

Circularidade e Engenharia de Polímeros

Resinas à base de água



Prof. Reinaldo Giudici

Departamento de Engenharia Química

Escola Politécnica - Universidade de São Paulo (USP)

(rgiudici@usp.br)





Roteiro

- Introdução
- Processos de polimerização em meio heterogêneo (tendo água como meio dispersante)
 - Polimerização em suspensão
 - Polimerização em emulsão
 - Polimerização em miniemulsão
- Exemplos de aplicação
- Redução de monômero residual e VOCs

Introdução

Polímeros

- Produção mundial $> 10^8$ ton/ano
- $\sim 30\%$ do total via radicais livres
- $\sim 25\%$ do total via processos heterogêneos
(polimerização em emulsão)

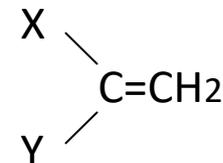
Polímeros base-água

- Monômeros hidrofóbicos (água=meio dispersante)
- Monômeros solúveis em água
 - Polimerização em cadeia (p.ex. radicais livres)
 - Polimerização em etapas (“policondensação”)

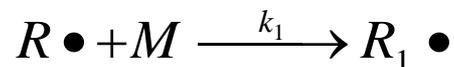
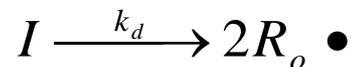
Mecanismo cinético

(polimerização via radicais livres)

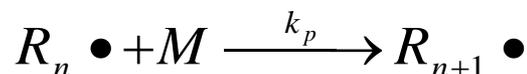
Monômero M



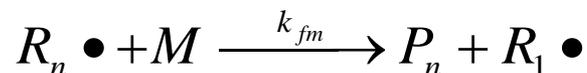
Iniciação



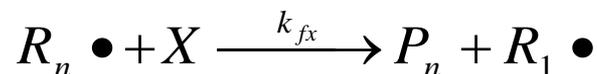
Propagação



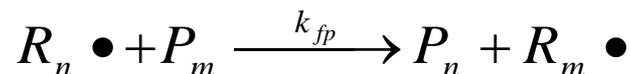
Transferência de cadeia para monômero



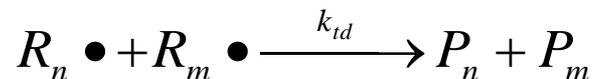
Transferência de cadeia para agente de transf. de cadeia



Transferência de cadeia para polímero



Terminação por desproporcionamento



Terminação por combinação



Polimerização em Massa

- ☹ aumento considerável da viscosidade → dificuldade em troca de calor, mistura, etc.

Polimerização em Solução

- 😊 solvente inerte, menor aumento da viscosidade
- 😊 se solvente volátil, maior remoção de calor via vaporização
- ☹ necessidade de remover e recuperar o solvente (se o produto for o polímero)
- ☹ menor produtividade (comparada à polimerização em massa)

Polimerização em Suspensão

- 😊 água como meio dispersante, menor viscosidade (comparada à polim. massa e solução)
- 😊 fácil separação do polímero
- ☹ menor produtividade (comparada à polimerização em massa)
- ☹ controle da DTP e estabilidade das partículas durante o processo

Polimerização em Emulsão

- 😊 água como meio dispersante, menor viscosidade (comparada à polim. massa e solução)
- 😊 maior taxa de reação (produtividade) e maior peso molecular
- 😊 permite mudar morfologia da partícula (p.ex. “core-shell”)
- ☹ difícil purificação do polímero (se a emulsão não for o produto final)
- ☹ controle da estabilidade da emulsão
- ☹ aspectos fundamentais muito mais complexos

Polimerização em emulsão

($d_p \sim 50$ a 500 nm)

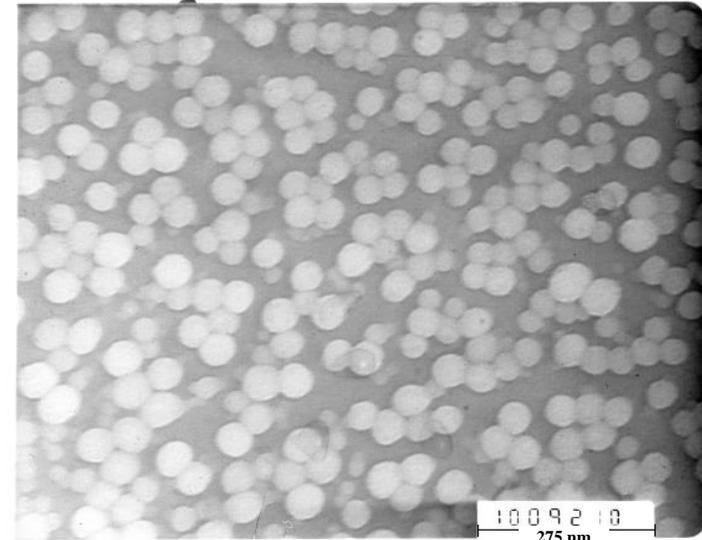
- Tintas (látex, acrílicos, vinílicos)
- Adesivos (PVA)
- Floculantes para tratamento de água
- PVC (couro artificial)
- SBR (borracha para pneus, recobrimento de papel)
- Kits para diagnósticos (imuno-ensaios)
- ...

Polimerização em suspensão

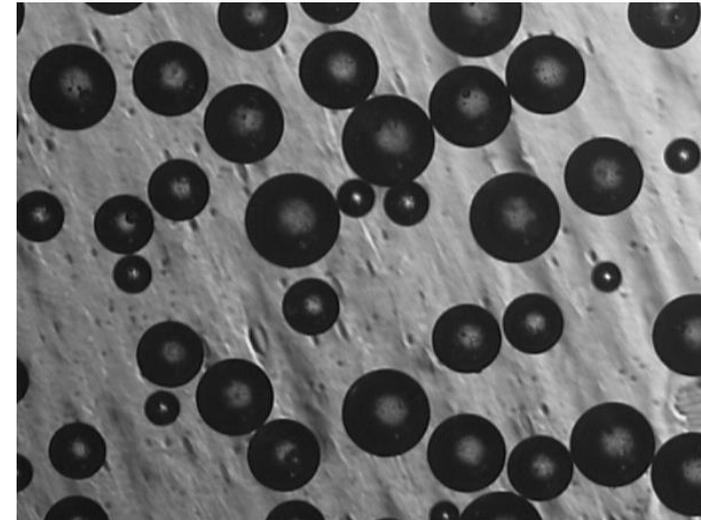
($d_p \sim 10$ μm a 5 mm)

- PVC (tubos e chapas, construção civil)
- PS (isopor EPS, HIPS)
- ...

TEM



275 nm



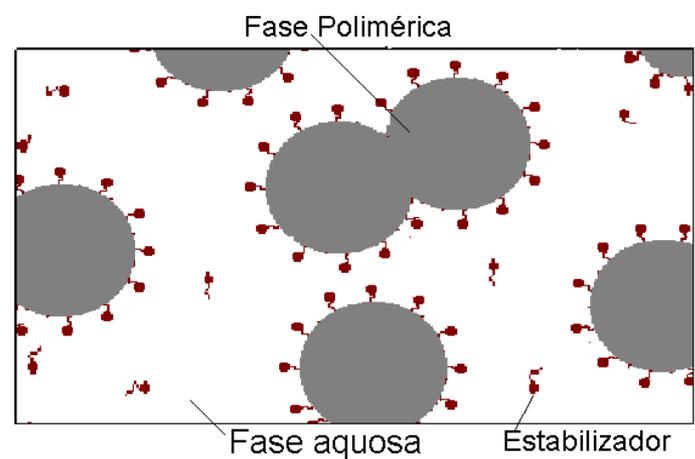
$D_{p_n} = 700$
 μm

Polimerização em Suspensão

- Monômero(s) (relativamente insolúvel na água)
25-50 vol. %
- Água (fase contínua)
- Iniciador (solúvel na fase orgânica)
- Agentes de suspensão (estabilizantes)
- Forte agitação
- Aditivos (ATC)

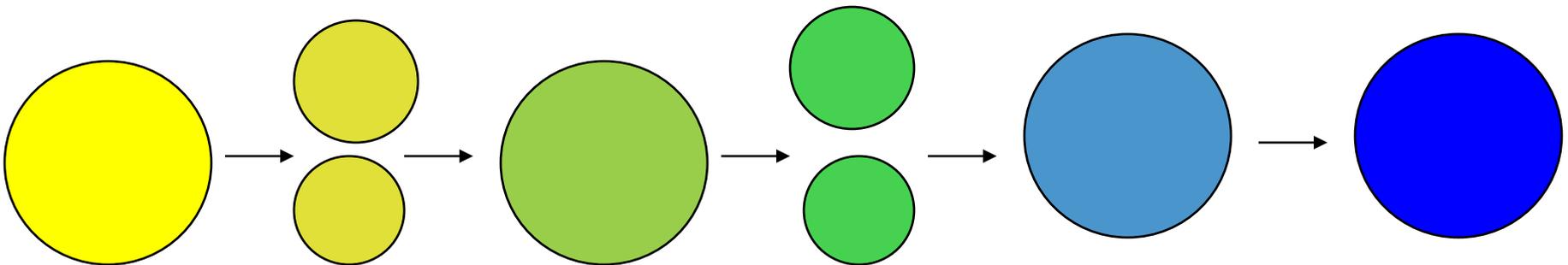
Tipos de Agentes de Suspensão:

- polímeros sintéticos solúveis na água :
 - polivinilpirrolidona, poli(álcool vinílico), poli(ácido acrílico), etc.
- polímeros naturais solúveis na água :
 - derivados da celulose (hidroxi etil celulose), gelatina, etc.
- pós inorgânicos :
 - hidróxido de magnésio, fosfato de cálcio, hidróxido de alumínio, etc.



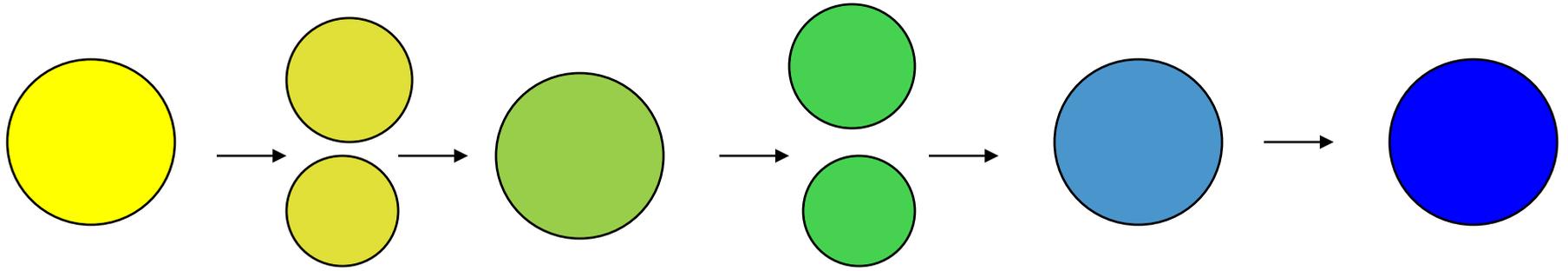
- $x < \sim 20\%$ → gotas de monômero
em estado líq. altamente móvel
- $\sim 20\% < x < \sim 60\%$ → gotas muito viscosas e pegajosas ("sticky")
- $x > \sim 70\%$ → partículas sólidas de polímero
("identity point")

**partículas de
polímero
10 μm a 5 mm**



Suspension polymerization

($d_p \sim 10 \mu\text{m}$ a 5 mm)



Monomer droplets

Coalescence x breakage

$f(\text{agitation, surfactant, ...})$

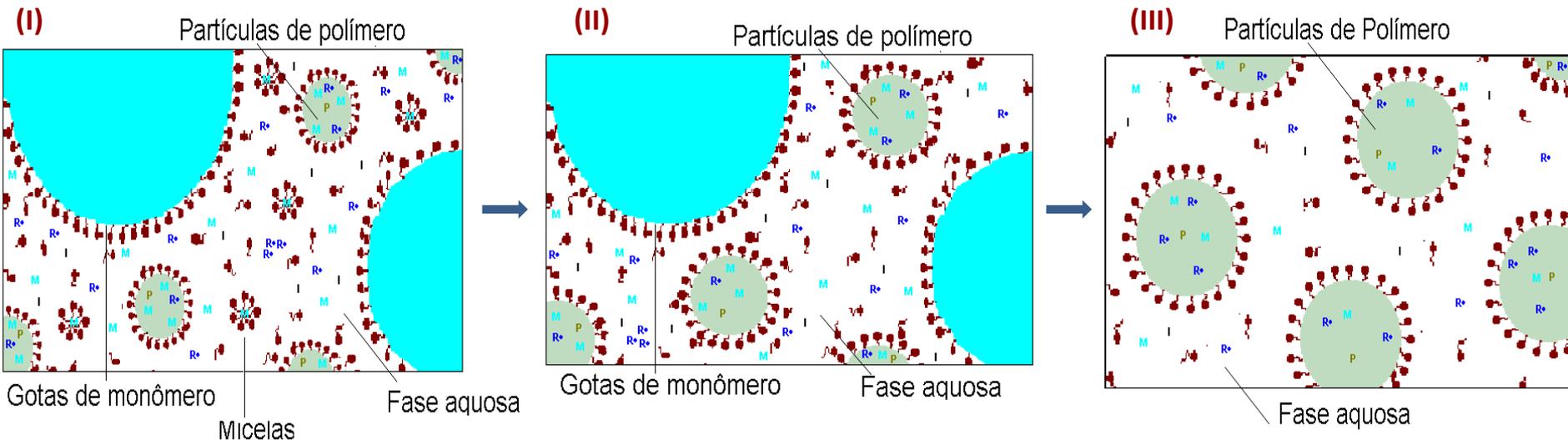
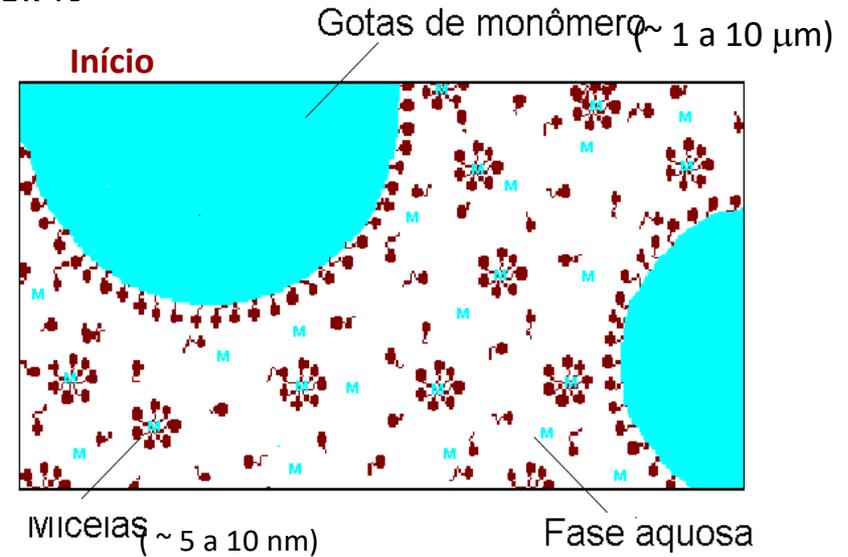
Particle identity point
 $x \sim 70\%$

Polymer particles

impossible to measure PSD off-line
(before the particle identity point)

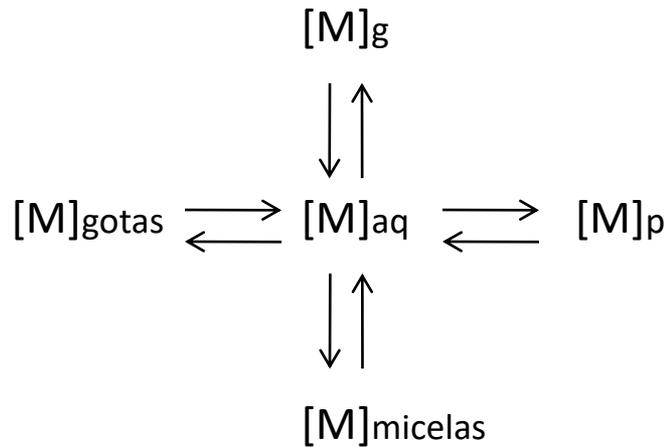
Polimerização em Emulsão

- Monômero(s) (pouco solúvel em água) 30-55 vol. %
- Água (fase contínua)
- Iniciador (solúvel na fase aquosa)
- Emulsificantes (acima da CMC → micelas)
- Agitação
- Aditivos (ATC)

