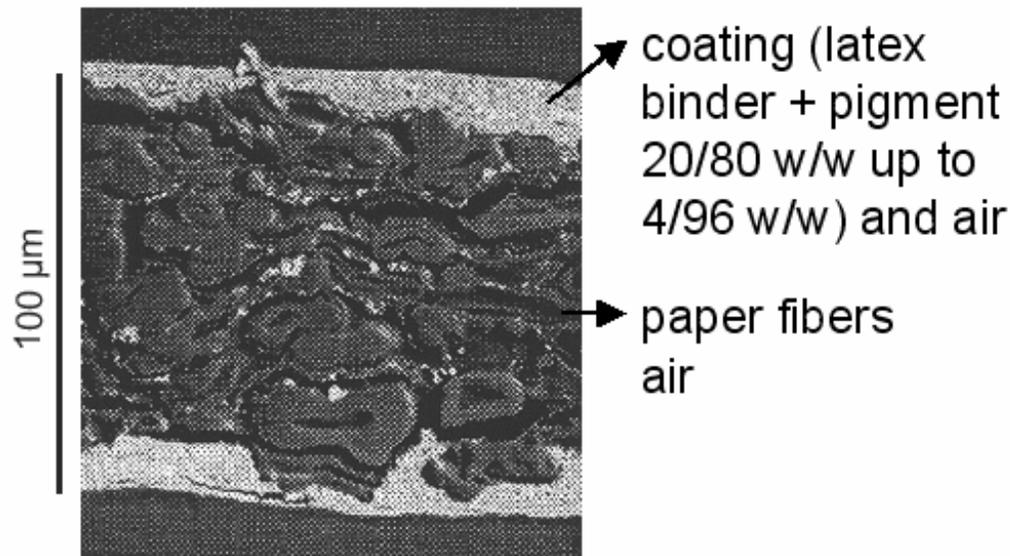
ca. 190.000.000 tons Polymers (world wide)

# Latex Applications

100% = 7.400.000 tons per year



# No Good Quality Paper Without Latexes

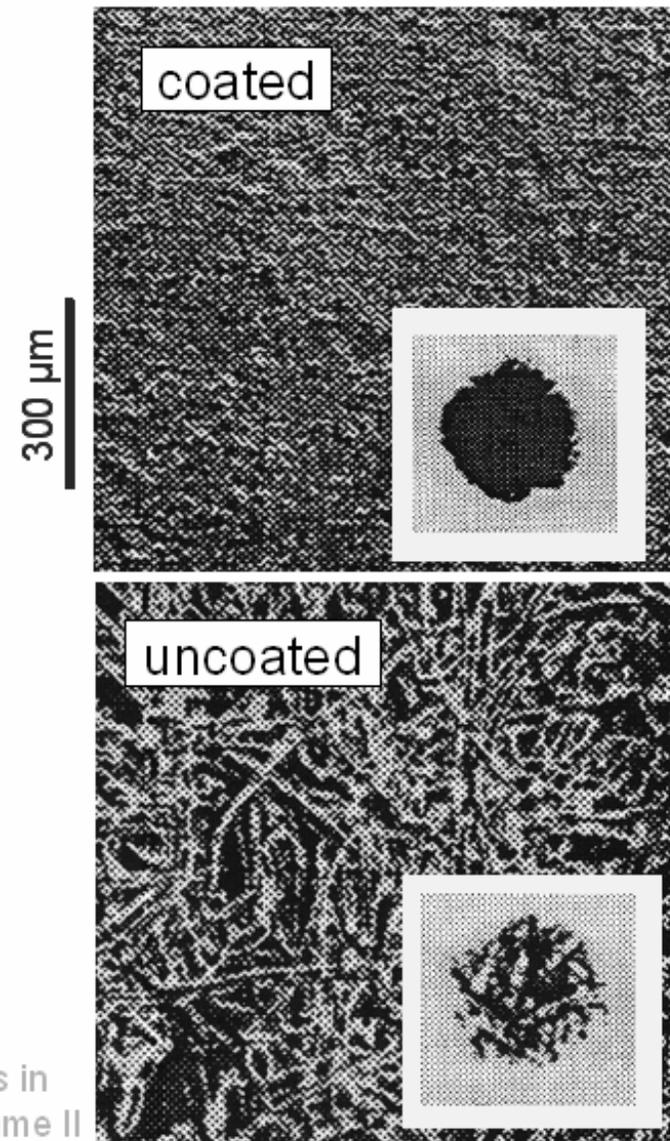


coated paper is a fiber-reinforced pigment-binder-air composite

## paper consumption:

USA 330 kg per head China 20 kg per head  
—→ there is to expect an increase in paper production of at least  $4 \cdot 10^{11}$  kg if the paper consumption will be equal in China and the US

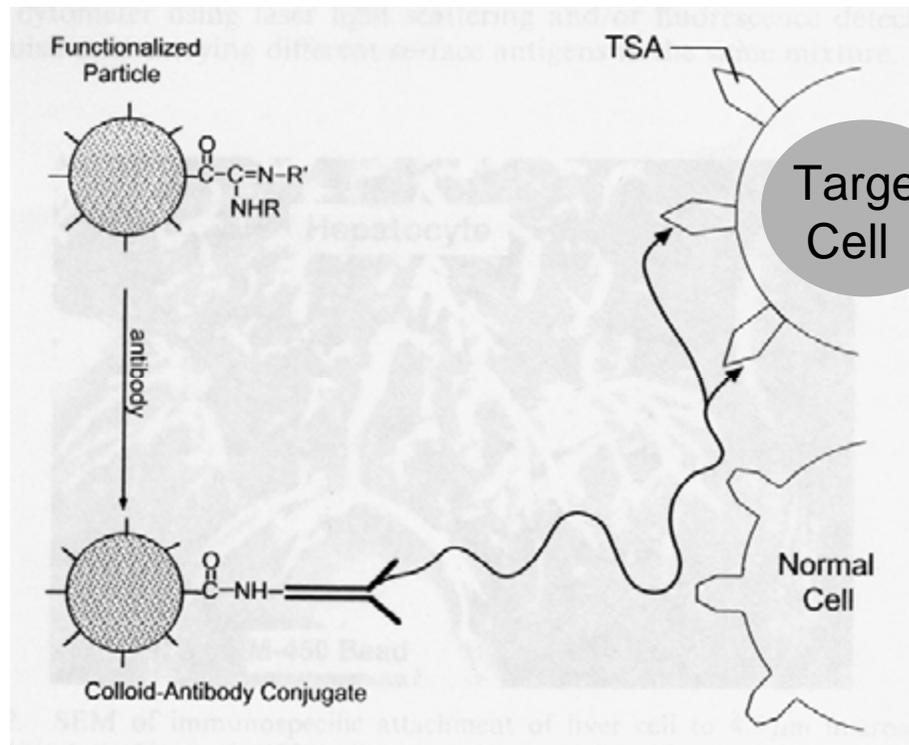
## paper with a halftone dot



# Biomedical Applications - Principle

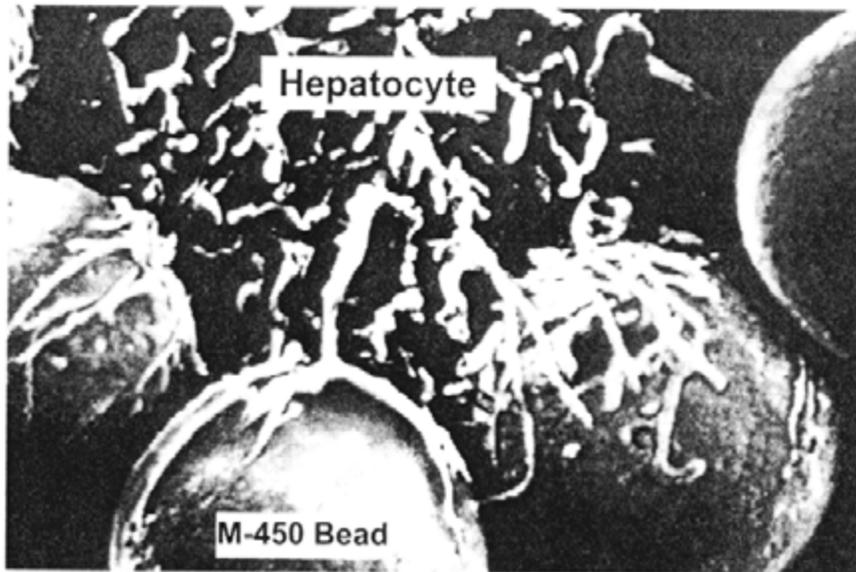
*benefits of latex particles for medicine & biotechnology*

take advantage of the large interfacial area and the possibility to tailor both surface and volume properties



separation by means of magnetic latex particles with special surface functionalities

# Biomedical Applications - Examples



R.M. Fitch "Polymer Colloids" , Academic Press, 1997, 164-172

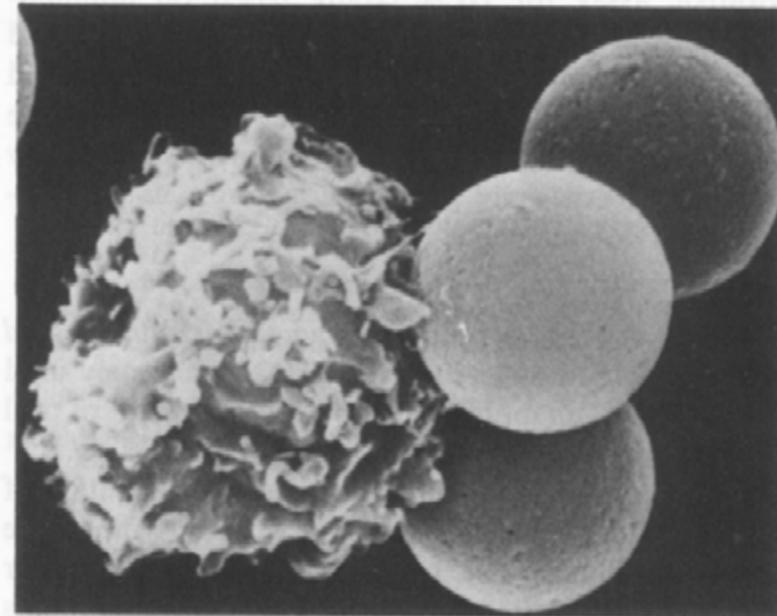


Fig. 3. Neuroblastoma cell isolated by means of M-450 Dynabeads®.