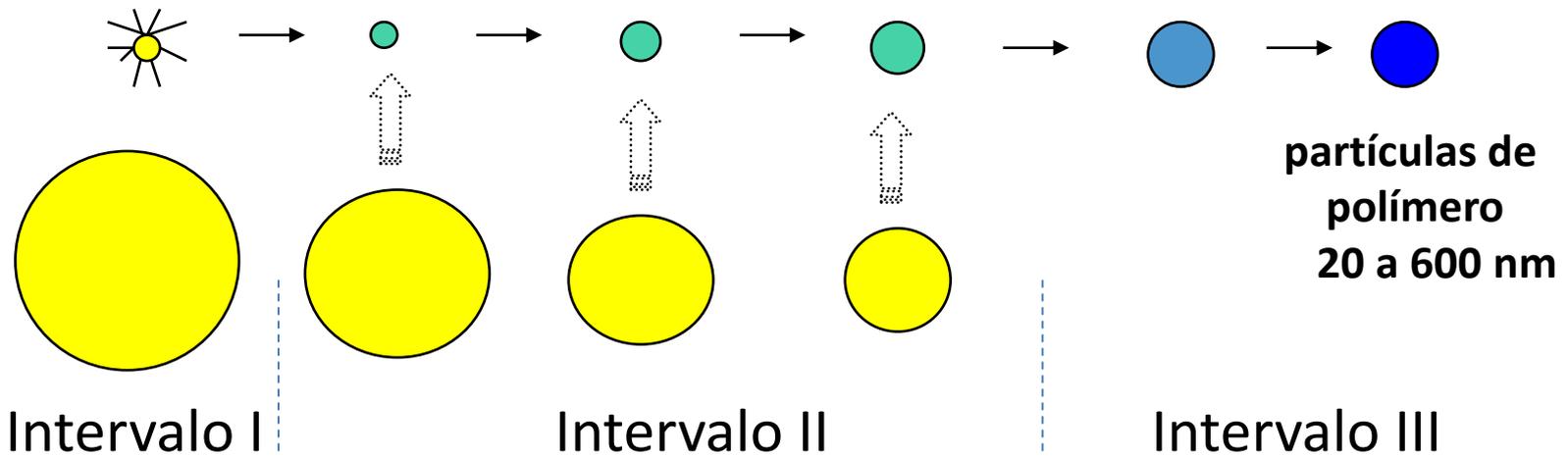
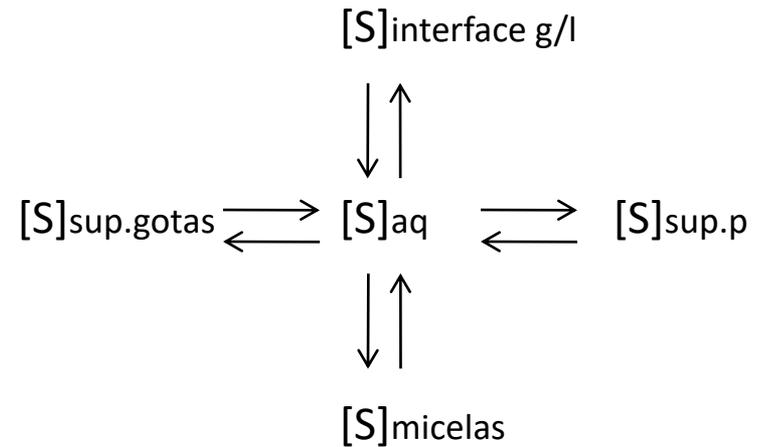


Polimerização em emulsão

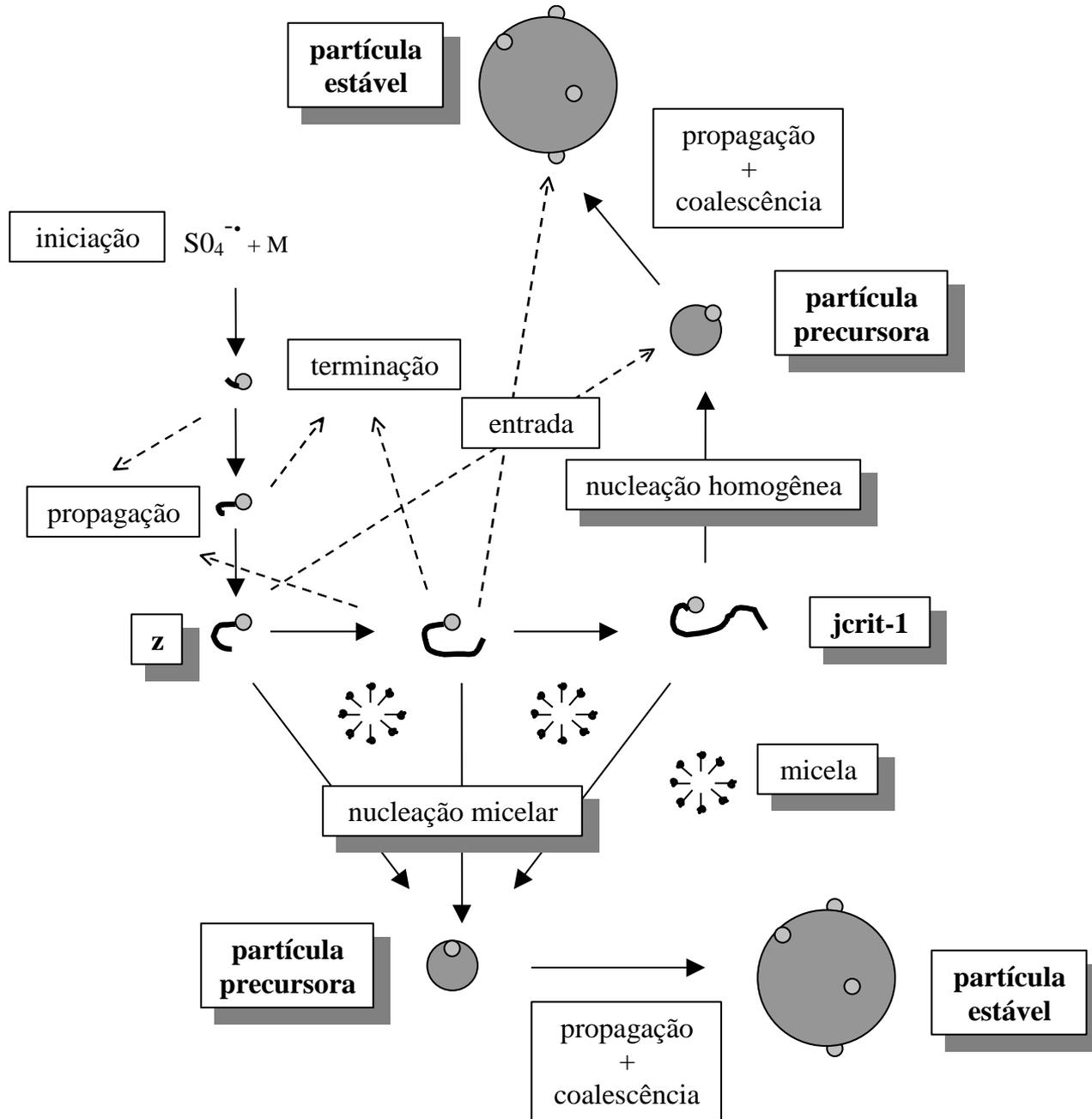
Partição de monômeros entre as fases



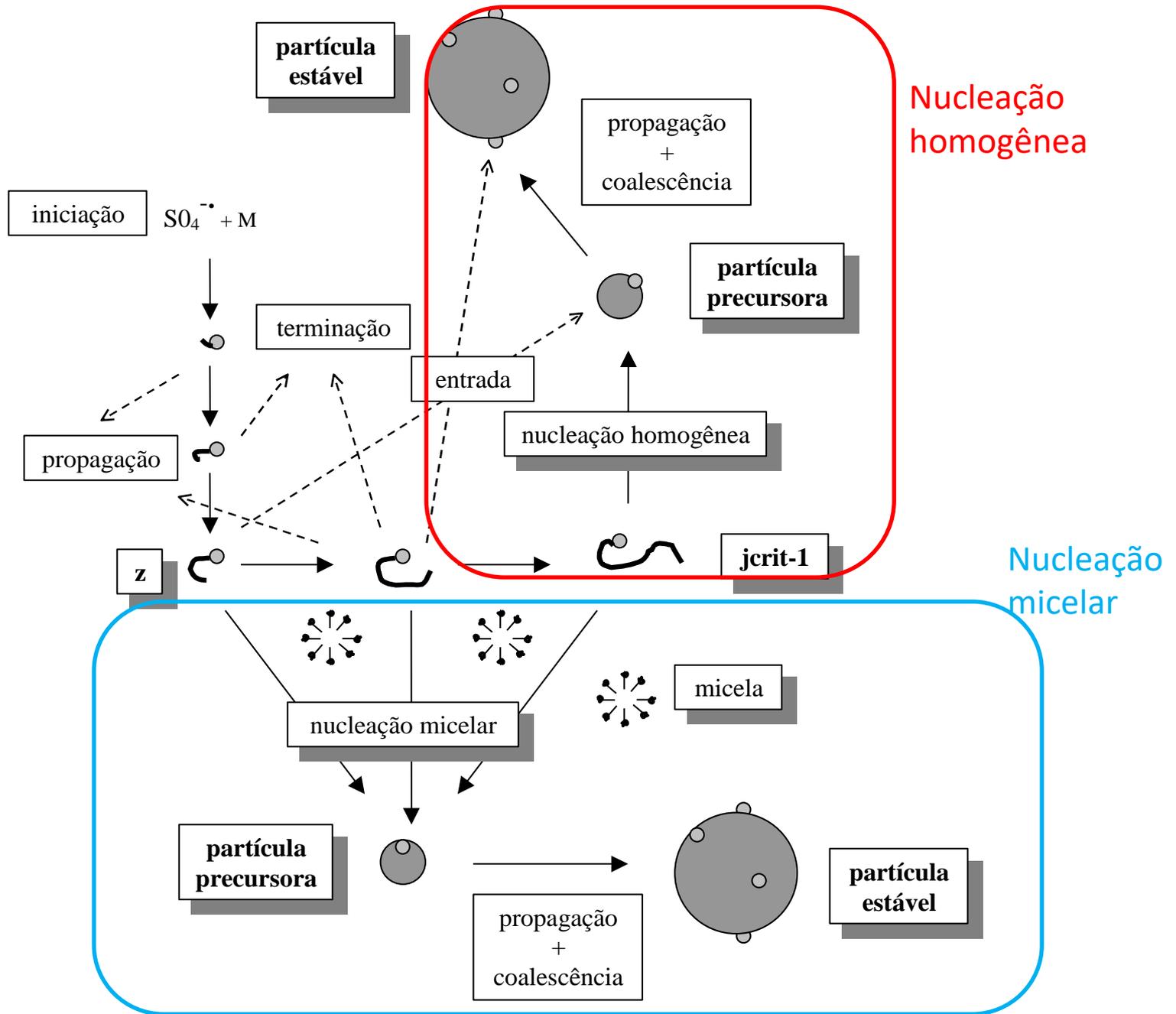
Partição de emulsificante entre as superf.



Polimerização em Emulsão (GILBERT, 1995).

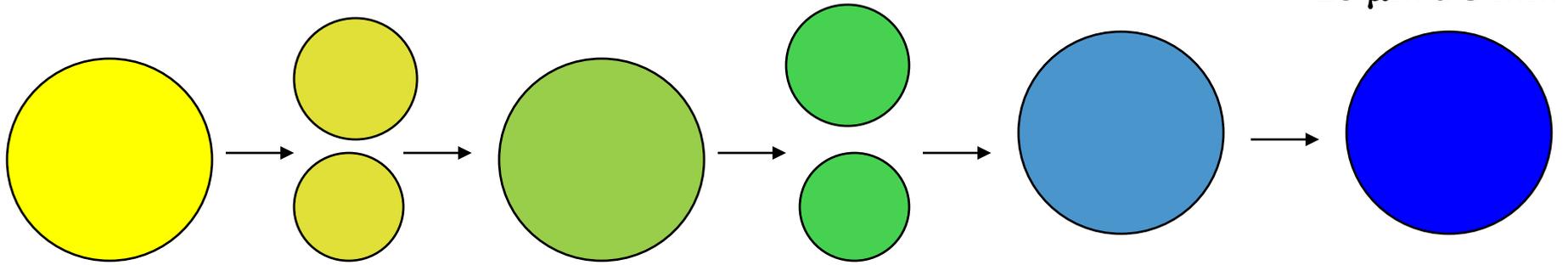


Polimerização em Emulsão (GILBERT, 1995).



Polimerização em suspensão ($dp \sim 10 \mu\text{m}$ a 5mm)

- iniciador solúvel no monômero



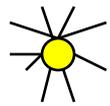
partículas de
polímero
 $10 \mu\text{m}$ a 5mm

Polimerização em emulsão ($dp \sim 20$ a 600nm)

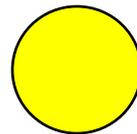
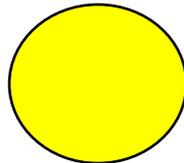
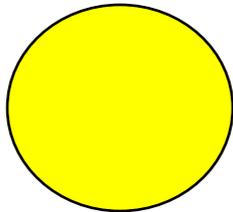
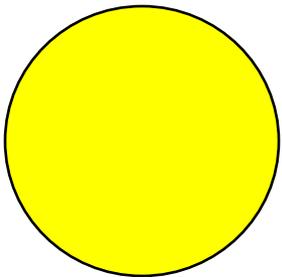
- iniciador solúvel na fase aquosa

- principal locus de polimerização \square partícula polimérica estabilizada

- gotas de monômero \square atuam somente como reservatório de monômero



partículas de
polímero
 20 a 600nm



Intervalo I

Intervalo II

Intervalo III

Importância do tamanho das partículas e da DTP

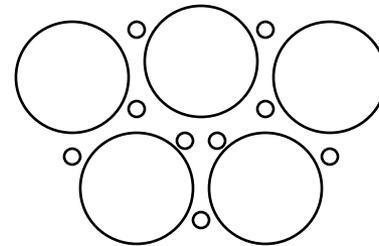
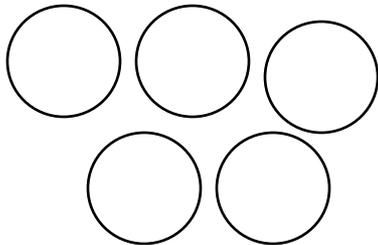
Polimerização em suspensão:

dp e DTP não afetam a cinética da polimerização, mas:

- Partículas muito pequenas prejudicam a separação do polímero na saída do reator, elevando as perdas e deterioram a qualidade do ambiente de trabalho.
- Partículas poliméricas muito grandes podem comprometer o processamento da resina, devido ao tempo necessário para fusão e dissolução da massa.

Polimerização em emulsão:

- dp e DTP afetam a cinética da polimerização (núm. médio de radicais/partícula)
- dp e DPT afetam a reologia do látex (emulsões com alto teor de sólidos)



Aumento do teor de sólidos em
polimerização em emulsão

Motivation

Incentives for **increasing solids content** in polymer emulsions

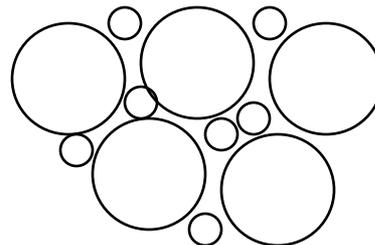
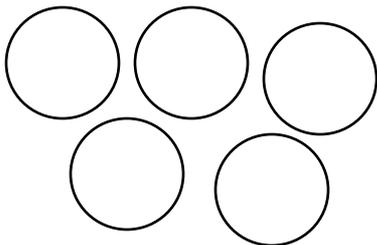
- Lower transportation and storage costs per unit mass of polymer
- Shorter drying and film formation times
- Higher productivity (per unit volume of reactor)

Difficulties:

- Risk of colloidal destabilization
- Keep the apparent viscosity manageable (low)

How?

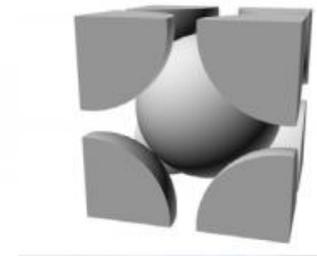
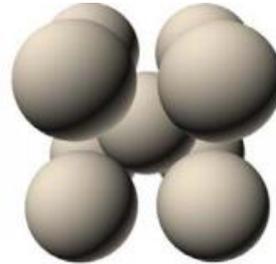
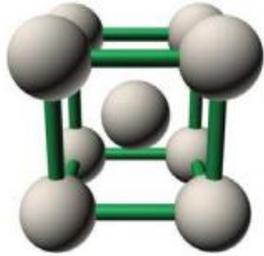
- Bimodal, trimodal, multimodal PSD



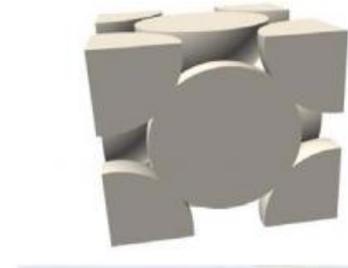
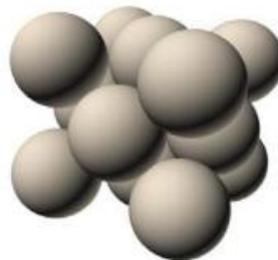
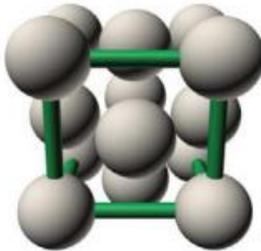
Seeded or ab initio
Competitive growth

• Fator de empacotamento esférico

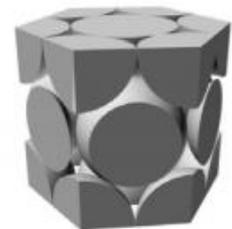
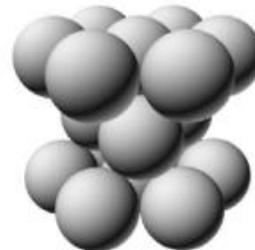
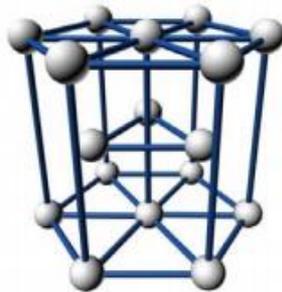
- Estrutura cúbica de corpo centrado (CCC) = 0.68



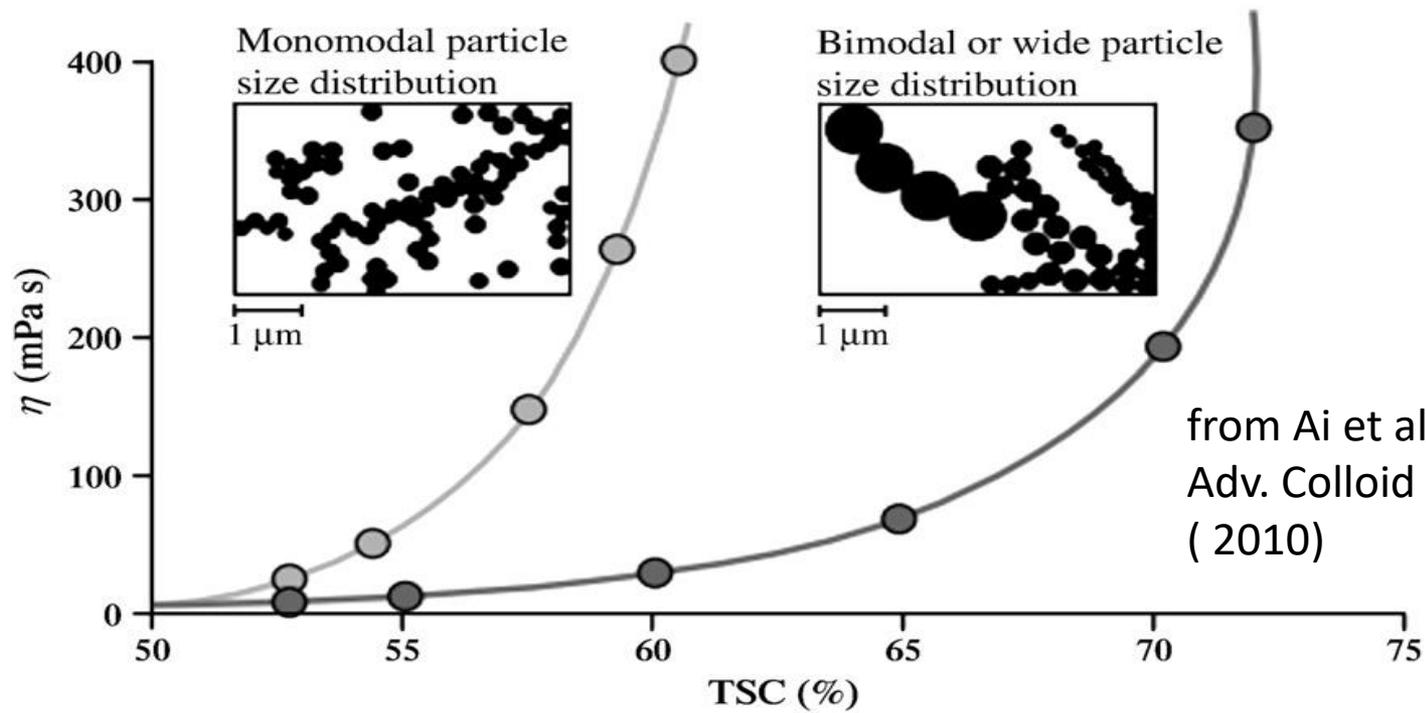
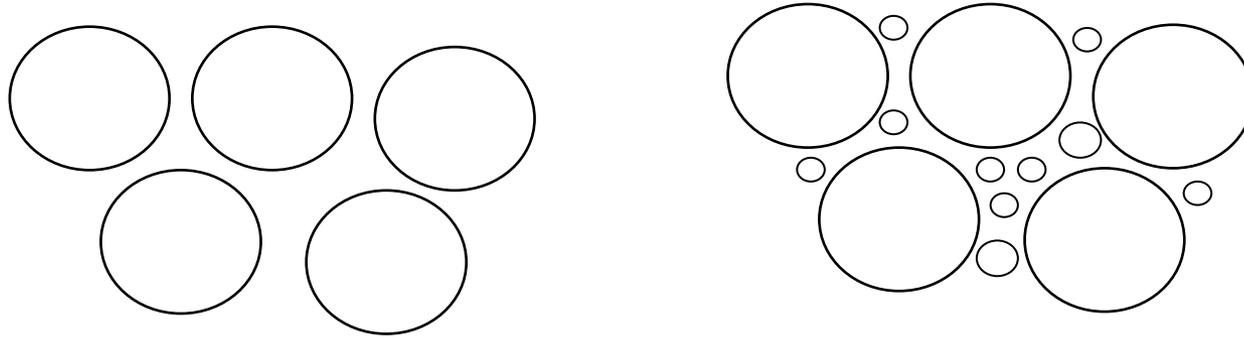
- Estrutura cúbica de face centrada (CFC) = 0.74



- Estrutura hexagonal compacta (HC) = 0.74



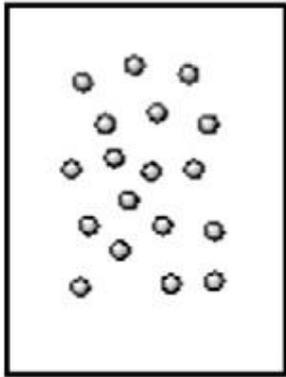
Polymer emulsions with high solids content



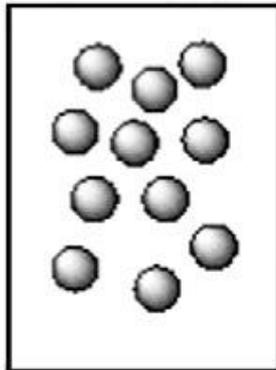
from Ai et al.,
Adv. Colloid Interf. Sci.,
(2010)

Operational strategy to produce HSC latex

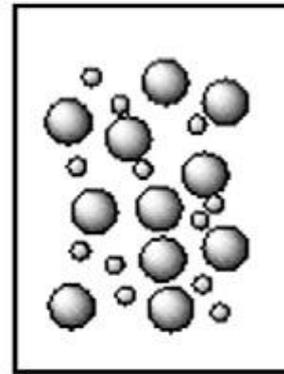
Stage 1:
nucleation



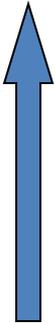
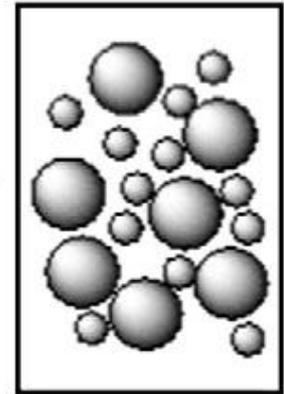
Stage 2:
growth



Stage 3:
Second nucleation



Stage 4:
Competitive growth

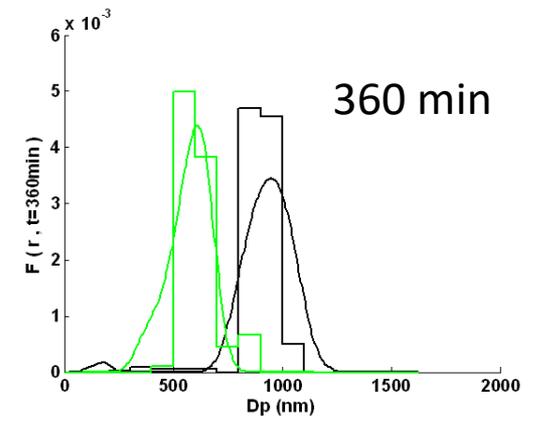
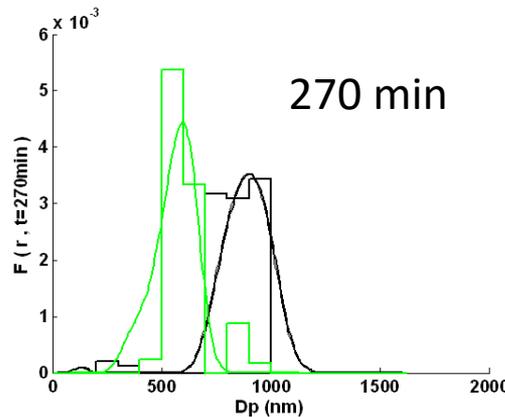
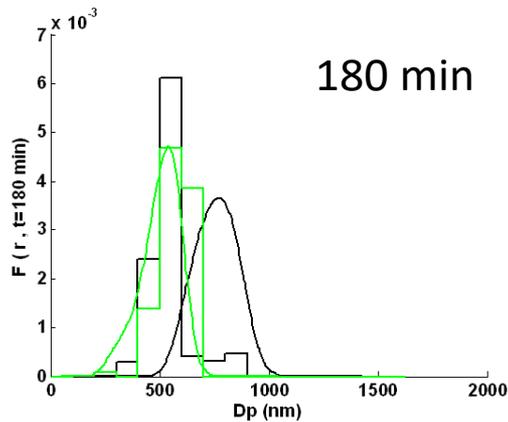
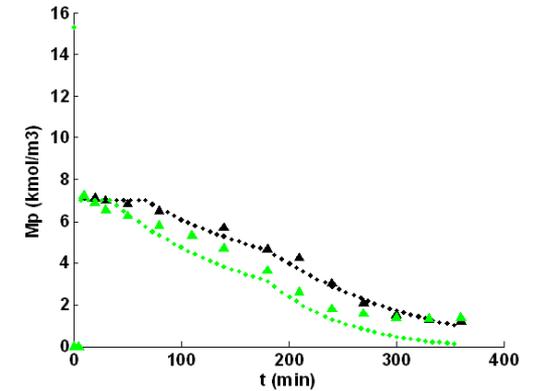
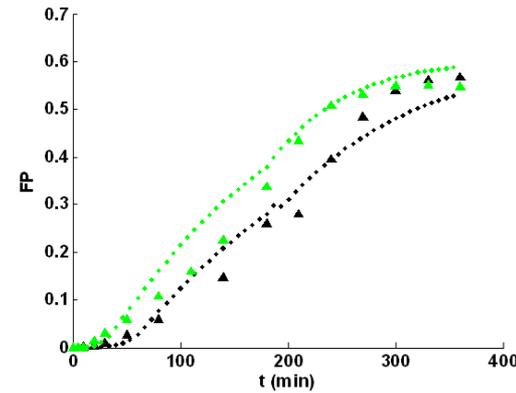
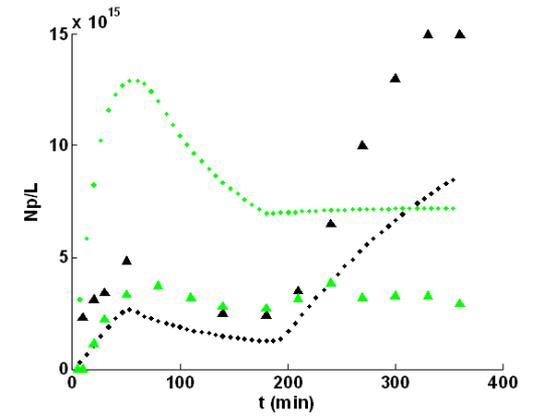
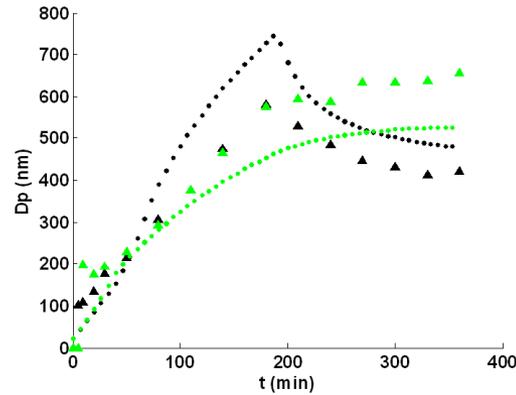


High solids content

Experimental and simulation results of runs BAS-03 and AS-23 for (Dp), (Np), (FP) and (Mp)

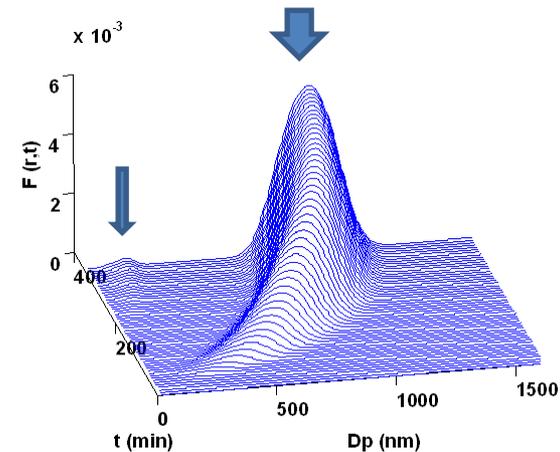
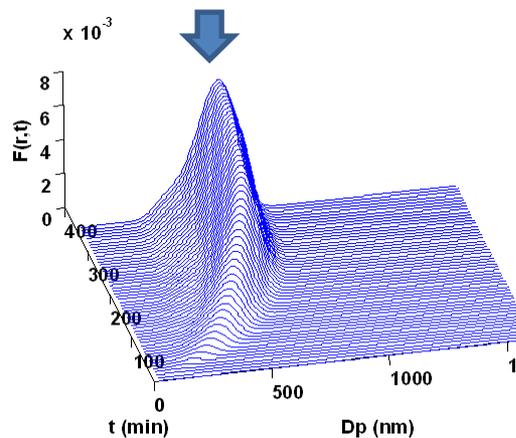
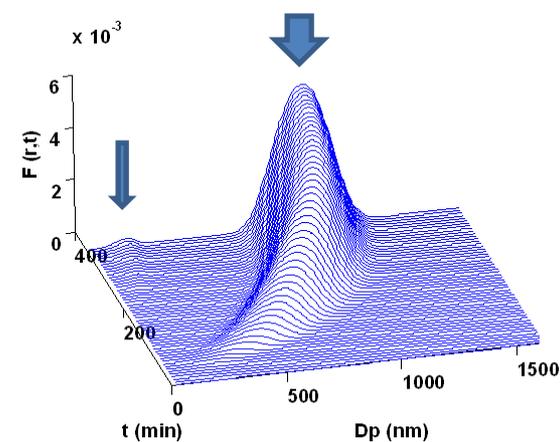
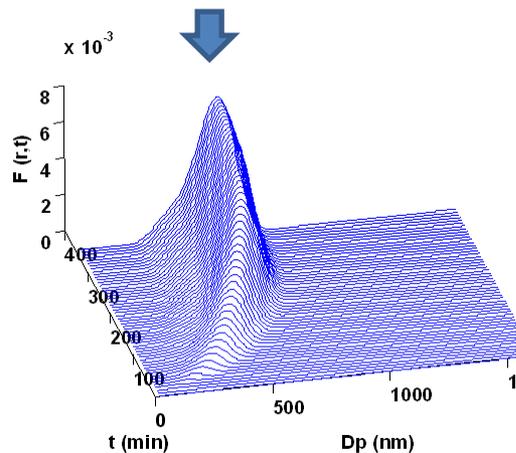
Green: Δ -experimental BAS-03;
 [.....]- model BAS-03;
 no shot (monomodal PSD)

Black: Δ -experimental AS-23;
 [.....]- model AS-23
 with shot of emulsifiers
 at t=190 min
 (bimodal PSD)