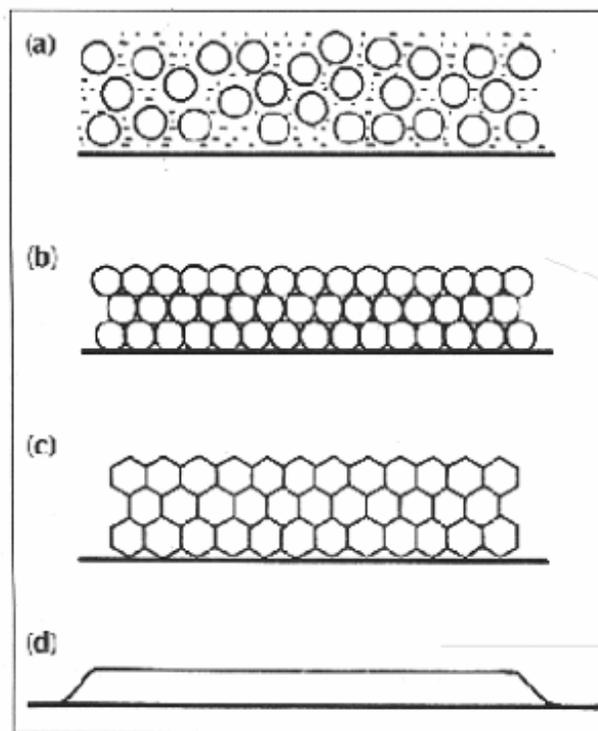
J. Ugelstad et al. Polymer Intern. 30 (1993) 157-168

- treatment of cancer of the nerve cells (neuroblastoma)
- bone marrow is taken from patient and slurried with magnetic, monosized 4.5 $\mu$ m particles which are immunospecific for the neuroblastoma cell surface

# Film Formation

## Synthetic Latexes

Schematic drawing



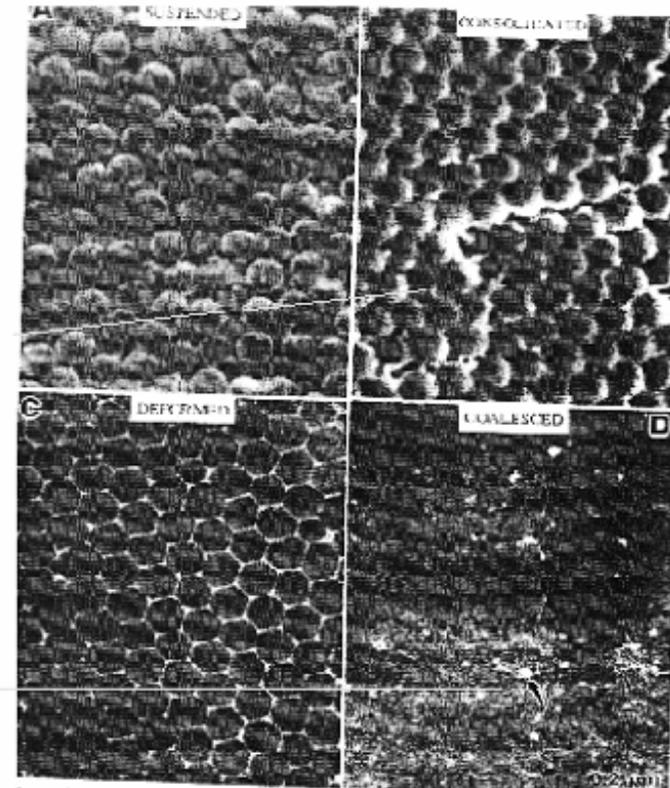
Suspended

Consolidated

Deformed

Coalesced

STY-BD-AA latex

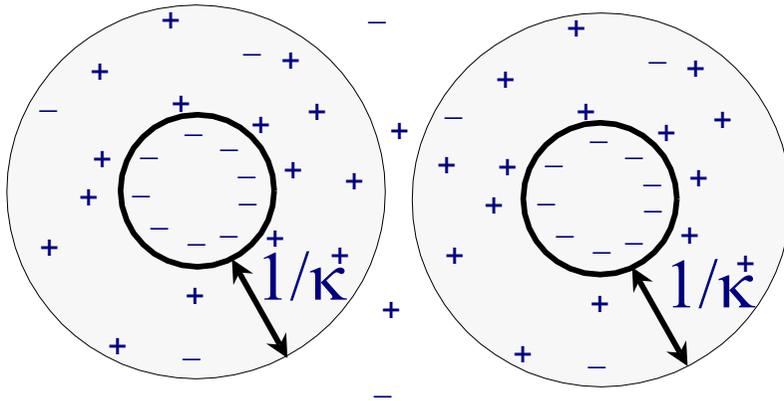


Ö.Pekcan, TRIP 2 (1994), 236-243

K. Takamura et al. TAPPI proceedings, Coating Conference 1995, 391-405

# Stabilization of Colloidal Particles - 1

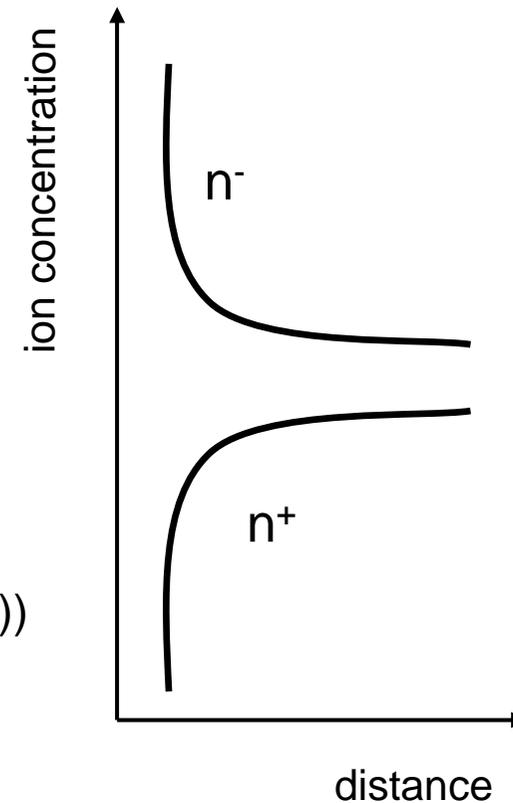
most important case:



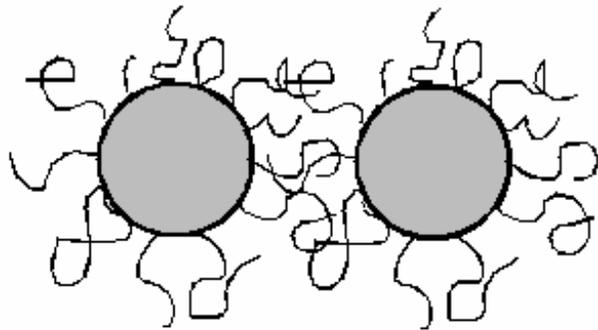
electrostatic

$$V_{\text{int}}(h) = \pi \cdot a \left( \underbrace{-\frac{H_{121}}{12\pi} \cdot \frac{1}{d_{\text{PP}}}}_{\text{electrostatic}} + \underbrace{\frac{64 \cdot k_B \cdot T \cdot C_0 \cdot \Gamma_0^2}{\kappa^2} \exp(-\kappa \cdot d_{\text{PP}})}_{\text{steric}} \right)$$

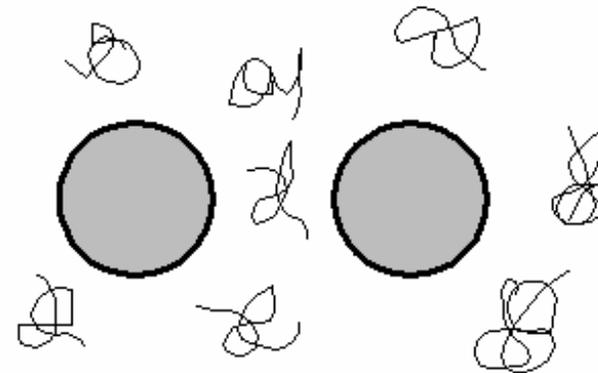
$$\Gamma_0 = \tanh\left(\frac{z \cdot e \cdot \Phi}{4 \cdot k_B \cdot T}\right)$$



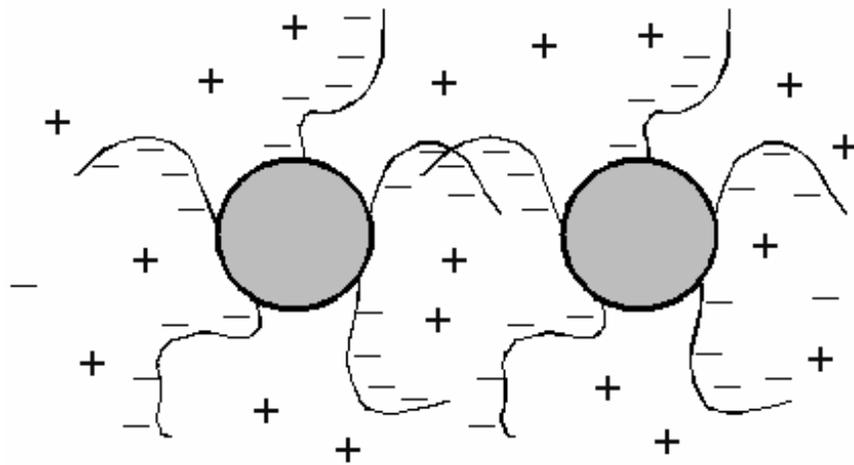
## Stabilization of Colloidal Particles - Charges + Polymers



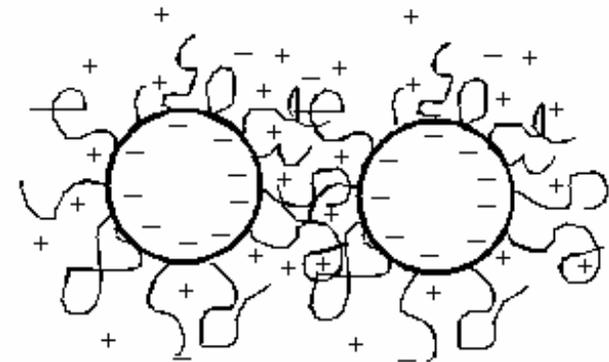
steric  
adsorbed, tethered



depletion stabilization.