High solids content

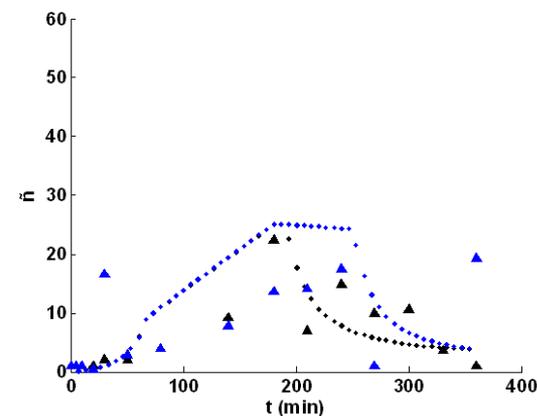
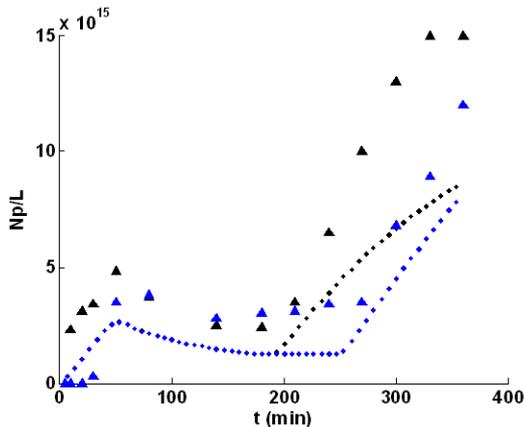
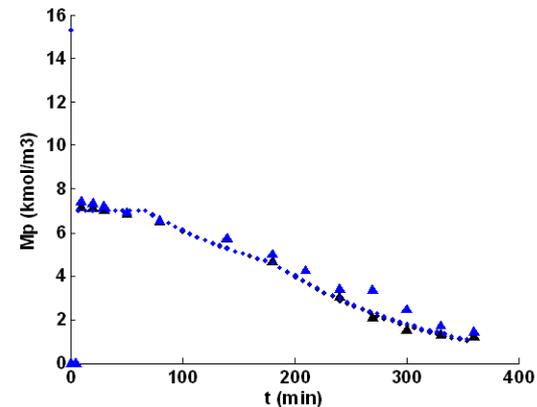
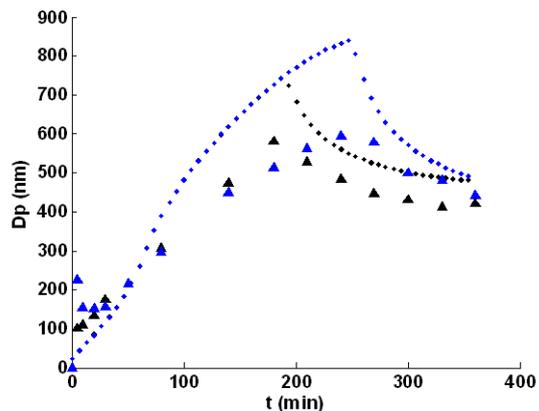
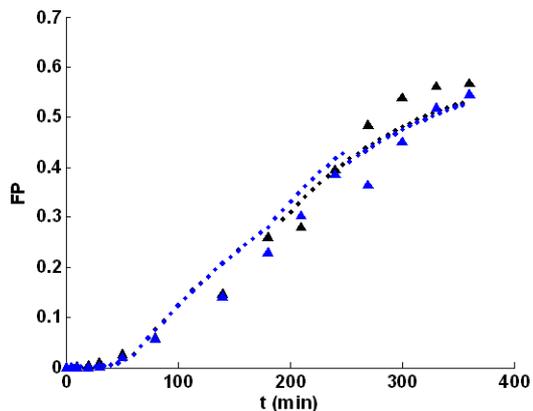
Marinangelo, Hirota, & Giudici ,
Chem. Eng. Sci. 66(23), 5875-5890 (2011)



Run	Solids content (wt%)	Apparent viscosity* η (mPa.s)	Coagulum content (ppm)
BAS-03	62	104.0	21909
AS-23		267.3	6406
BAS-04	64	244.0	41226
AS-22		4273.0	8118

*measured at T=20°C under shear rate 46.5 s⁻¹

Time evolution of the particle size distribution, according to the model predictions, for runs: (a) AS-23; (b) BAS-03; (c) AS-22 and (d) BAS-04. Table 4 – Characteristics of the final latexes.



High solids content

BAS-03 ($t_{shot}=190\text{min}$) and
BAS-05 ($t_{shot}=250\text{min}$)

Run	Solids content (wt%)	Apparent viscosity* η (mPa.s)	Coagulum content ppm
BAS-03	62	104.0	21909
BAS-05		89.0	11024

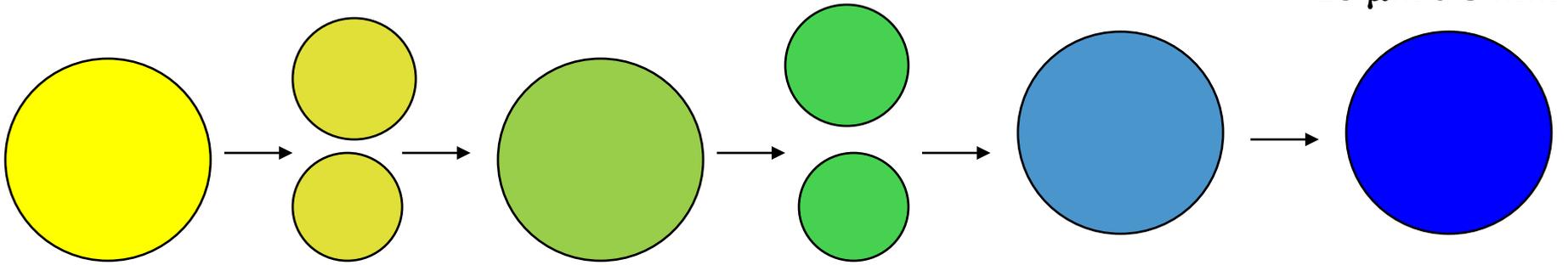
*measured at $T=20^\circ\text{C}$ under shear rate 46.5 s^{-1}

Marinangelo, Hirota, & Giudici ,
Semi-batch emulsion copolymerization of styrene and
butyl acrylate for production of high solids content
latexes: Experiments and mathematical model.
Chem.Eng. Sci. 66(23), 5875-5890 (2011).

Polimerização em miniemulsão

Polimerização em suspensão ($dp \sim 10 \mu\text{m}$ a 5mm)

- iniciador solúvel no monômero



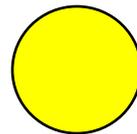
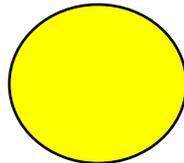
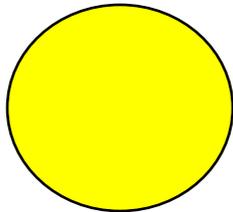
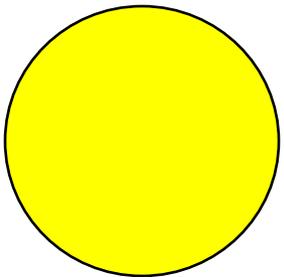
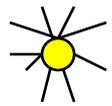
partículas de
polímero
 $10 \mu\text{m}$ a 5mm

Polimerização em emulsão ($dp \sim 20$ a 600nm)

- iniciador solúvel na fase aquosa

- principal locus de polimerização \square partícula polimérica estabilizada

- gotas de monômero \square atuam somente como reservatório de monômero



partículas de
polímero
 20 a 600nm

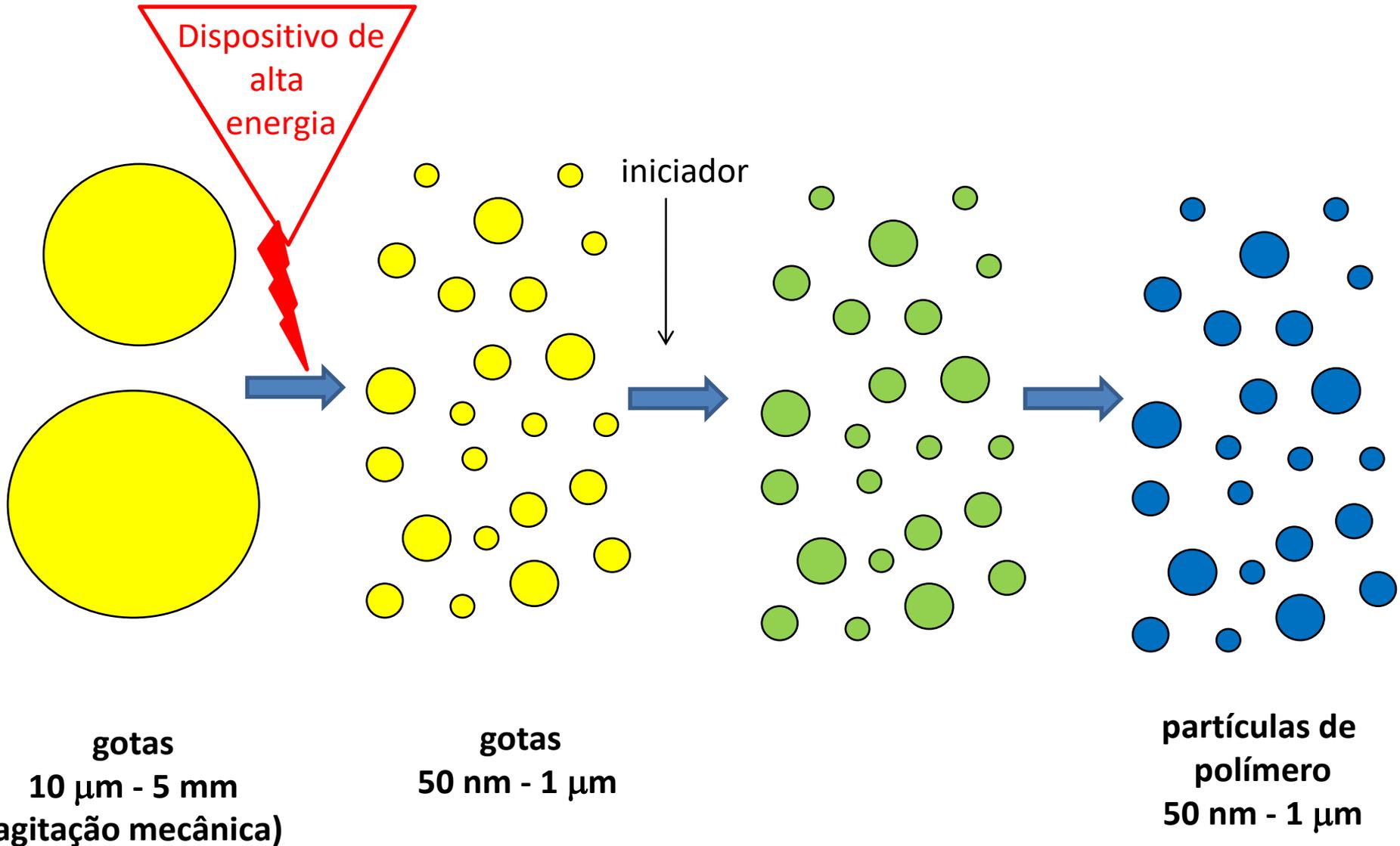
Intervalo I

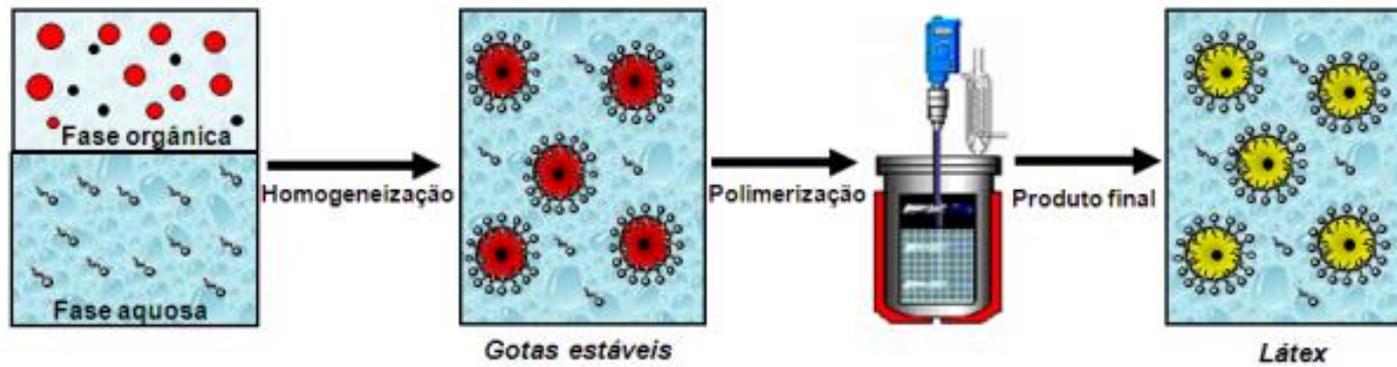
Intervalo II

Intervalo III

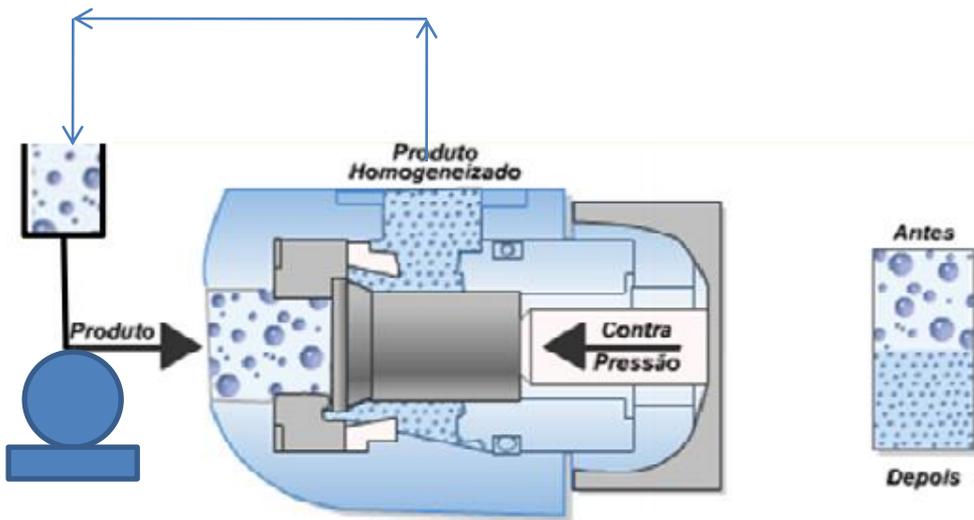
Polimerização em miniemulsão ($dp \sim 50 \text{ nm} - 1 \mu\text{m}$)

- iniciador solúvel no monômero ou na fase contínua

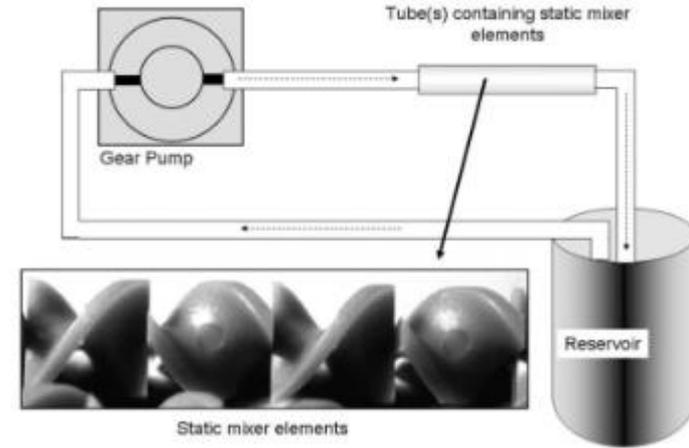




LANDFESTER, 2003



Homogenizador de alta pressão (Gaulin)



Misturadores estáticos

(JAPS,114,3875–3881(2009)

DOI 10.1002/app.30343)

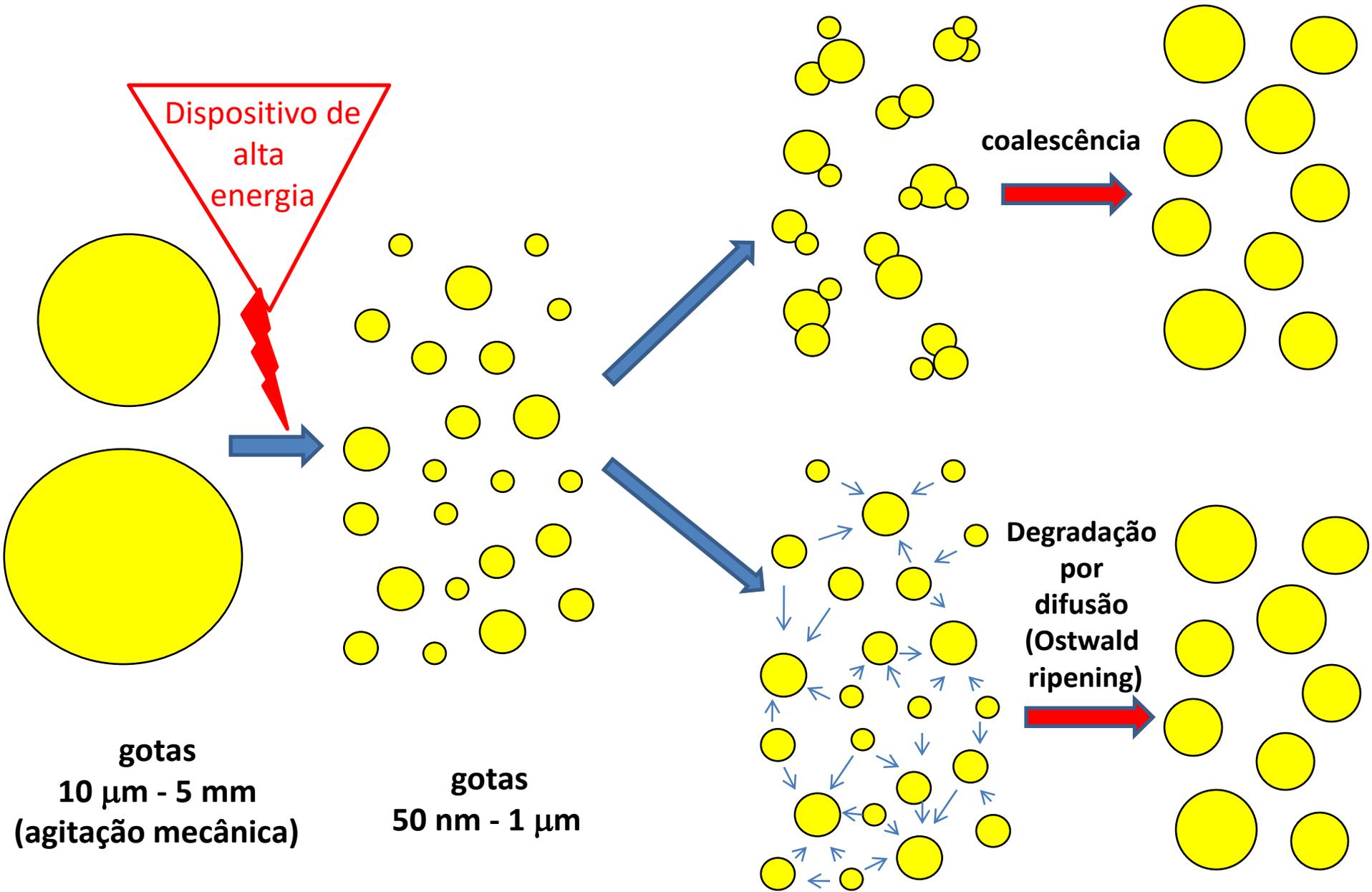


Rotor-estator (UltraTurrax)

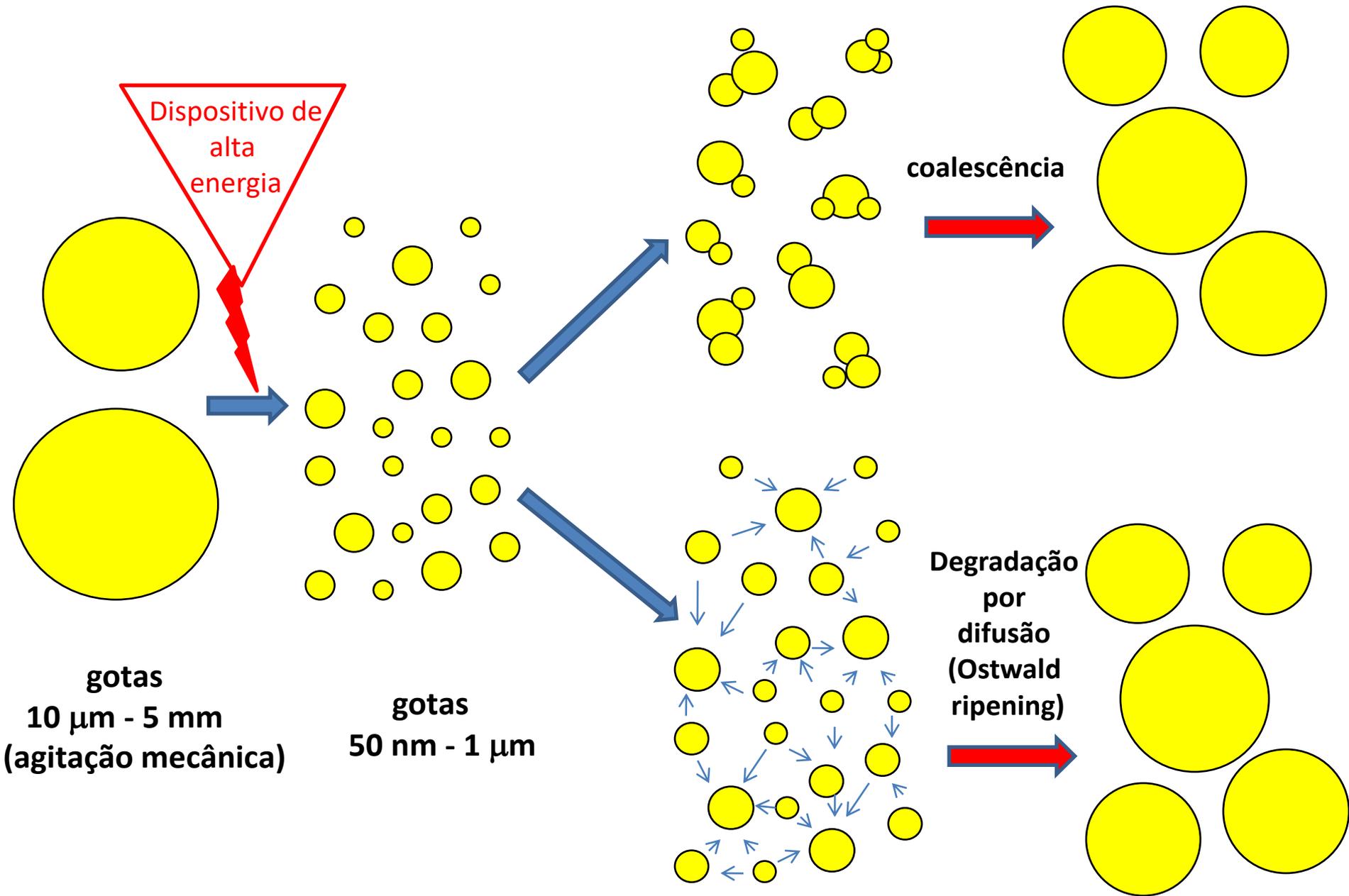


Ultrasonicador

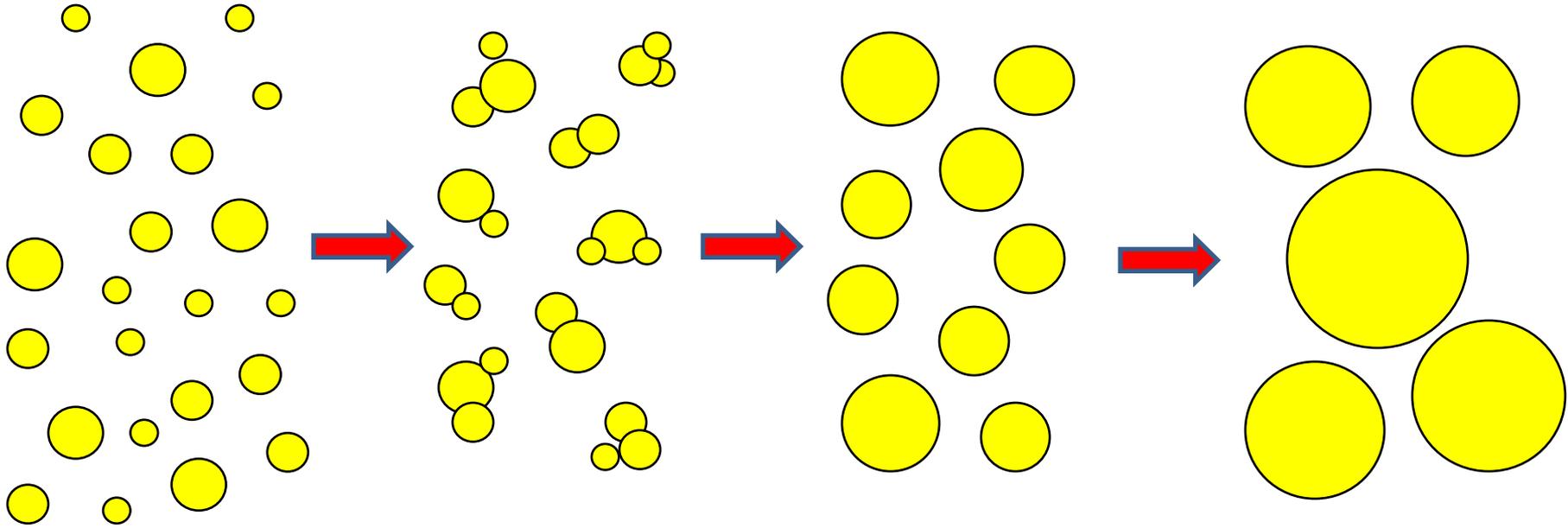
Polimerização em miniemulsão ($dp \sim 50 \text{ nm} - 1 \mu\text{m}$)



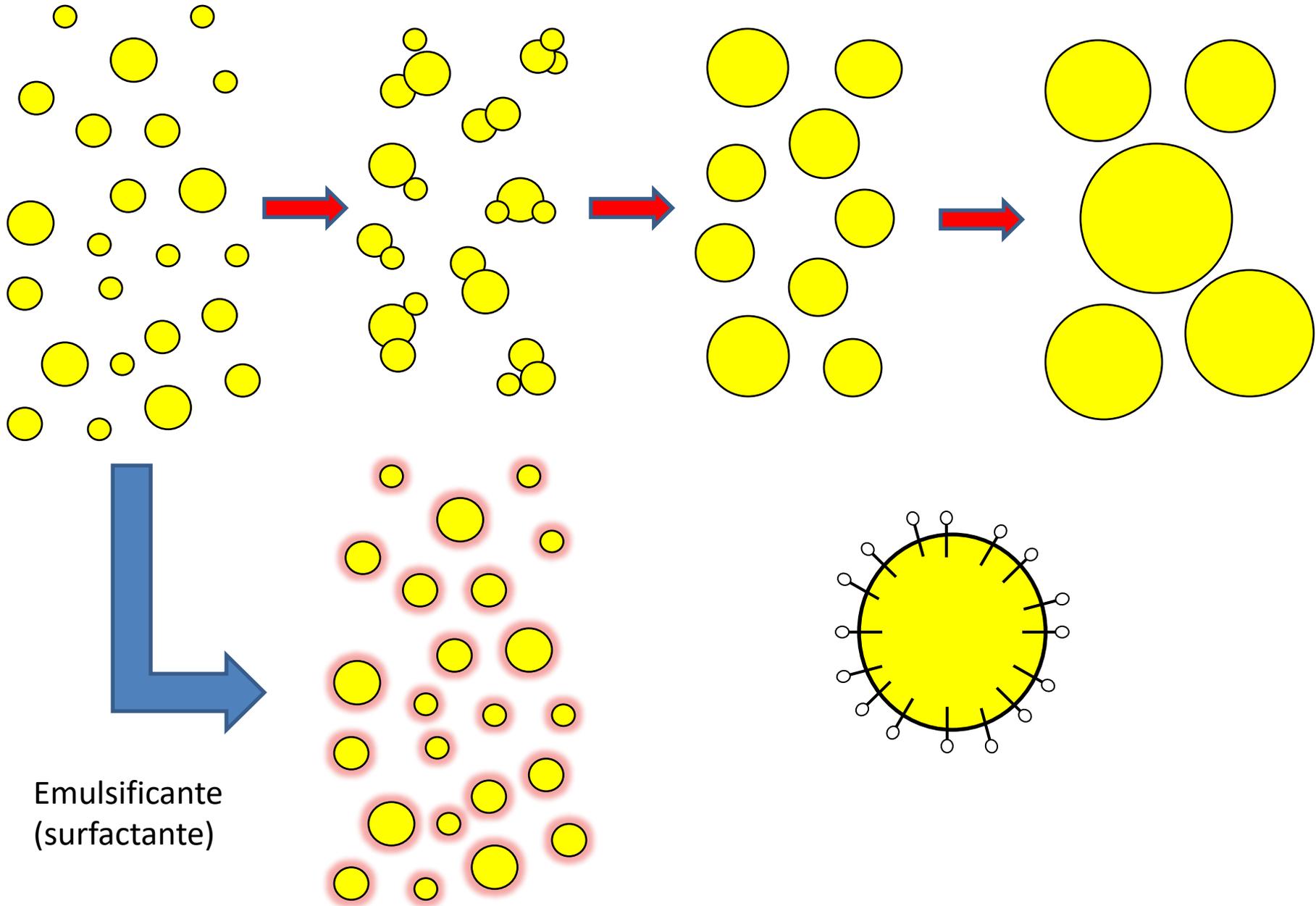
Polimerização em miniemulsão ($dp \sim 50 \text{ nm} - 1 \mu\text{m}$)