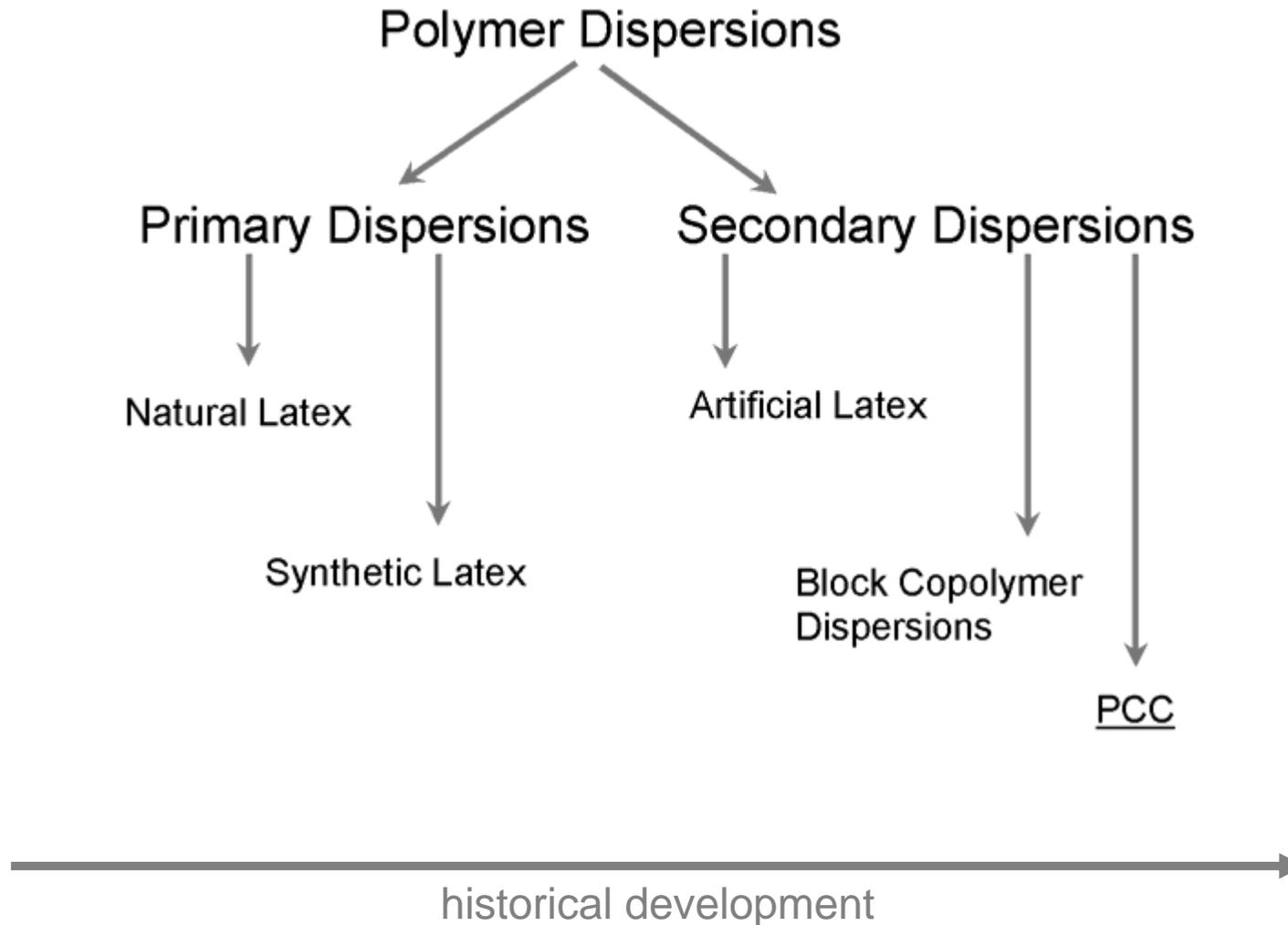
charged polymer, adsorbed or tethered



charges on particle surface and  
polymer adsorbed or tethered

# Polymer Dispersions

a family tree



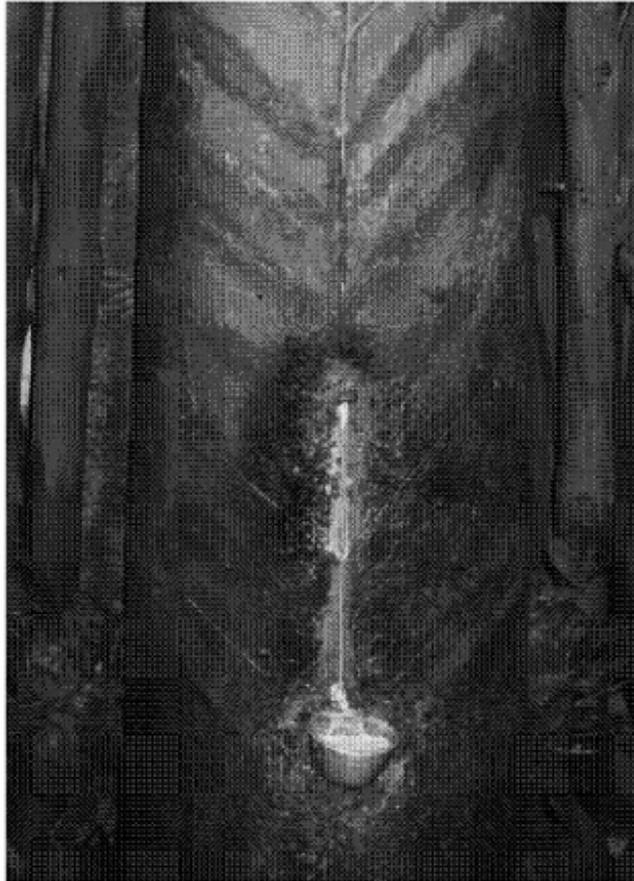
# Natural Rubber (NR)

Occurrence: in over 1000 species of plants (dikotyledonen)  
as white liquid (milky sap) = natural latex

European plants: Gänsedistel (*sonchus oleraceus*)  
salad (*lactua sativa*)

Economic importance: *hevea brasiliensis* tree  
sole source of natural rubber (99%)  
height: 20 m; diameter: 0.7 m  
productivity: 10 g latex a day (33% solid)

# The Rubber Tree Reactor



Natural rubber is produced in a system of tubular vessels in the tissue of the tree. Freshly collected latex contains all the enzymes necessary for the formation of rubber from the sugars photosynthesized in the leaves of the tree.

Continuous tubular reactor (L: 20m; D: 0.7m)

Pressure: 1.38 bar

Productivity: 10 g/day

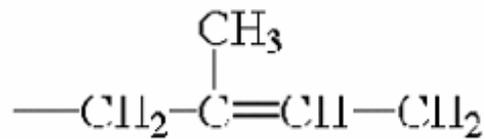
World production: 5 million tons/year

Application: rubber with high elasticity

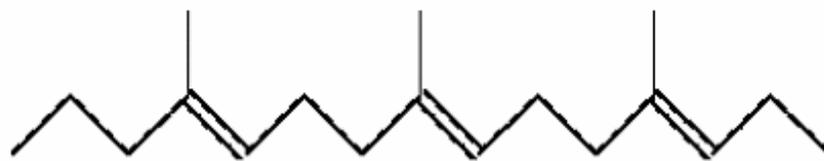
Price: about 1 US-\$ per kg

# Natural Latex Polymer

- enzymatic catalysed biosynthesis

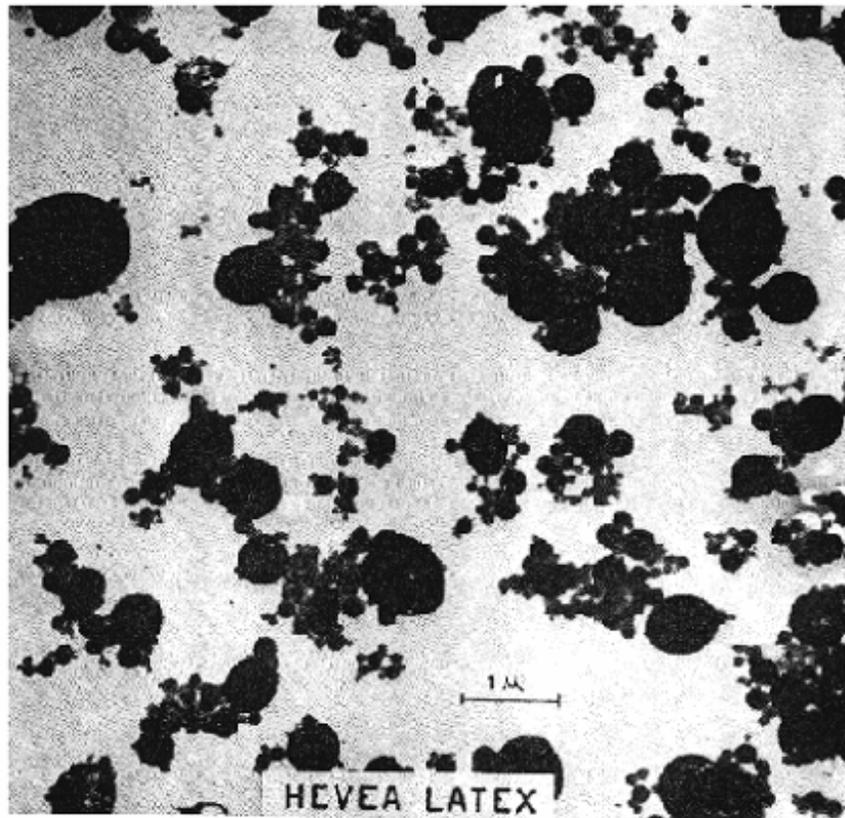


polyisoprene repeating unit



guttapercha, balata

# Natural Latex



The natural latex of the *Hevea brasiliensis* tree is a cytoplasmic system consisting of cis-polyisoprene particles in an aqueous phase electro-sterically stabilized by proteins (1-2%) and phospholipids (0.4-0.8%).  
[pH: 6.5-7.0;  $\rho$ : 0.98 g cm<sup>-3</sup>; SC: 33%]

PSD: 50 nm up to 1.6 μm  
DP: 8.000 - 30.000

TEM photograph taken from F.A. Bovey, I.M. Kolthoff, A.I. Medal and E.J. Meehan "Emulsion Polymerization", Volume IX High Polymers, Interscience 1955

# Heterophase Polymerization Techniques

Technique	Components
Suspension Pm. <sup>o</sup> Microsuspension Pm. <sup>o</sup> Dispersion Pm. Emulsion Pm. <sup>o</sup> Miniemulsion Pm. Microemulsion Pm.	Dispersion Medium Monomer Polymer Stabilizer

Technique	Components
Precipitation Pm.	Dispersion Medium Monomer Polymer

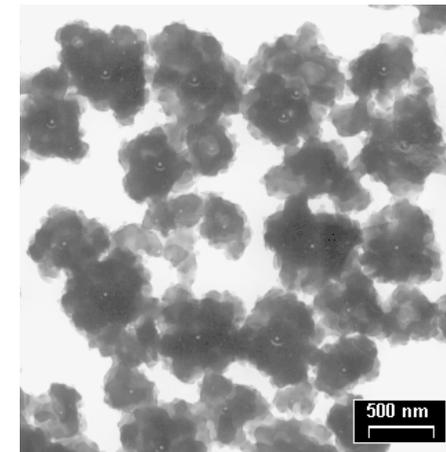
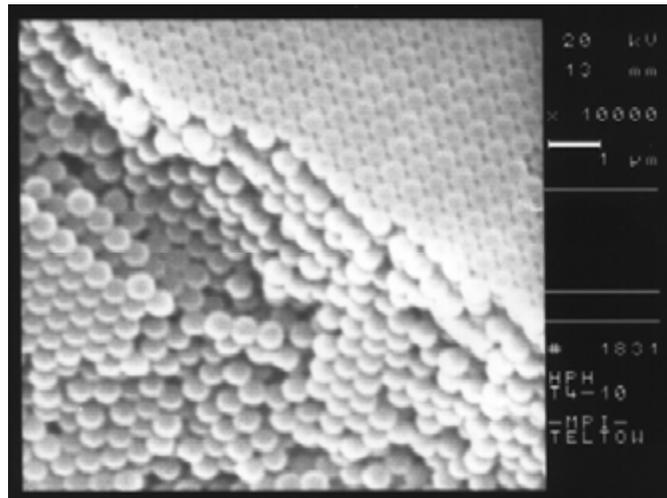
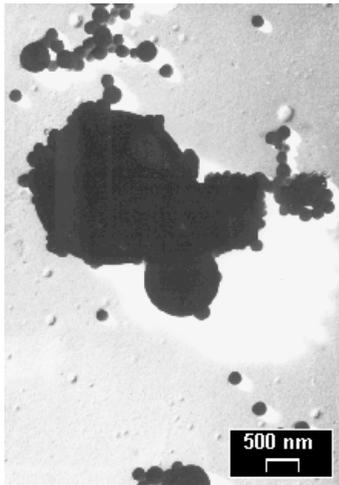
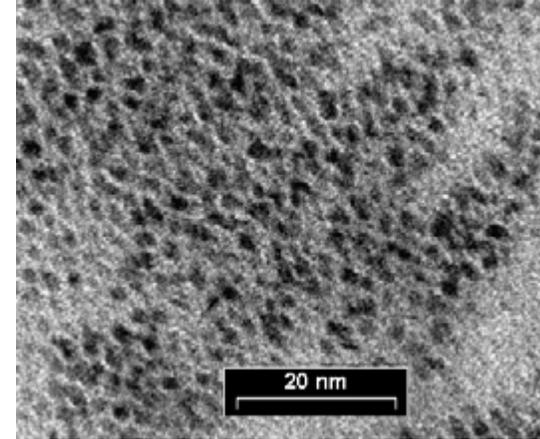
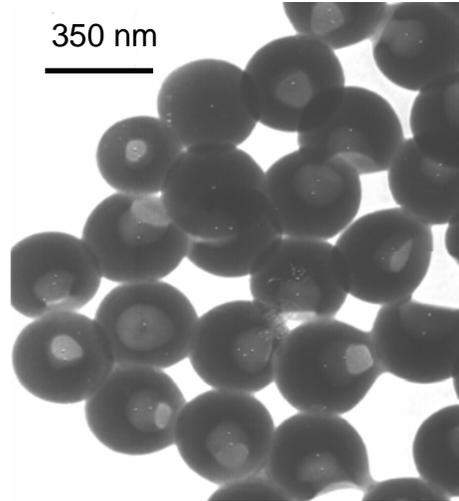
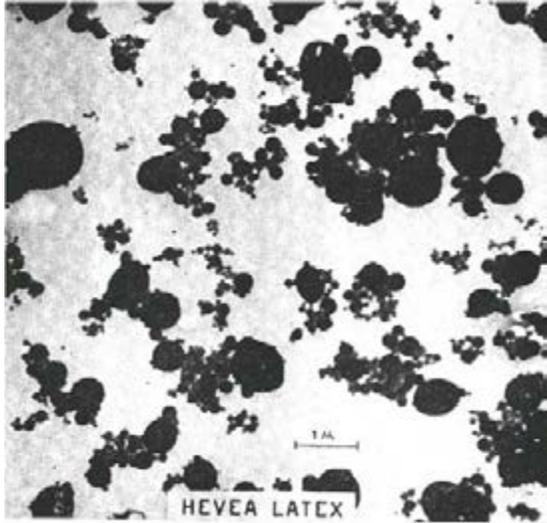
Technique	Components
Bulk Pm.	Monomer
Gas Phase Pm.	Polymer