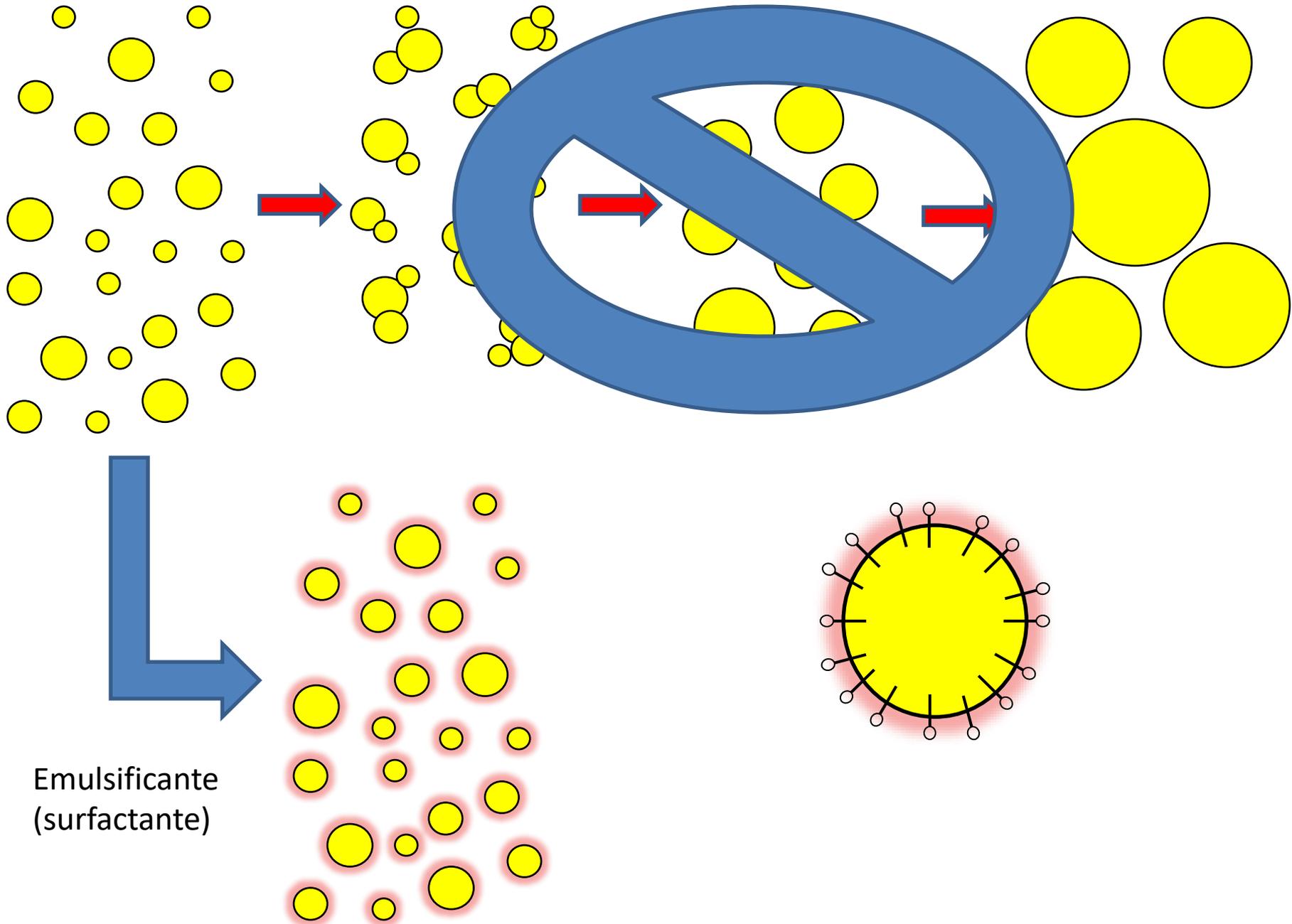
Coalescência das gotas de monômero



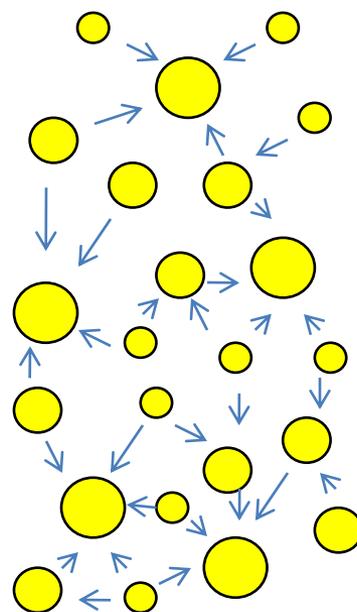
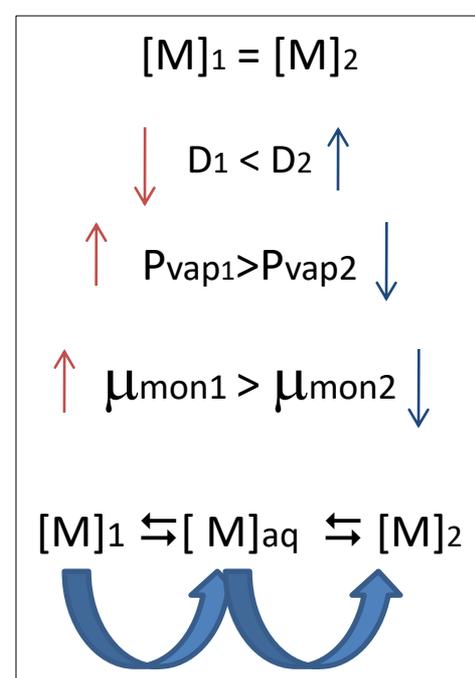
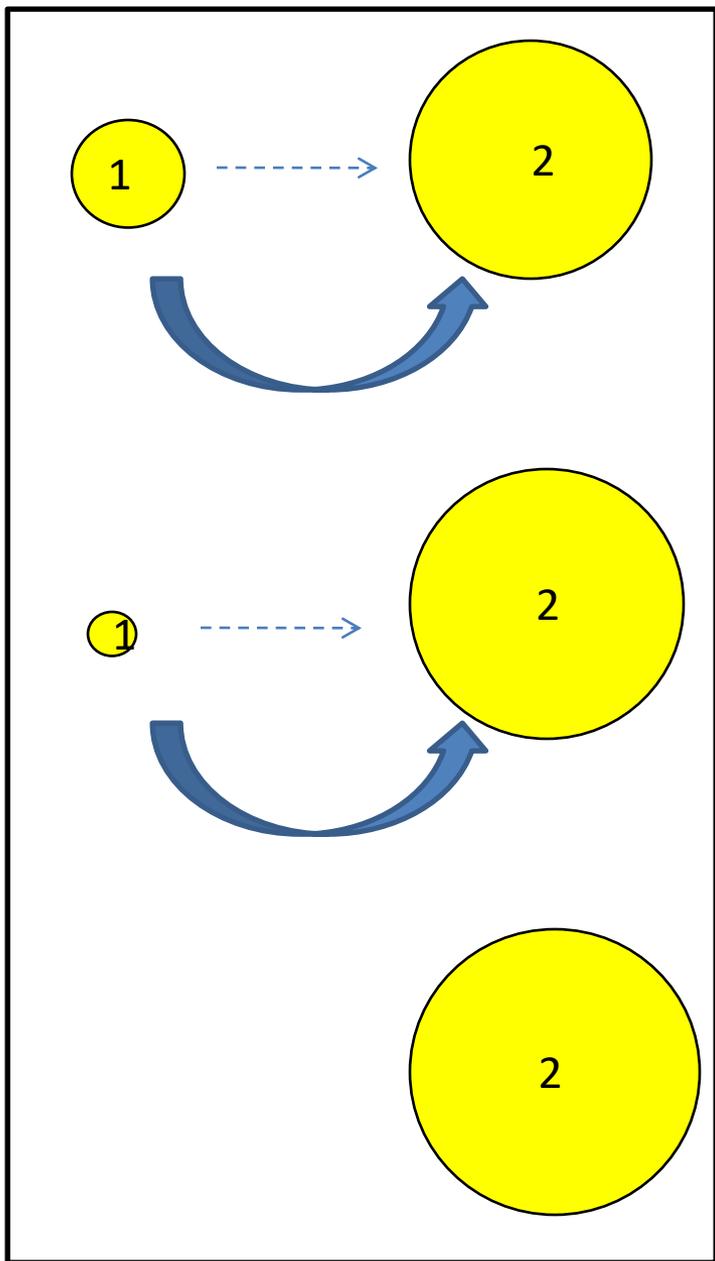
Coalescência das gotas de monômero



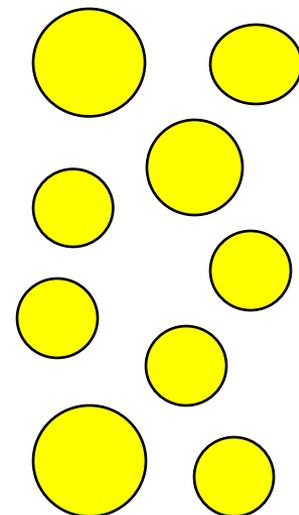
Coalescência das gotas de monômero



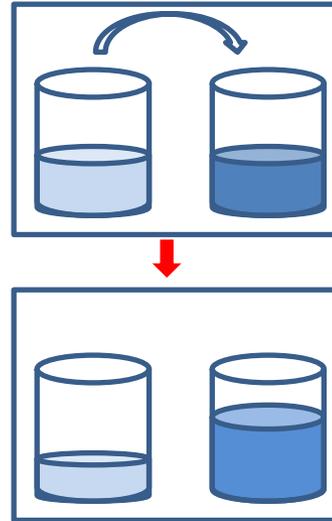
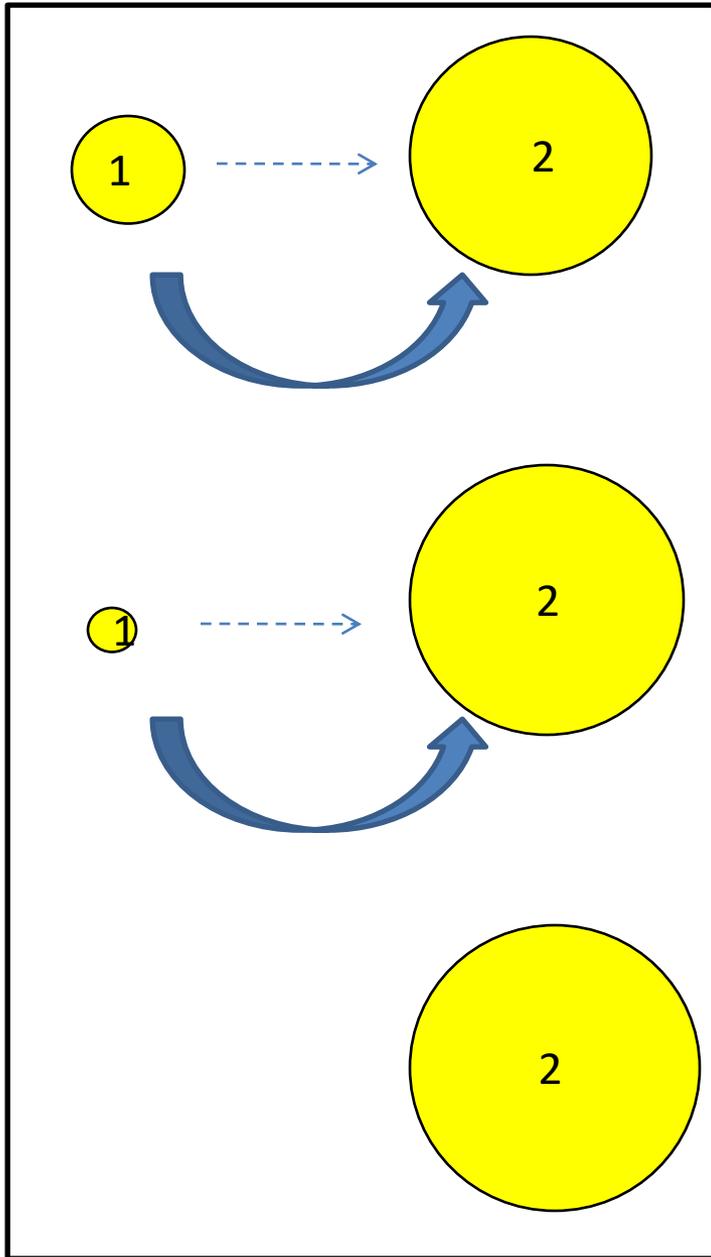
Degradação por difusão (Ostwald ripening)



Degradação por difusão (Ostwald ripening)



Degradação por difusão (Ostwald ripening)



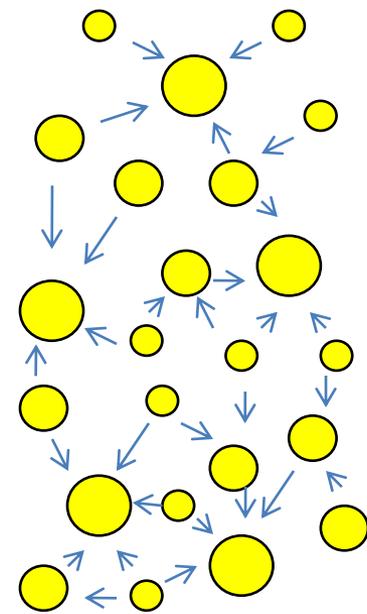
$[M]_1 = [M]_2$

$\downarrow D_1 < D_2 \uparrow$

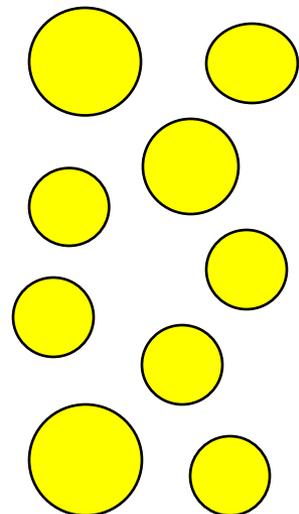
$\uparrow P_{vap1} > P_{vap2} \downarrow$

$\uparrow \mu_{mon1} > \mu_{mon2} \downarrow$

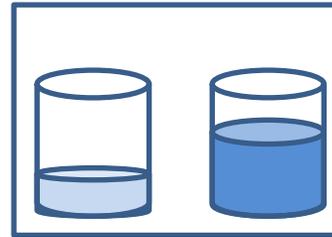
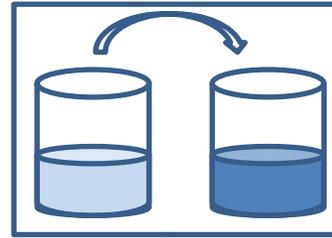
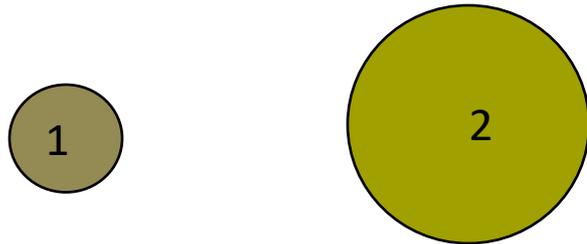
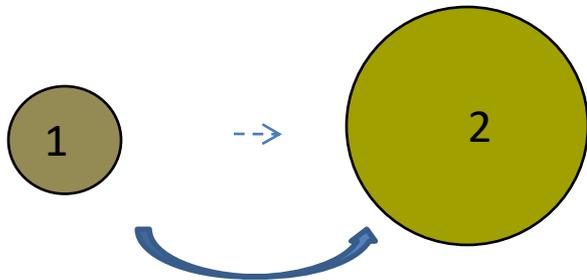
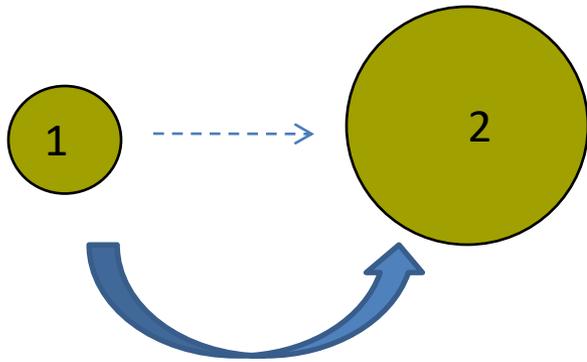
$[M]_1 \rightleftharpoons [M]_{aq} \rightleftharpoons [M]_2$



Degradação por difusão (Ostwald ripening)



Degradação por difusão (Ostwald ripening)



\uparrow [soluto]₁ > [soluto]₂ \downarrow

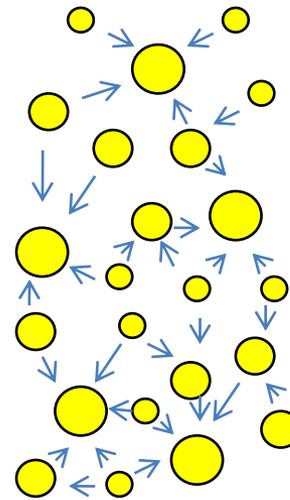
$D_1 < D_2$

\downarrow P_{vap1} > P_{vap2} \uparrow

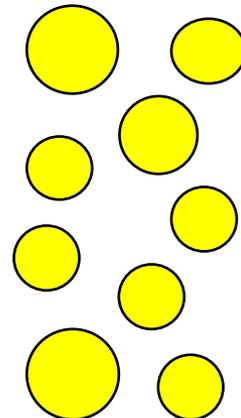
\downarrow μ_{mon1} > μ_{mon2} \uparrow

$[M]_1 \rightleftharpoons [M]_{aq} \rightleftharpoons [M]_2$

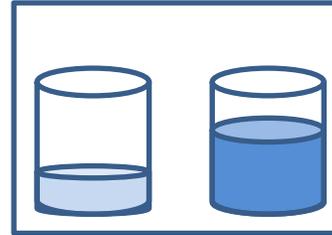
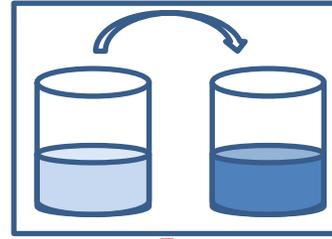
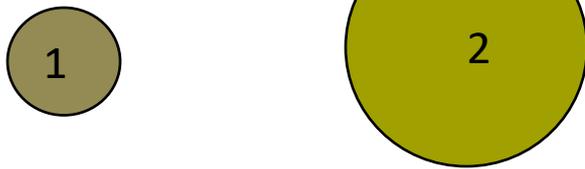
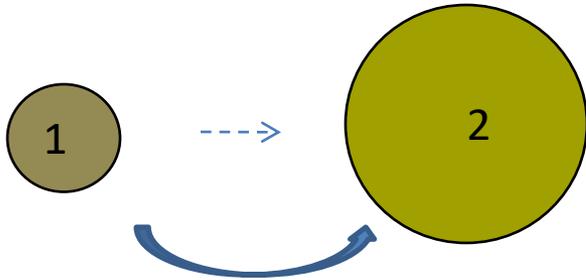
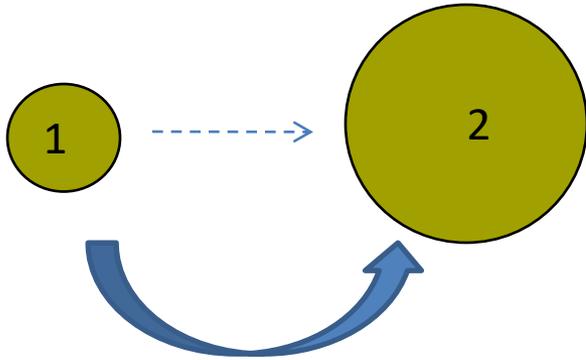
Acrescentar ao monômero um “soluto” (COESTABILIZANTE)
(bem mais insolúvel em água que o monômero)



Degradação
por
difusão
(Ostwald
ripening)



Degradação por difusão (Ostwald ripening)