Basic Principle: polymer is insoluble / immiscible in the medium

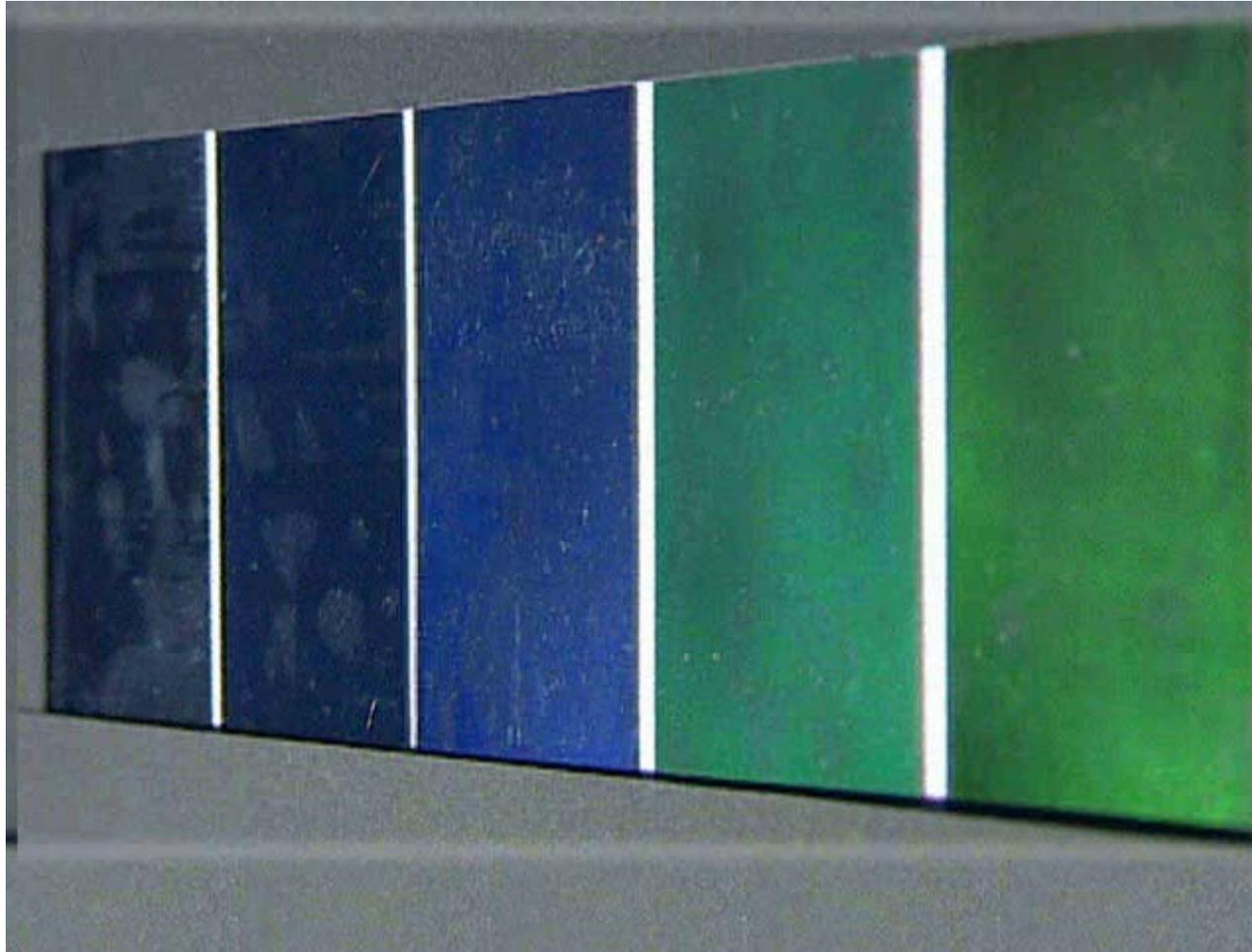
- of technical importance

# Heterophase Polymerization - A Simple Definition

- a generic term for methods to produce different kinds of polymer particles:



monodisperse particles



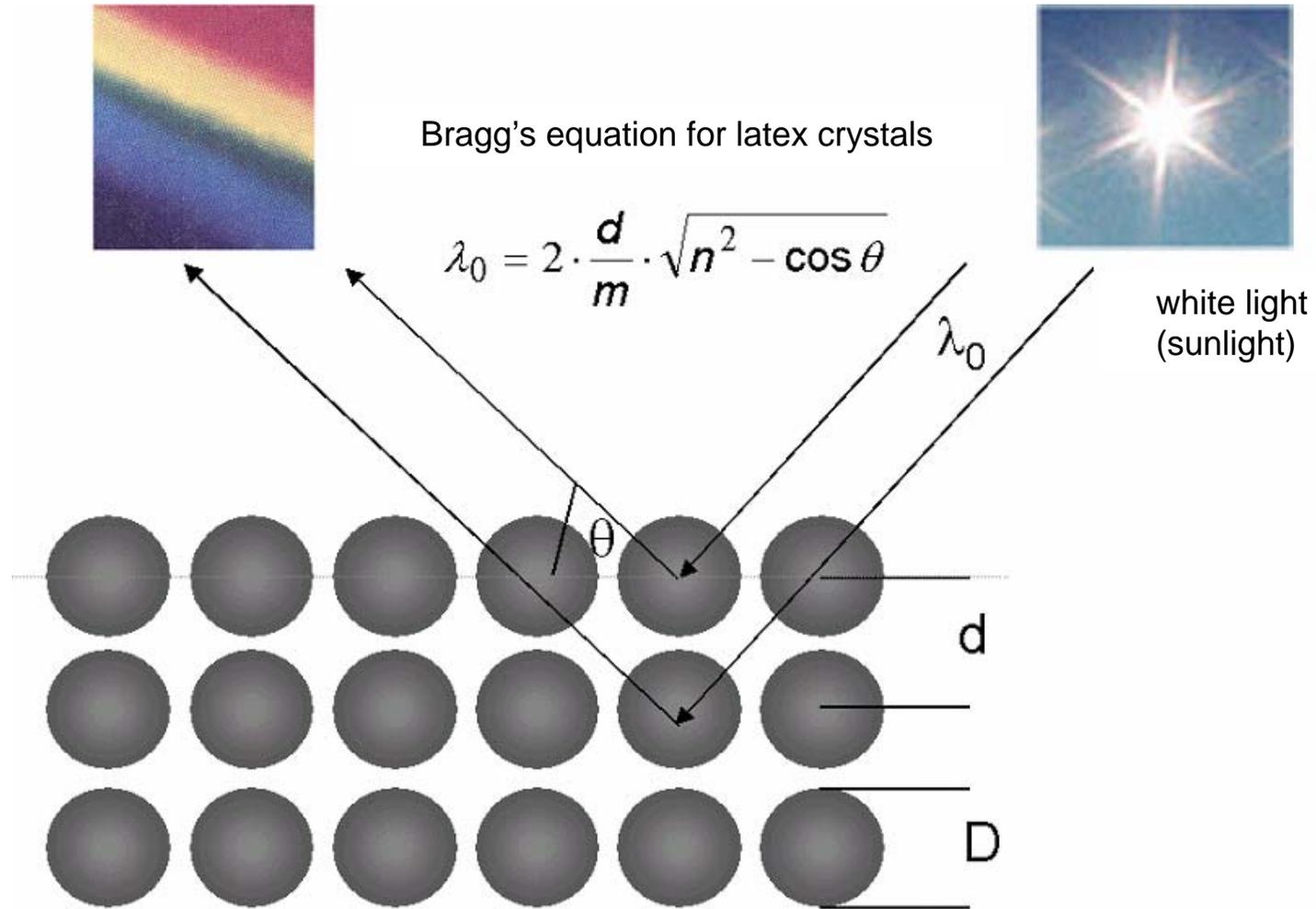
color without dyes (BASF AG, Ludwigshafen)

## **„Color by transparent latex particles“**

**Monodisperse polymer particles can arrange in a quasi crystalline ordered structure and produce an angle dependent color effect due to Bragg diffraction at the 'crystal' planes. When the lattice parameter is comparable with the wavelength of visible light and a refractive index difference between the particle and the matrix exists, an intensive iridescent color will be observed. The polymer films used here were made from an emulsion made by two step emulsion polymerisation. A crosslinked hard core particle is formed in the first step, followed by the film forming outer phase in the second step. Both the mechanical properties and the color effects of the films could be varied by changing the particle size and the thickness of the outer phase.**

**The color changes from red through yellow to green the more acute the viewing angle is. This is because the apparent distance between two particles decreases the more oblique the angle of observation. Also the amount of shell material and thus the distance between the nanoparticles is changed, and results in different colors. As the size of the core-shell particles decreases, the color, when observed from a vertical perspective, changes from red through yellow to green and even blue. Depending on the viewing angle, the same area appears for example either as glowing red or bright green. The particle size has to be accurately chosen, since even minor changes of about 20 nanometers have a clear effect on the color.**

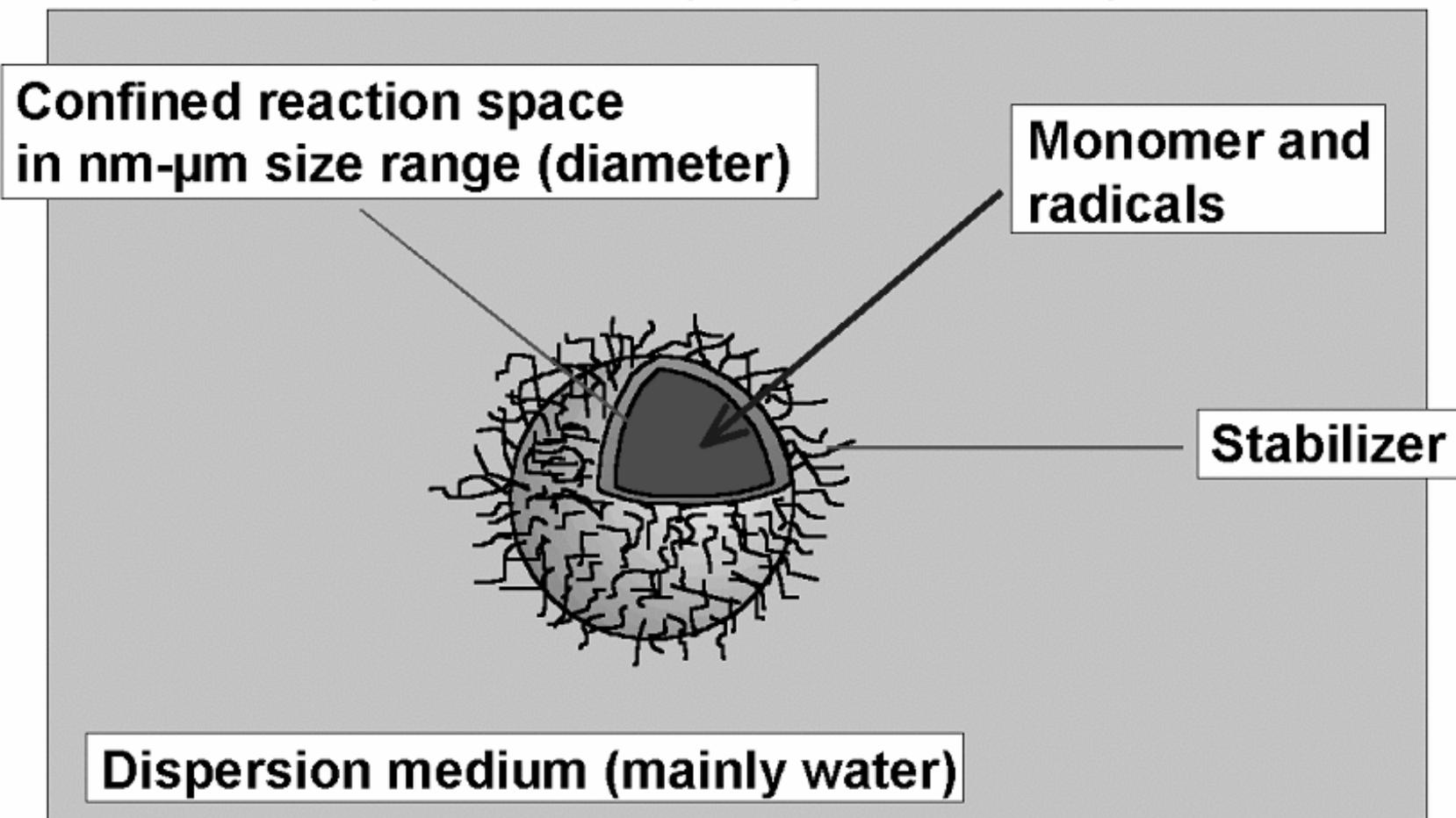
# “colors without dyes”



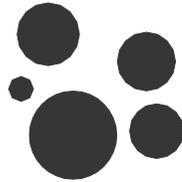
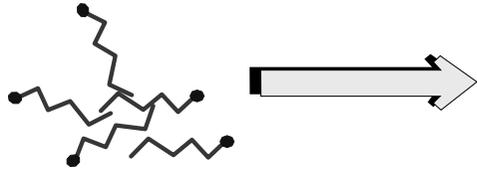
reflexion (and color) depends on the wave length of incoming light and the observation angle

## Common Features of Heterophase Polymerizations

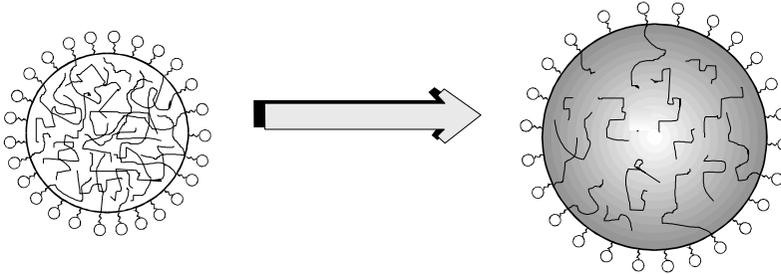
Heterogeneous system; spatial density differences;  
at least two phases; transport processes; equilibria;....



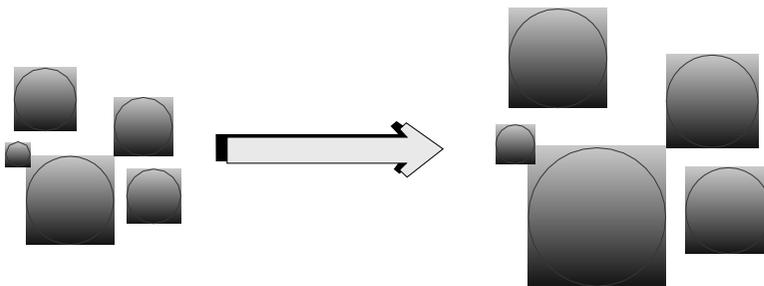
# Curriculum Vitae of a Latex Particle



nucleation



swelling



growth

**some unusual examples  
(regarding morphology)**

# Advantages of Heterophase Polymerization Techniques

- Easiness of polymerization heat removal
- Viscosity of the reaction mixture is low and independent of the polymer molecular weight
- Monomer and emulsion feed procedures are possible as the monomer consumption takes place outside the monomer droplets
- Monomer concentration at the reaction loci can be kept stationary at its highest level so that the rate of polymerization is high during the entire reaction
- The particle size distribution as well as the average particle size can be tailored over wide ranges
- Product properties can be changed nearly unlimited

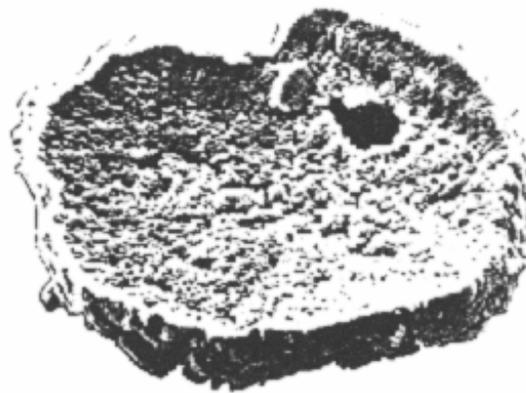
—————> most important mechanism today: radical polymerization

# Suspension Polymerization

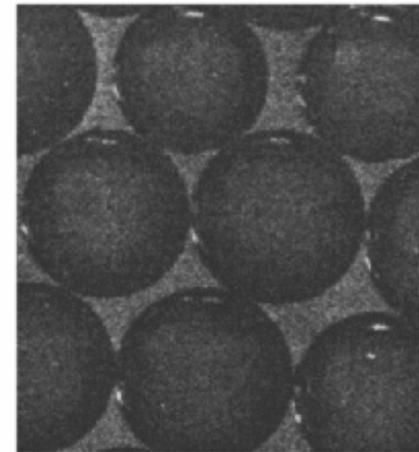
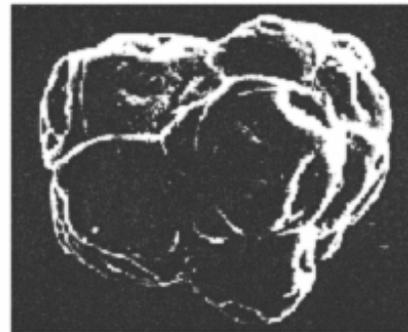
- Water, monomer, oilsoluble Initiator, protective colloid ( water soluble polymers: Polycarboxylic acids, cellulosic materials, poly(vinylalcohol))
- Reaction product is a slurry of suspended polymer particles with a particle size in between 50 - 400  $\mu\text{m}$
- Particle size is determined by monomer typ, stabilizer, and agitation
- Technical very important ( styrenic ion exchange resins, VC homo and copolymers, tetrafluorethylene, vinyl acetate)
- Bulk polymerization in the monomer droplets
- Reactor sizes up to 200  $\text{m}^3$ , cycle times before cleaning the reactor around 500; radical scavengers at the reactor walls to prevent fouling and water phase polymerization

# Suspension Polymerization

## Particle Morphology



100  $\mu\text{m}$

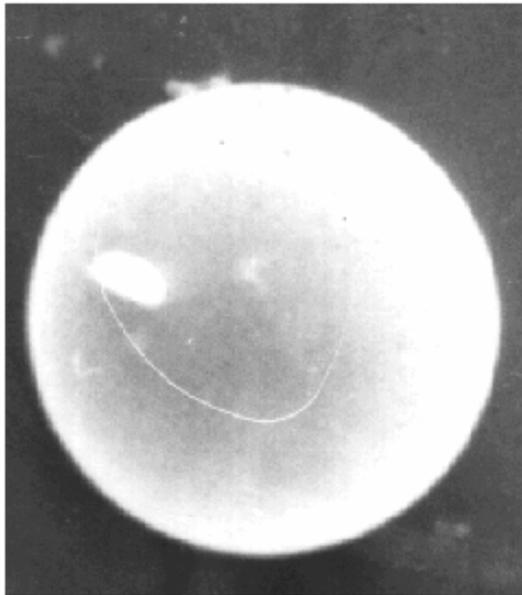


# Microsuspension Polymerization

- Smaller droplet sizes than in suspension polymerization
- Microsuspension preparation with homogenizers; stabilization of the monomer droplets
- Special surfactant system (mixture with polymeric stabilizers PVAL)
- Particle sizes in the  $\mu\text{m}$ -range
- Monomer soluble initiators
- Crucial point: to avoid emulsion polymerization
- Technical important for the production of special PVC-types

# Example: Microsuspension Polymerization

## Staining a monomer emulsion



Vinyl Chlorid droplet  
emulsifier free polymerization  
diameter 13.1  $\mu\text{m}$

B.R. Paulke, PhD 1985

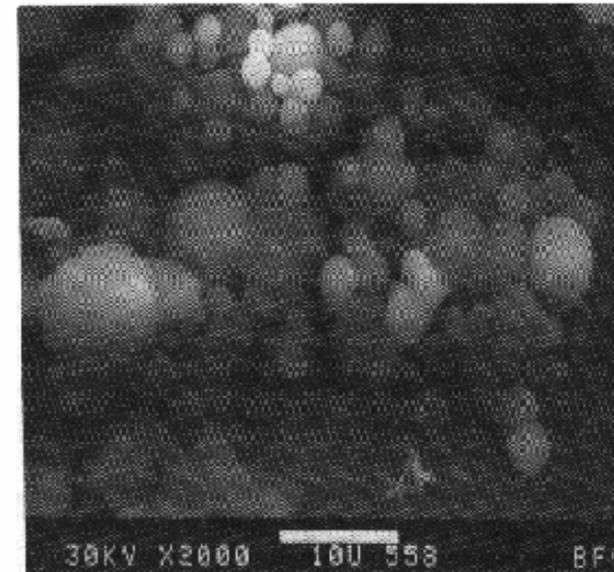


FIG. 4. Vinyl chloride droplets in the microsuspension recipe.  
 $\mu$ -emulsion: 40%VC, 59% water,  
1 suspension agent, 1100 rpm 30 min.  
bar indicates 10  $\mu\text{m}$

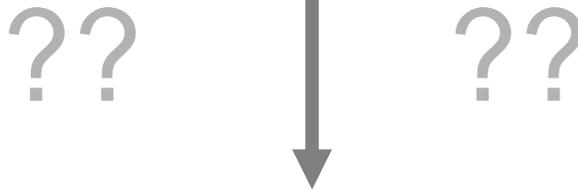
H.W.H. Yang, J.Macromol.Sci.-Phys. B20 (1981) 199-206

# Polymerization of or in monomer emulsions

Question: whether or not it is possible to convert the characteristic features of monomer droplets into that of polymer particles???