\uparrow [soluto]₁ > [soluto]₂ \downarrow

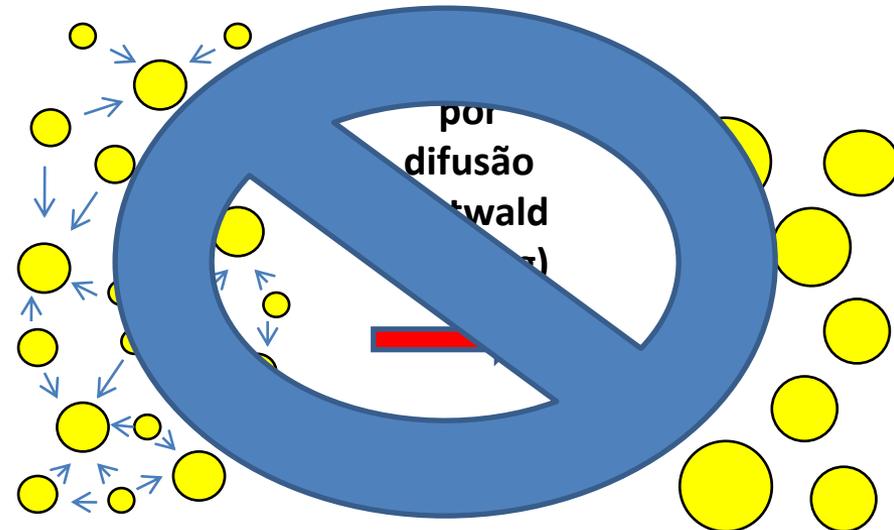
$D_1 < D_2$

\downarrow $P_{vap1} > P_{vap2}$ \uparrow

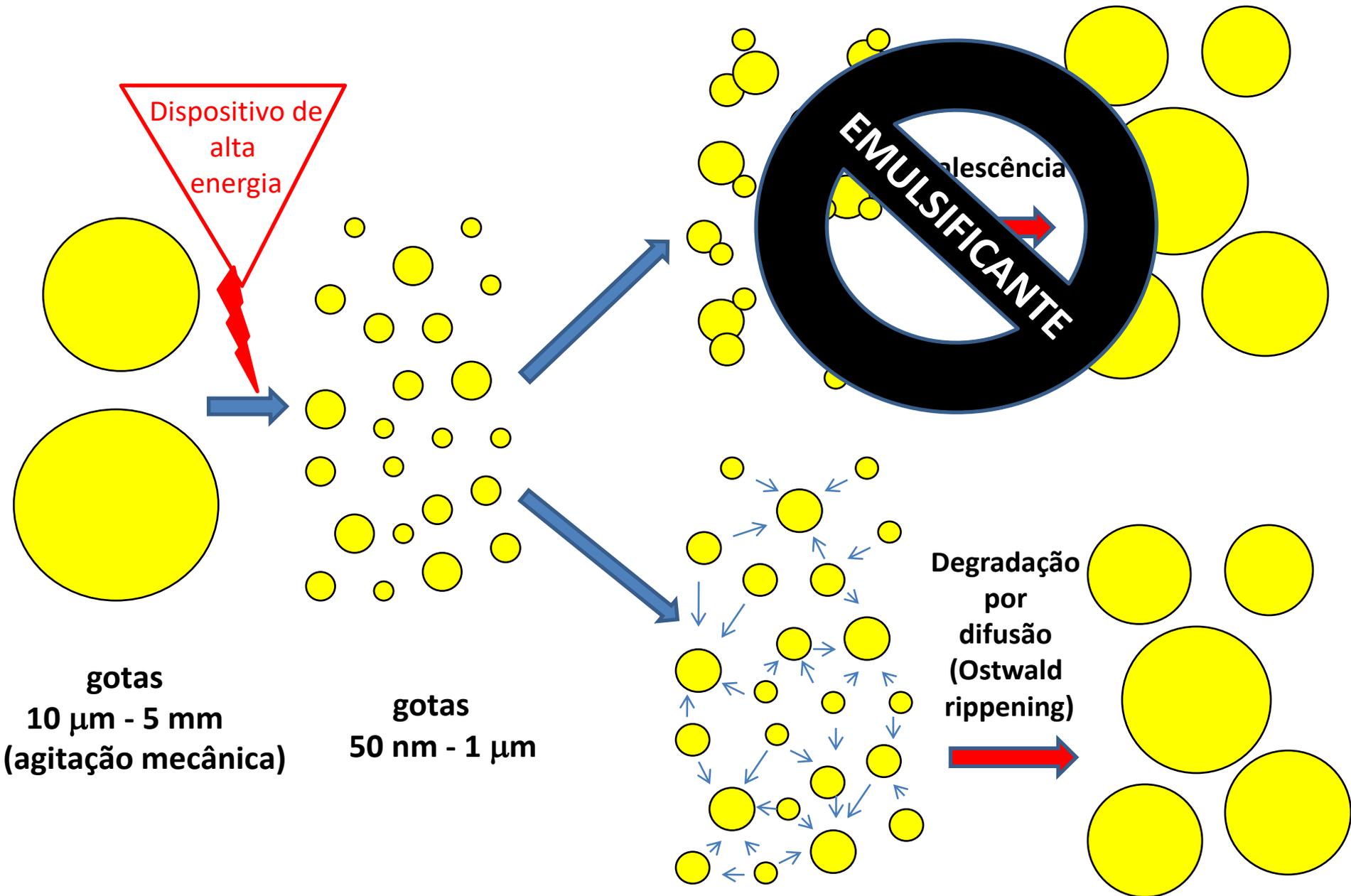
\downarrow $\mu_{mon1} > \mu_{mon2}$ \uparrow

$[M]_1 \rightleftharpoons [M]_{aq} \rightleftharpoons [M]_2$

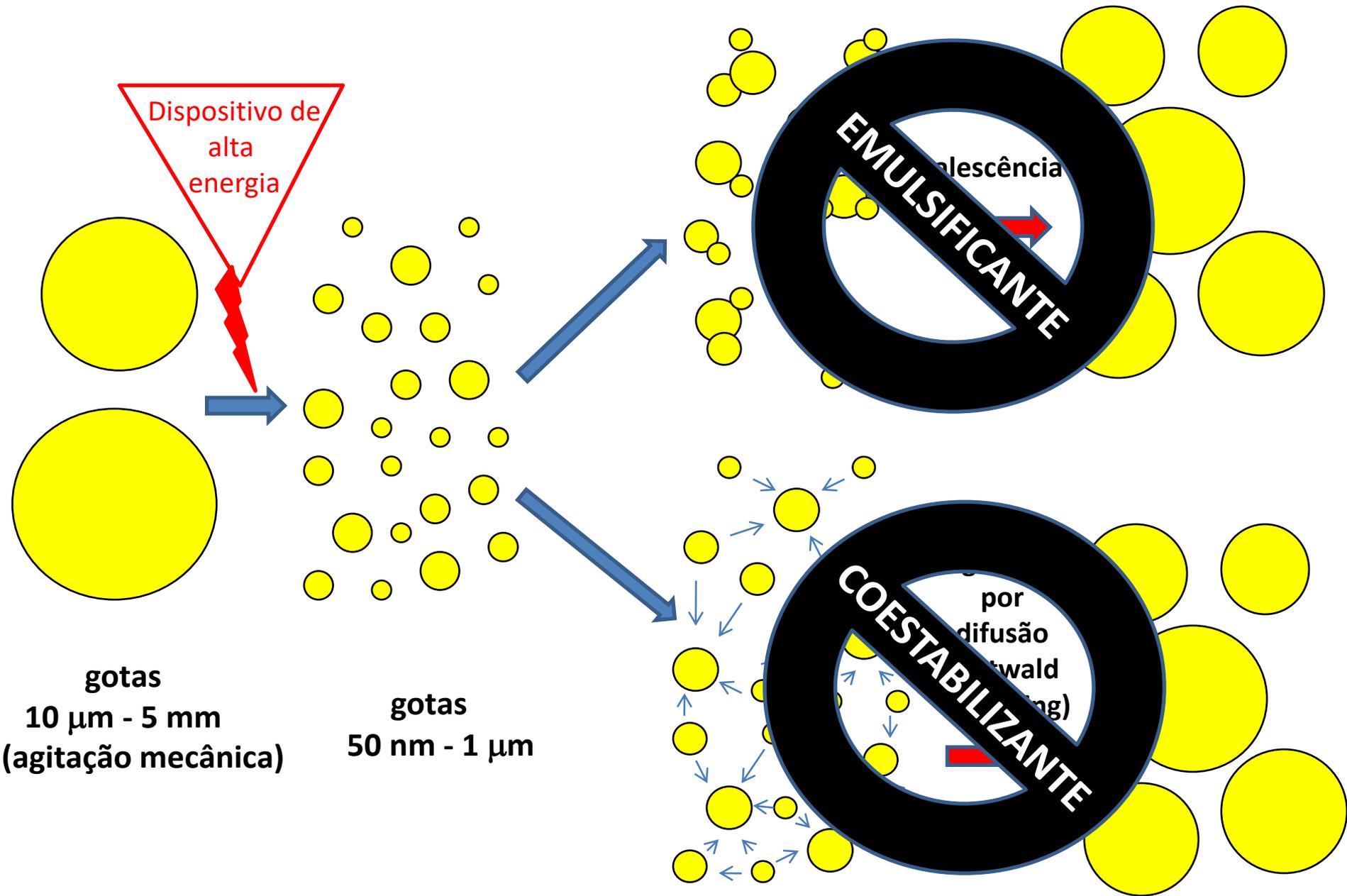
Acrescentar ao monômero um “soluto” (COESTABILIZANTE)
(bem mais insolúvel em água que o monômero)



Polimerização em miniemulsão ($dp \sim 50 \text{ nm} - 1 \mu\text{m}$)

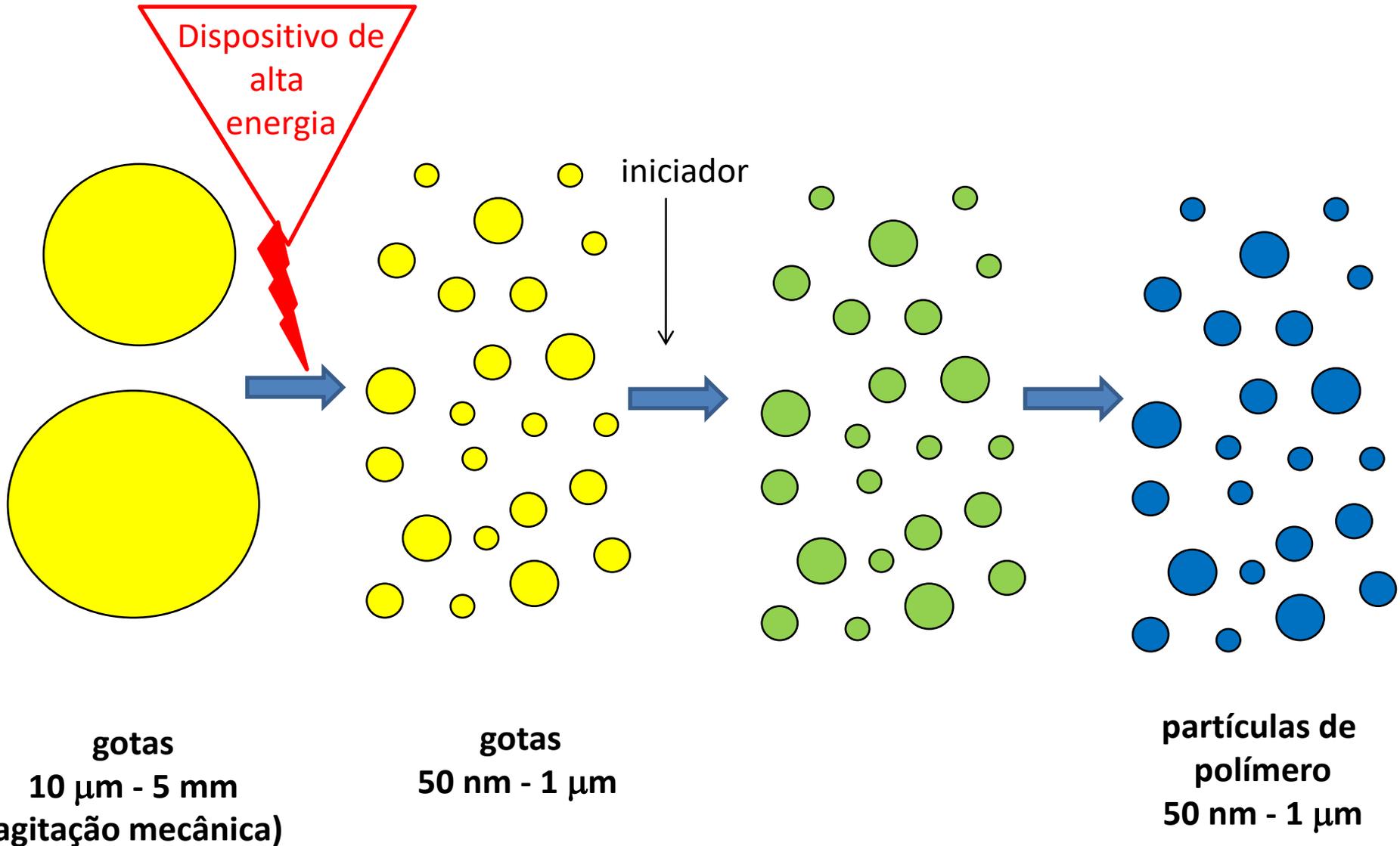


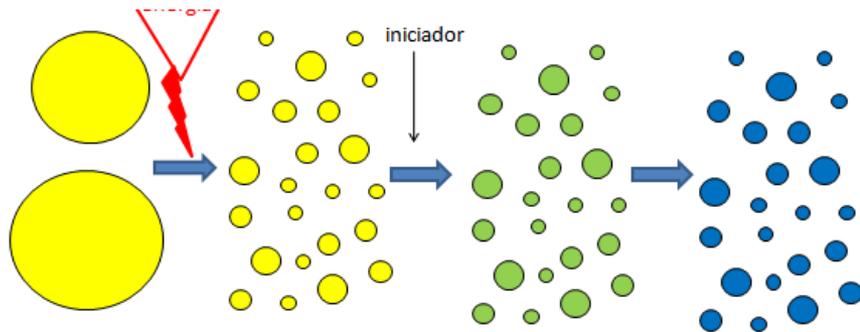
Polimerização em miniemulsão ($dp \sim 50 \text{ nm} - 1 \mu\text{m}$)



Polimerização em miniemulsão ($dp \sim 50 \text{ nm} - 1 \mu\text{m}$)

- iniciador solúvel no monômero ou na fase contínua





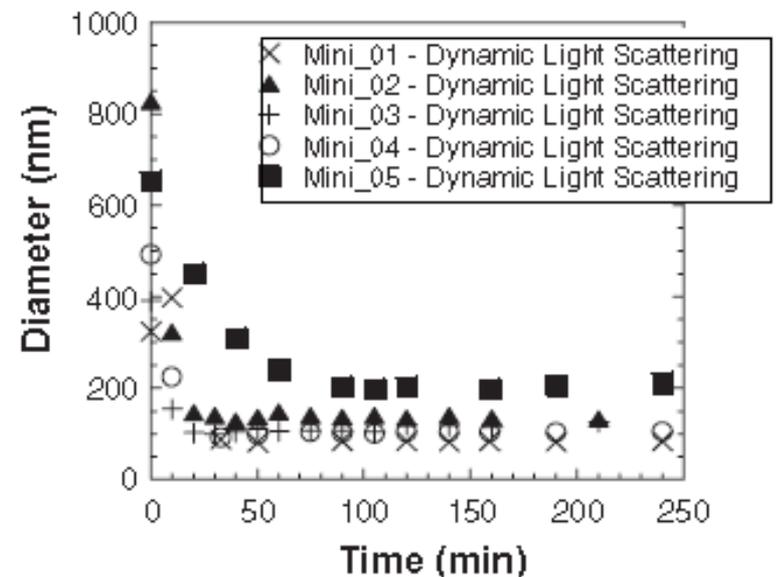
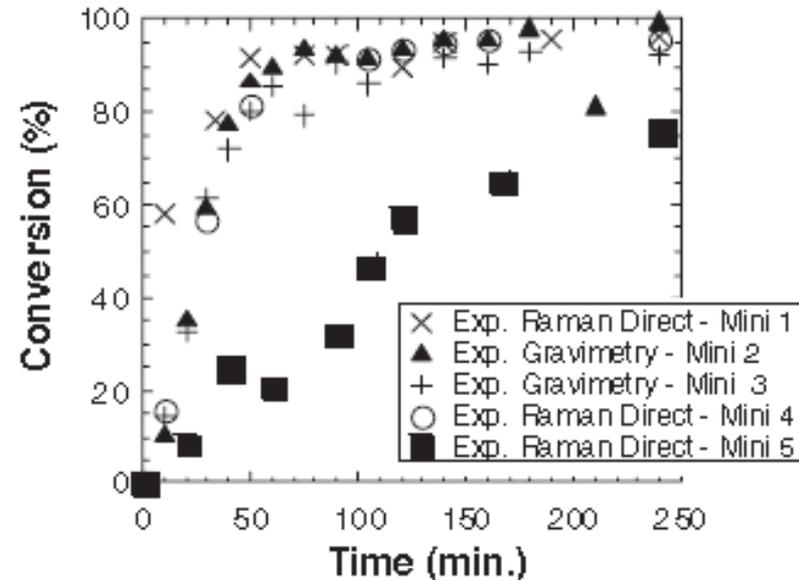
Polimerização em miniemulsão

Cópia (uma gota → uma partícula)

... nem sempre

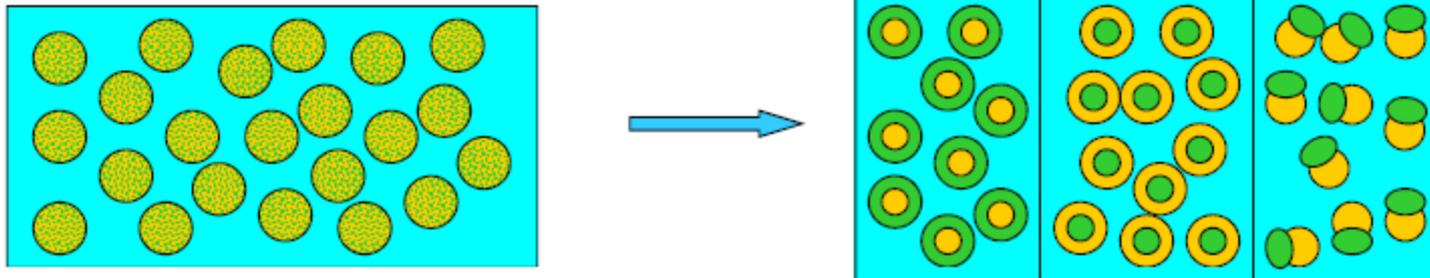
(podem ocorrer nucleações secundárias)

Sty, HD/PS, SLS, KPS, water



Ambrogi, Colmán & Giudici, MRE (2017)
<https://doi.org/10.1002/mren.201600013>.