Answer: yes, by seed and feed techniques, even in large scale

Suspension, miniemulsion and emulsion polymerization

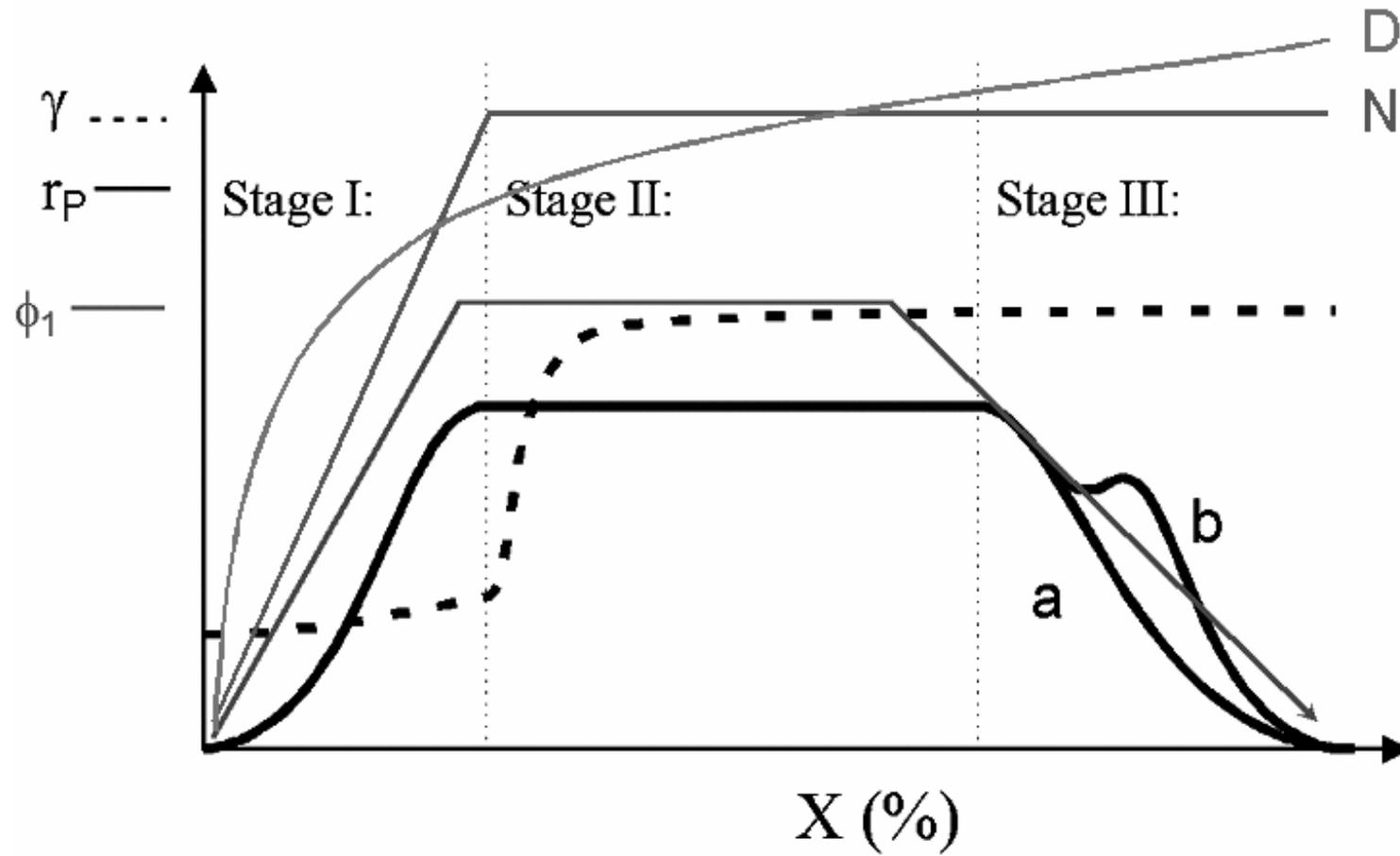


to preserve the droplet properties during polymerization  
(in the sense to make a 1:1 copy)

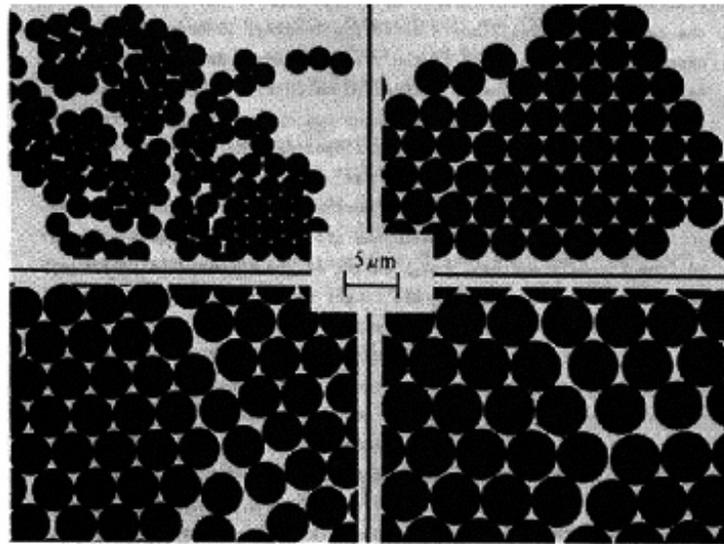
# Emulsion Polymerization

- Recipe: Monomer, water, emulsifier(s), water soluble initiator
- Result: polymer latex with a particle size in between 20 nm and several  $\mu\text{m}$  depending on the recipe and polymerization conditions
- The heterophase technique with the most technical realizations, the greatest flexibility, and the most economic importance
- From the scientific point of view the most exciting technique
- It is more than 80 years old but with increasing importance especially due to environmental demands

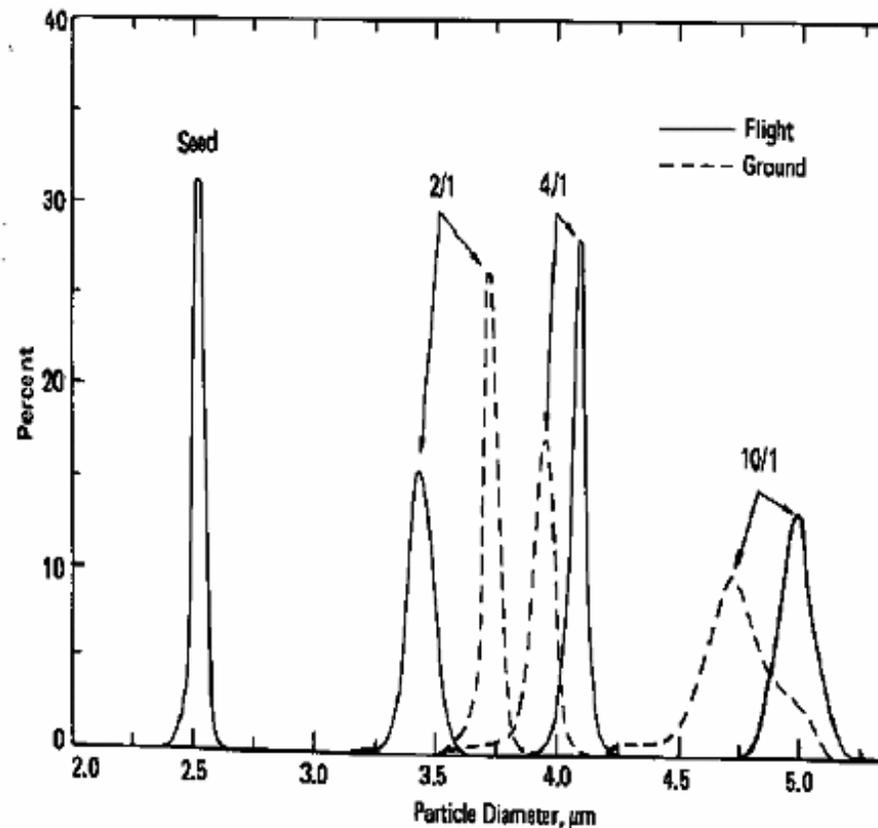
# Ideal Behavior of an EP



# Space emulsion polymerization - but worldly results



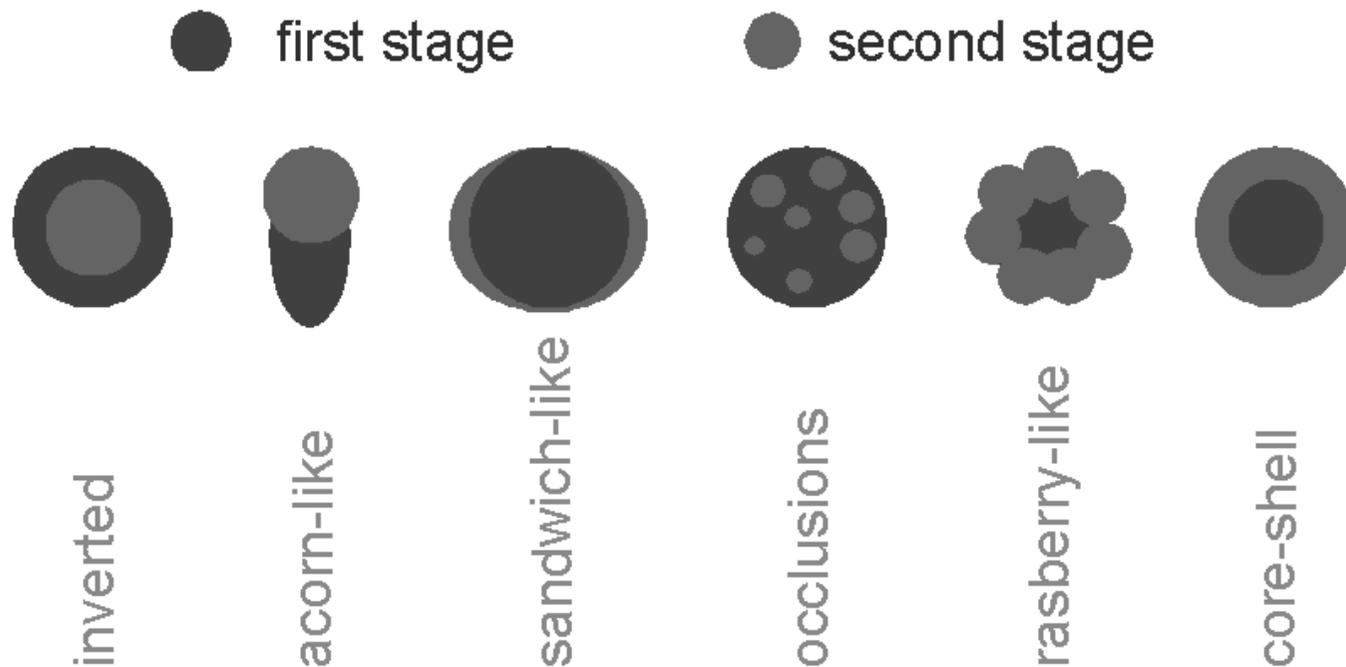
J. W. Vanderhoff et al. J. Disp. Sci. Technol. 5 (1984) 231-246



1983, in zero gravity aboard the Challenger STS-6: the first products ever made in space - polystyrene latex particles (certified as standard reference materials for calibrating microscopic objects); J. W. Vanderhoff & M. S. El-Aasser (Lehigh University, USA)

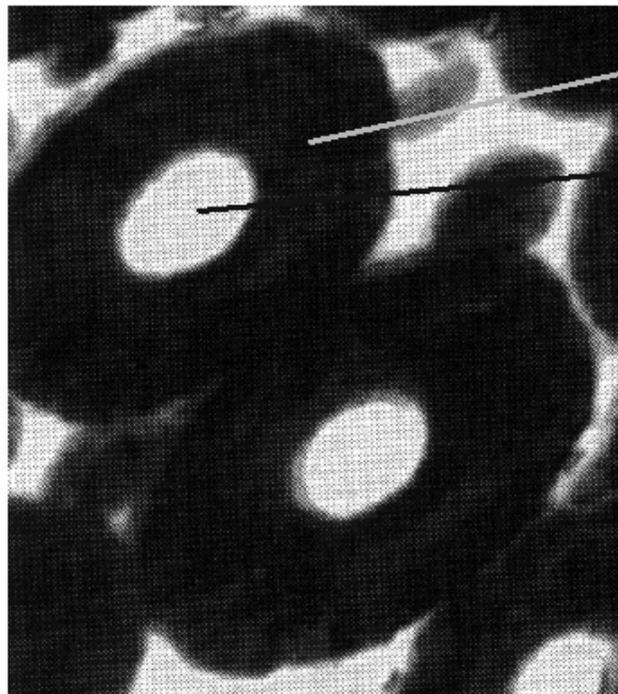
# Particle Morphologies in a Two Stage Emulsion Polymerization

Schematic Drawing of Various Morphologies



# Core - Shell Particles (1)

Problem: a hydrophilic core and a hydrophobic shell



polystyrene (2nd stage monomer)

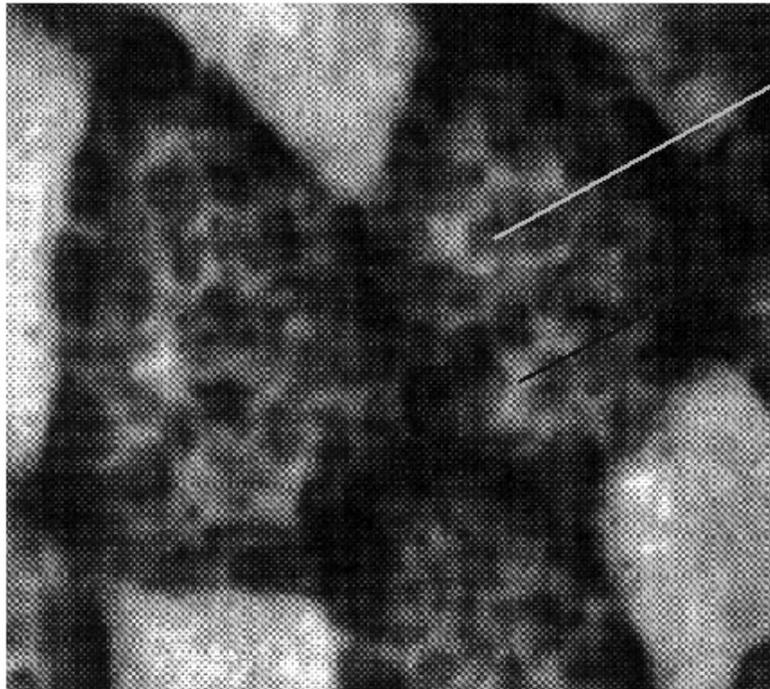
PMMA (1st stage monomer)

Successful solution:

two stage semi-batch polymerization  
with slow monomer-emulsion feed and  
redox initiation at 21°C  
(high core viscosity and low mobility  
inside the core, respt.)

## Core - Shell Particles (3)

Problem: a hydrophilic core and a hydrophobic shell



polystyrene (2nd stage monomer)  
dark areas

PMMA (1st stage monomer)  
bright areas

Failure:

two stage batch polymerization with  
KPS initiation at 60°C  
(low core viscosity and high mobility  
inside the core, respt.)

# Dispersion Polymerization

- Monomer is soluble in the dispersion medium (it starts as homogeneous solution)
- Polymer precipitates at a certain chain length (it ends as dispersion of polymer particles)
- Polymeric stabilizer (poly(ethylene glycol), poly(vinyl pyrrolidone, hydroxypropyl cellulose))
- Solvency of the dispersion medium has a strong influence (ethanol, methanol, mixtures with water)
- Particle size in the range of 1-10  $\mu\text{m}$   
monodispers particle size distributions
- Structured particles (change of the dispersion medium)

## Dispersion Polymerization in Supercritical Fluids

### CO<sub>2</sub> as dispersion medium

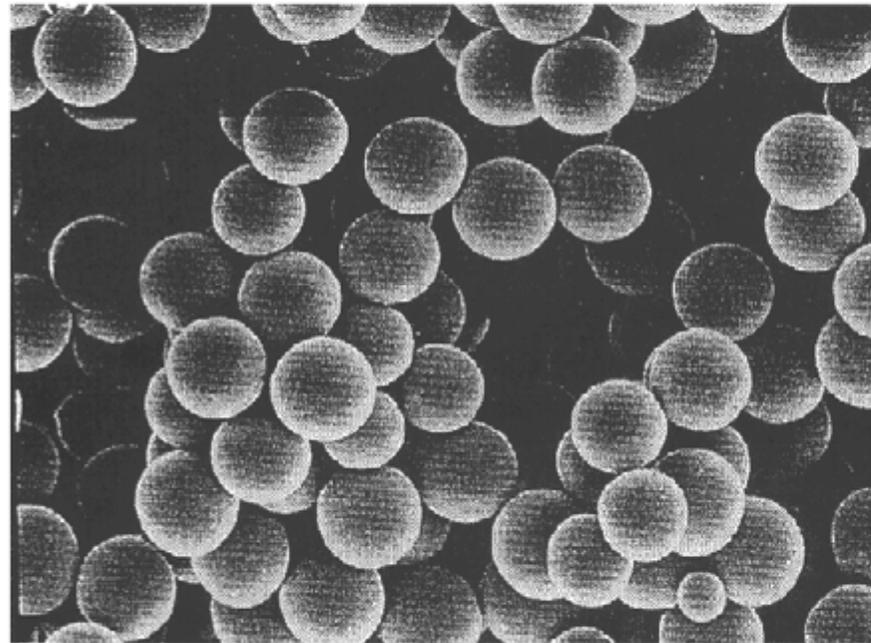
- Polymerization above the critical temperature and the critical pressure of the dispersion medium
- Density variation of the dispersion medium over a wide range
- Precipitation polymerization
- Advantage of carbon dioxide: it evaporates without environmental damage
- For a dispersion polymerization special stabilizers are needed (fluorinated)
- 1968 radical solution polymerization
- 1986 BASF Canada heterogeneous free-radical polymerization
- All kinds of polymerizations are possible; CO<sub>2</sub> is inert

## Dispersion Polymerization in Supercritical Fluids

### Some data

2  $\mu\text{m}$

Solvent	$T_{\text{crit}}$ ( $^{\circ}\text{C}$ )	$P_{\text{crit}}$ (bar)
$\text{CO}_2$	31.1	73.8
$\text{C}_2\text{H}_6$	32.2	48.8
$\text{C}_3\text{H}_8$	96.7	42.5
$\text{C}_4\text{H}_{10}$	152.0	37.8
$\text{CHClF}_2$	96.2	49.9



PMMA particles prepared in  $\text{CO}_2$

K.A. Shaffer, J.M. DeSimone TRIP Vol.3, (1995) 146-153

# Microemulsion Polymerization

- Polymerization in microemulsions starts in the early eighties
- Thermodynamic stability due to very low interfacial tensions (down to 0.001 mN/m) that compensates the dispersion entropy
- Extreme surfactant to monomer ratios up to 10/1 per weight (emulsion polymerization with a very high surfactant concentration)
- Surfactant / cosurfactant (alcohol) or single surfactant system
- Large overall surface area: 100 m<sup>2</sup> per ml dispersion
- Optical transparency and thermodynamic stability
- Small particle size: down to 10 nm
- Great variety of structures and a unique microenvironment
- New morphologies are accessible

F. Candau NATO ASI "Recent Advances in Polymeric Dispersions", Spain 1996

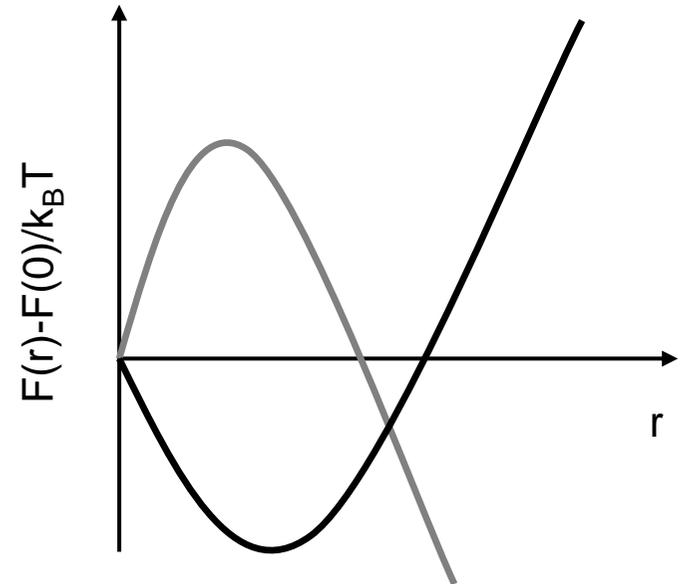
# μ-Emulsion Droplets

droplet thermodynamics (classical textbooks)

$$F = -\Delta P \cdot V + \sigma \cdot A = -\frac{4 \cdot \pi}{3} \Delta P \cdot r^3 + 4\pi \cdot \sigma \cdot r^2$$

$$\frac{\partial F}{\partial r} = 0$$

$$\Delta P = \frac{2\sigma}{r_c}$$



$$F = -\frac{4 \cdot \pi}{3} \Delta P \cdot r^3 + 4\pi \cdot \sigma \cdot r^2 + 8\pi\kappa \left(1 - \frac{r}{r_s}\right)^2 + 4\pi \cdot \bar{\kappa}$$

(Helfrich, 1973)

# Microemulsion Polymerization

## Some basic results

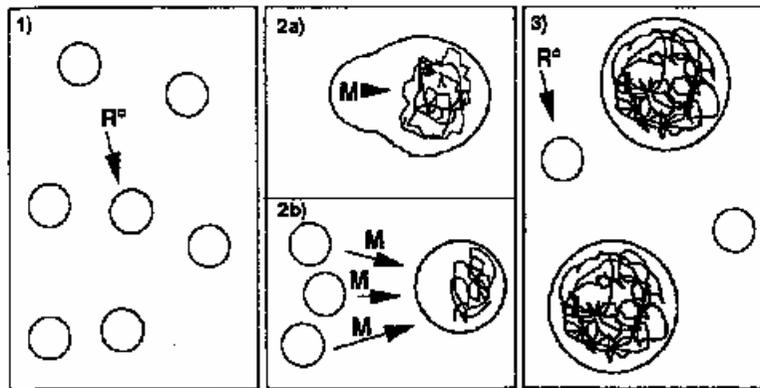


Figure 3. Microemulsion polymerization mechanism : 1) Before polymerization : monomer swollen micelles ( $d \sim 5-10\text{nm}$ ). 2) Polymer particle growth a) by collisions between particles ; b) by monomer diffusion through the continuous phase. 3. End of polymerization : polymer particles ( $d \sim 40\text{nm}$ ) + small micelles ( $d \sim 3\text{nm}$ ).

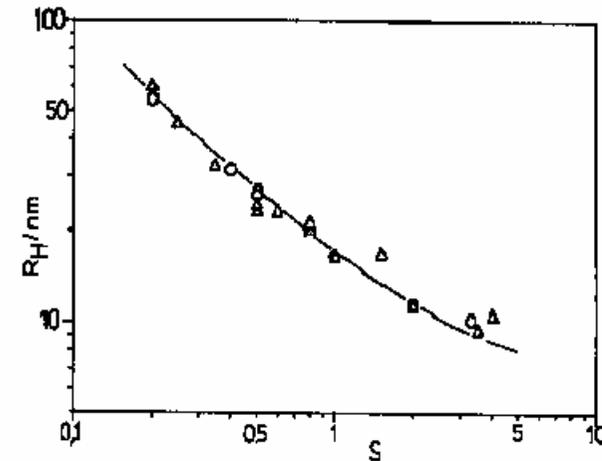


Figure 3. Hydrodynamic radius  $r_H$  of the latices in dependence of the relative amount of surfactant  $S$  for DTMA ( $\Delta$ ) and CTMA ( $\circ$ ). The straight line represents the calculated behavior corresponding to eq 1 and an interlayer thickness  $b = 3.5$ .

F. Candau NATO ASI "Recent Advances in Polymeric Dispersions", Spain 1996

M. Antonietti et al.  
Macromolecules 24 (1991) 6636-6643

# $\mu$ -EP common case

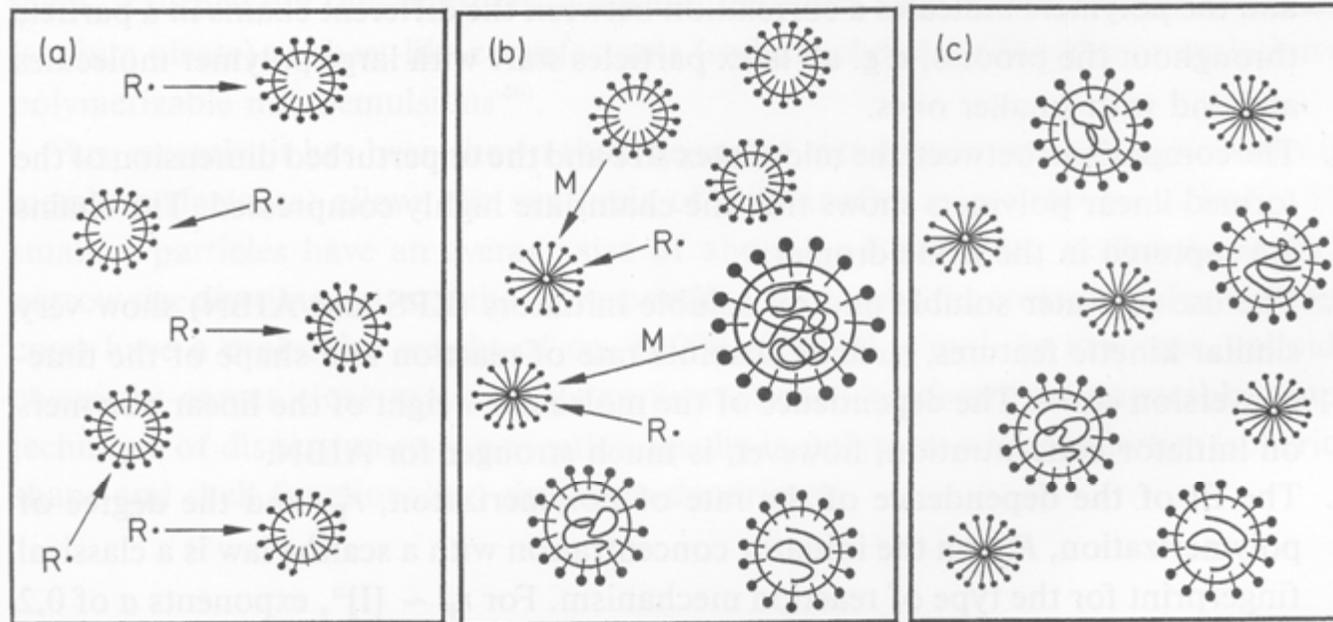


Fig. 1. Schematic scenario of the CLF-model: (a) Parental microdroplets of equal size are initiated by radicals formed in the aqueous phase. (b) Monomer transport from unpolymerized microdroplets through the aqueous phase results in growth of particles containing a polymer-chain. Empty micelles are formed which allow continuous nucleation of new latex particles. (c) At the end of the polymerization, latex particles larger than the primary microdroplets coexist with a large surplus of empty micelles

# Microemulsion - Results

[KPS] (%)	UMSATZ (%)	D <sub>p</sub> (nm)	N <sub>p</sub> 1/mL
1.50	22.06	54.0	5,1241 E+13
	51.31	52.0	1,3332 E+14
	65.43	49.0	2,0587 E+14
	99.16	45.0	3,9671 E+14
0.90	23.22	58.0	2,0847 E+14
	49.02	55.0	2,2163 E+14
	65.54	53.0	2,4254 E+14
	98.53	51.0	2,6671 E+14
0.30	23.87	61.0	3,7131 E+13
	55.75	59.0	9,5845 E+13
	63.54	57.0	1,2137 E+14
	95.37	55.0	2,0266 E+14

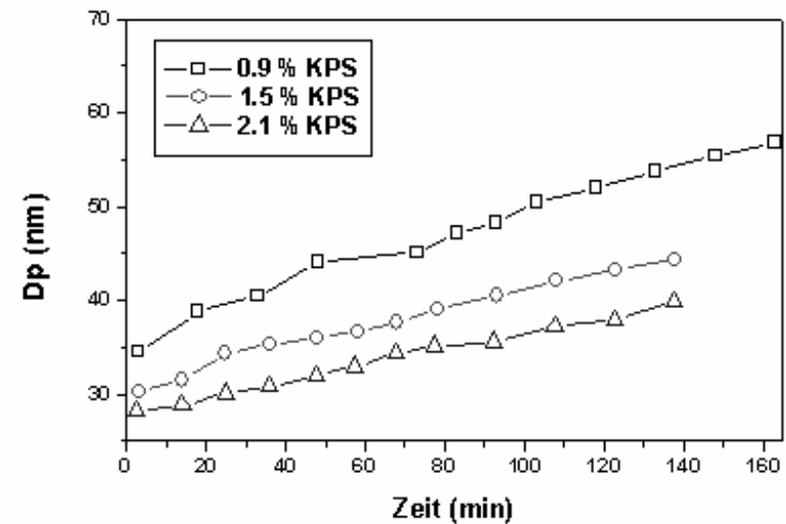
←  
batch

## Recipe:

97.216 g water  
 1.488 g SDS  
 0.496 g AOT  
 0.012 g KPS  
 0.9 g BuA

32.067 g BuA (feed)

↓  
semibatch

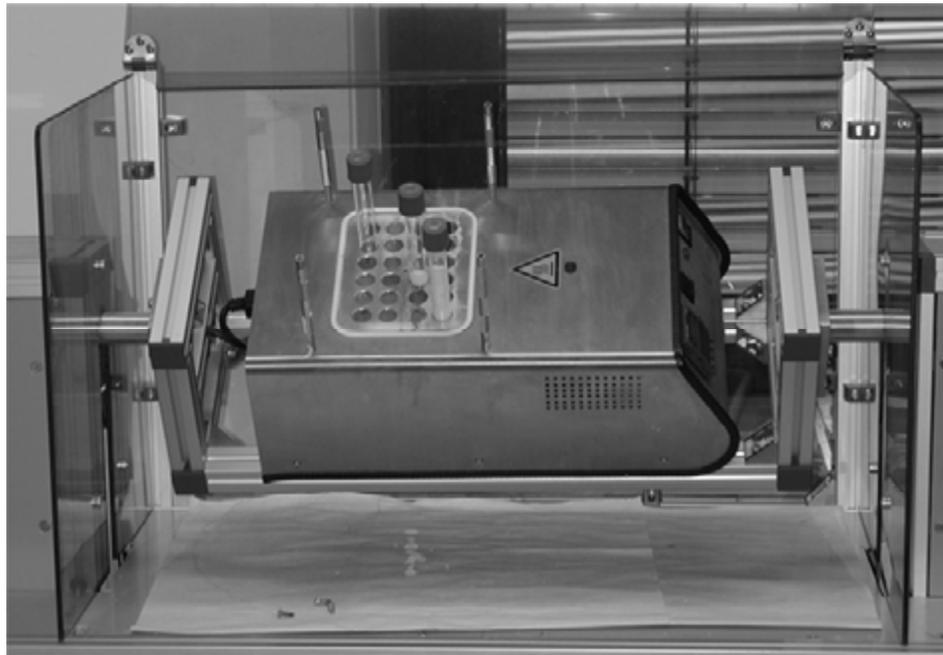


# Reactors & Procedures

## Emulsion Polymerization

- In principal emulsion polymerization doesn't require any special apparatus
- But for special products you need sophisticated recipes and procedures
- The wide variety of emulsion polymerization based products requires a wide variety of recipes and procedures
- Batch, semi-batch, and continuous procedures have been developed
- Seed procedures are very popular to avoid the uncertainties of particle nucleation

# Labscale Reactors





# Continuous Emulsion Polymerization

18 EMULSION POLYMERIZATION

Vol. 6

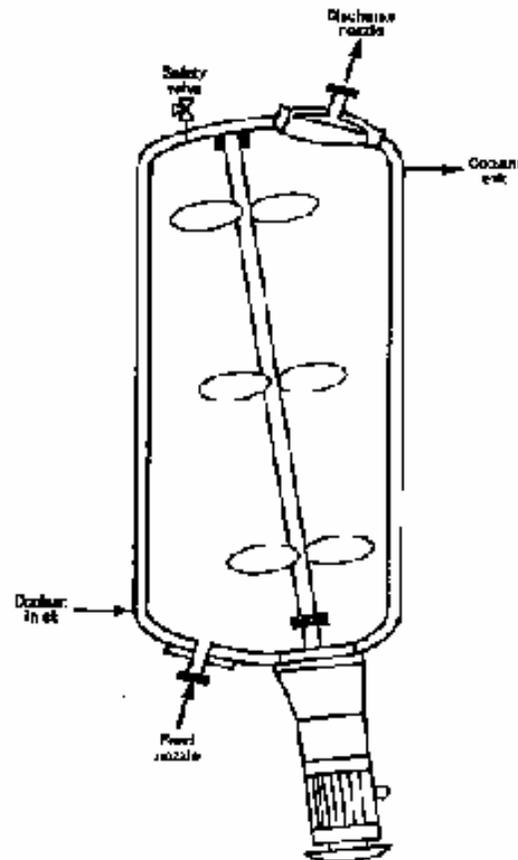


Fig. 10. Bayor continuous reactor for chloroprene (19).

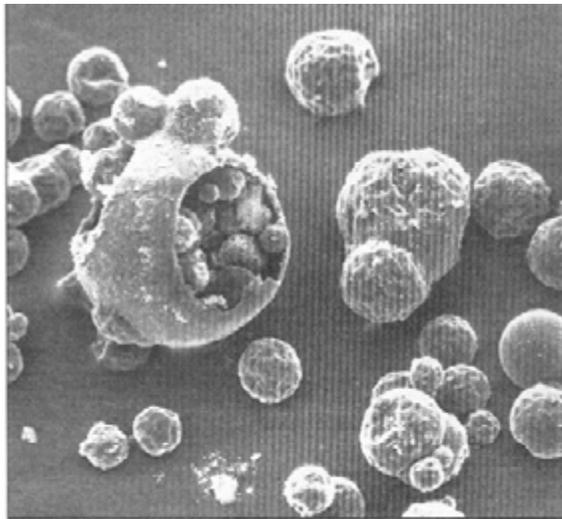
Continuous processes are used for high production amounts with constant quality; easiness of on-line control; Problems: sustained oscillations of latex properties may occur

Encyclopedia of Polymer Science and Engineering, Volume 6, J. Wiley & Sons 1986

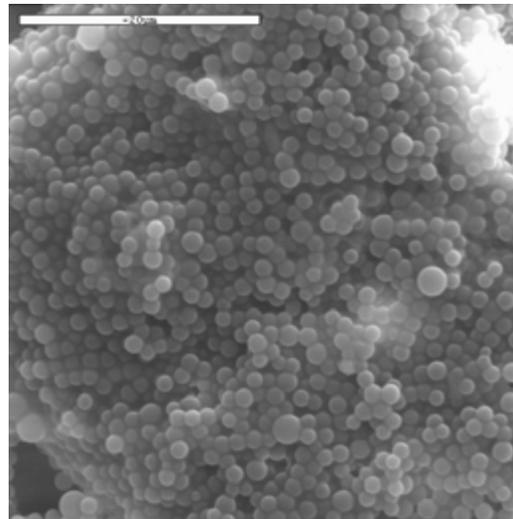


# Summary

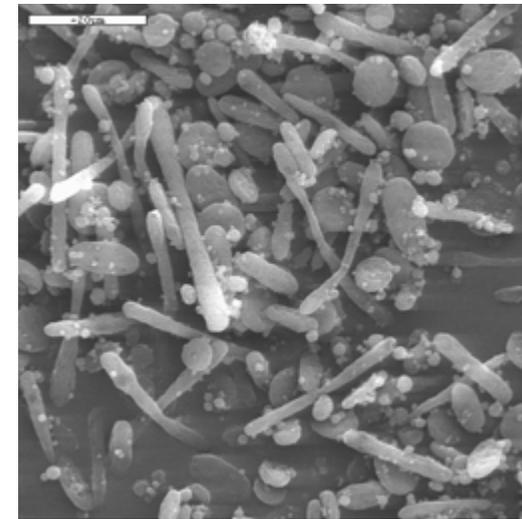
polymer dispersions are a fascinating area of colloid science



50  $\mu\text{m}$  poly(vinyl acetate)



Lmph2o2b, polystyrene



eur82-h, polystyrene

D. Distler "Wäßrige Polymerdispersionen"  
Wiley-VCH, 1999

MPI, Golm

aqueous polymer dispersions are the future form of all polymers

# Literature

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„Heterophase Polymerization“

in „Encyclopedia of Polymer Science and Technology“, 3<sup>rd</sup> edition

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