Polimerização em miniemulsão

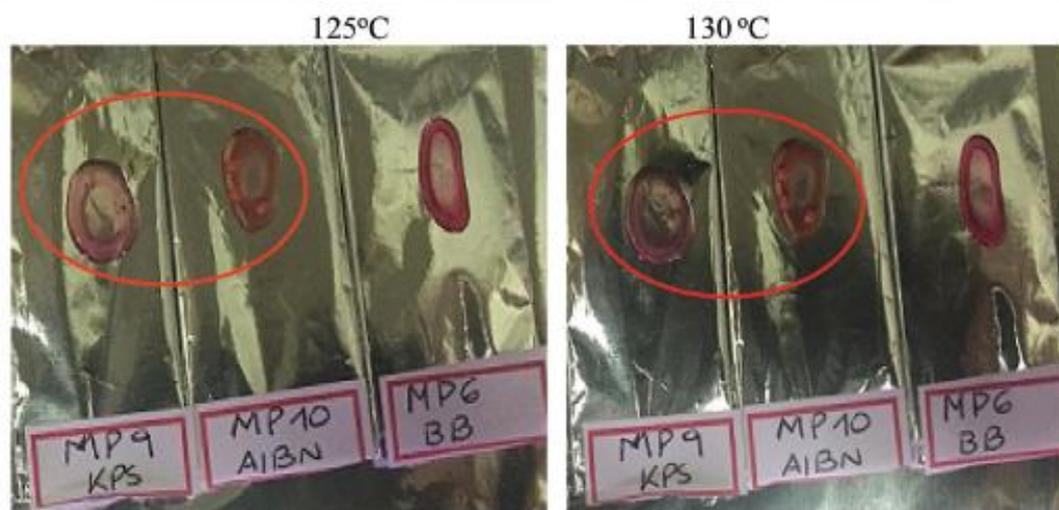
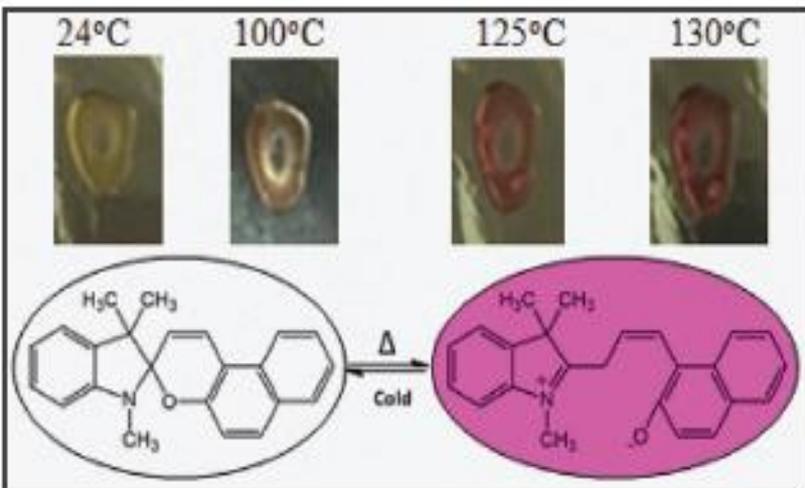


Partículas de polímero contendo
corante termocrômico

(para formar filmes de polímero
com propriedades termocrômicas)

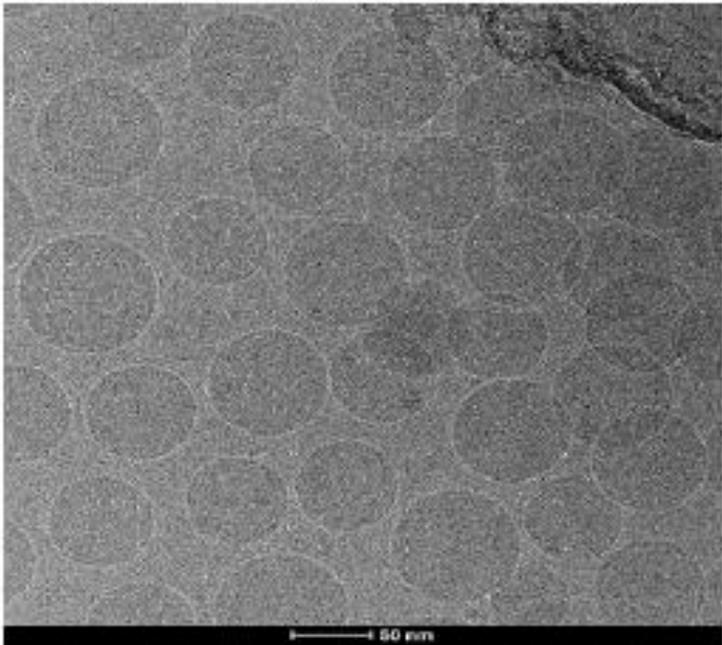
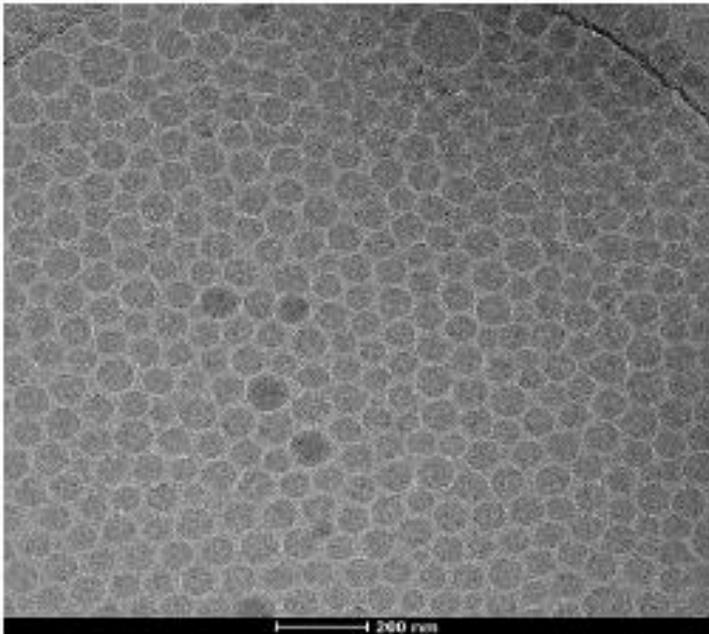
POLIMERIZAÇÃO EM MINIEMULSÃO

Poli-(S-co-BuA) e poli-(S-co-MMA) contendo pigmento termocrômico
(1,3,3-Trimethylindolino- β - naphthopyrylospira)

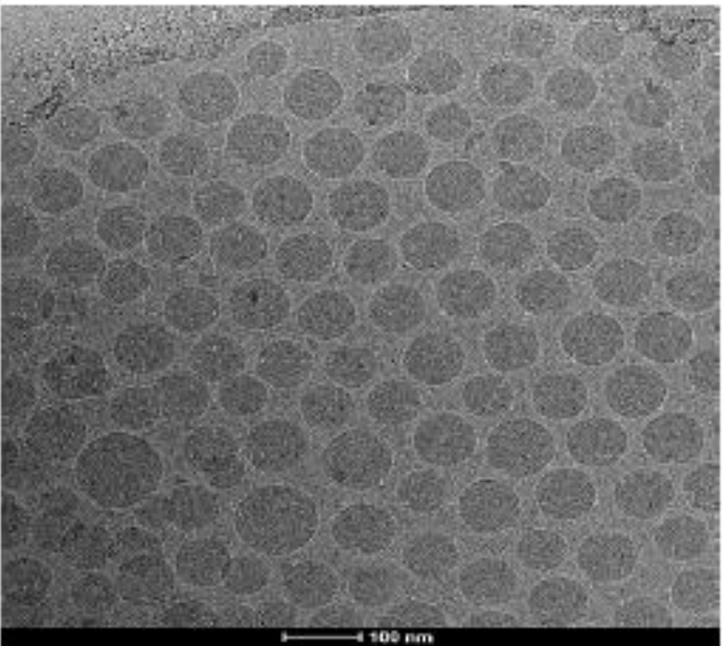
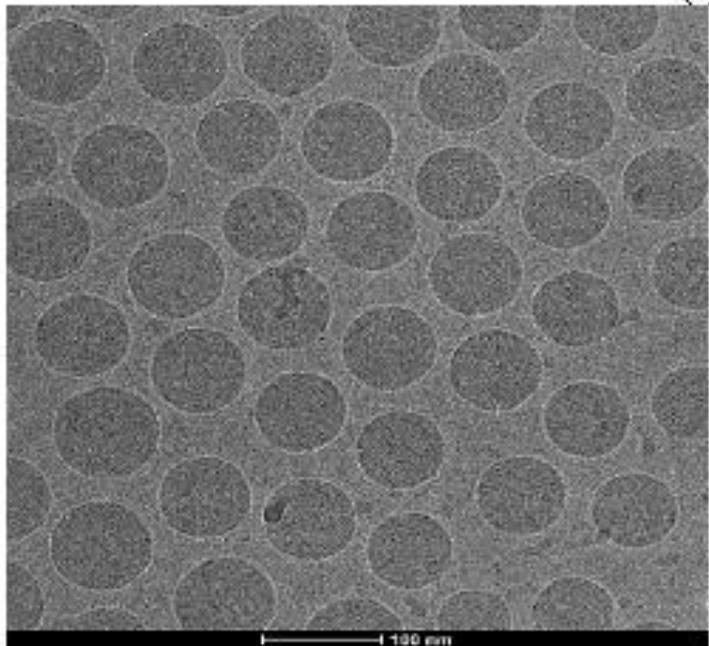


Colmán, García Valdez, George, Cunningham, Laqua & Giudici, *Macromol. React. Eng.* 13(3), 1900009 (2019)

Crio-TEM



(a)

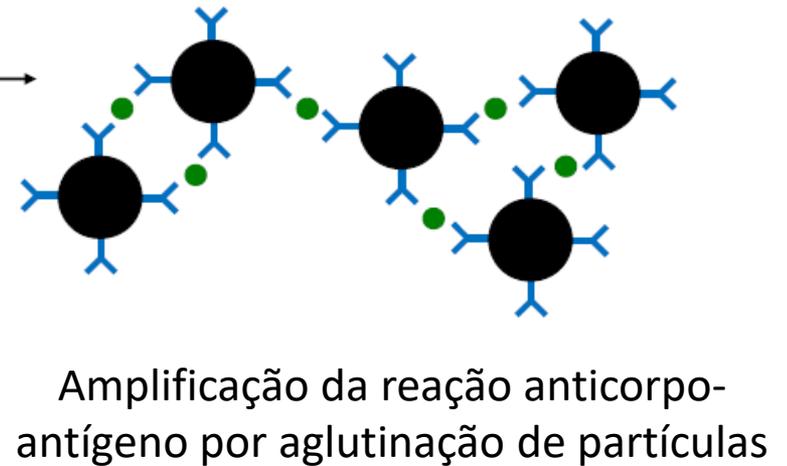
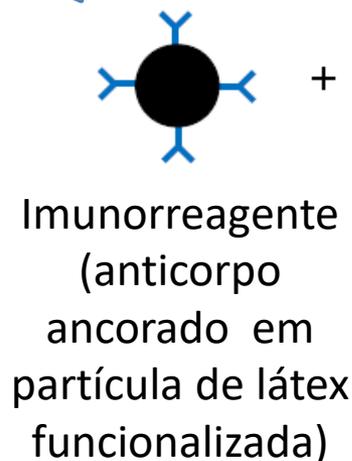


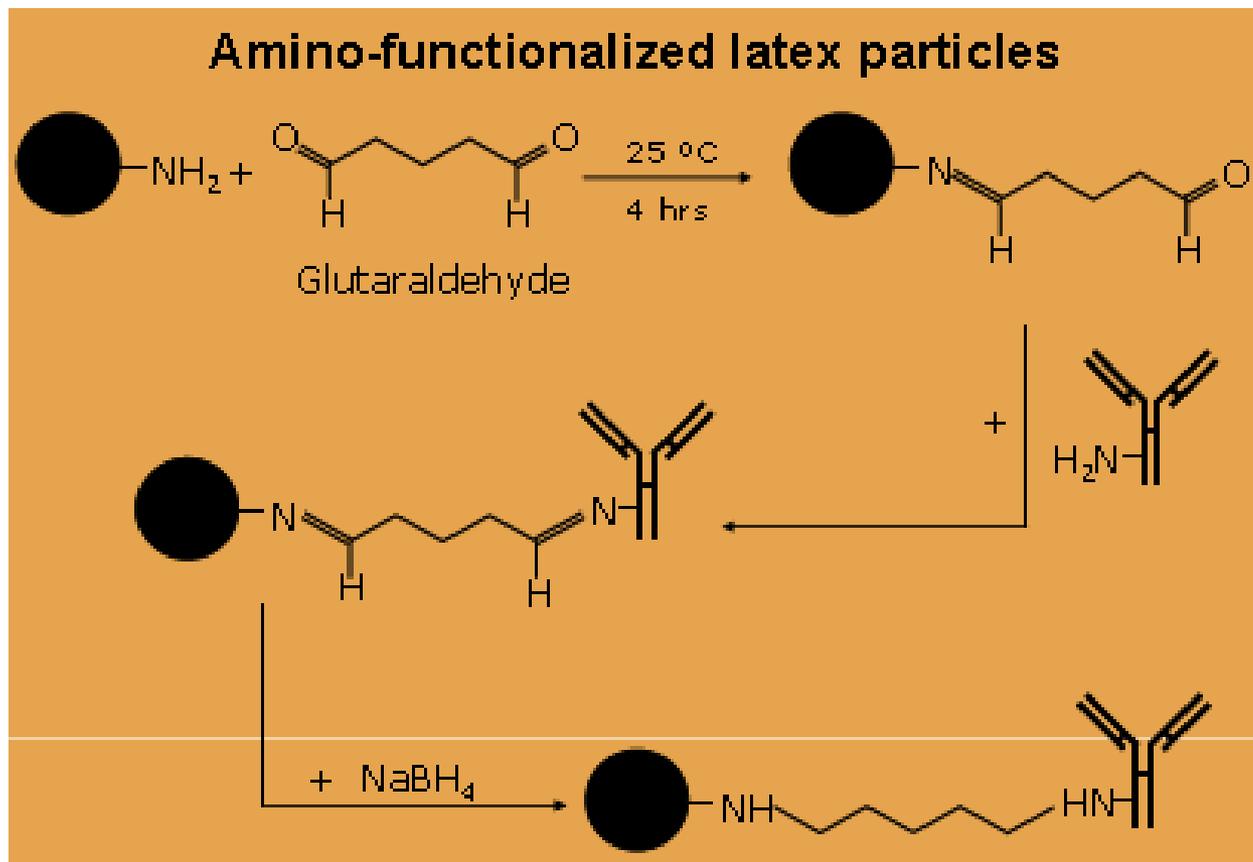
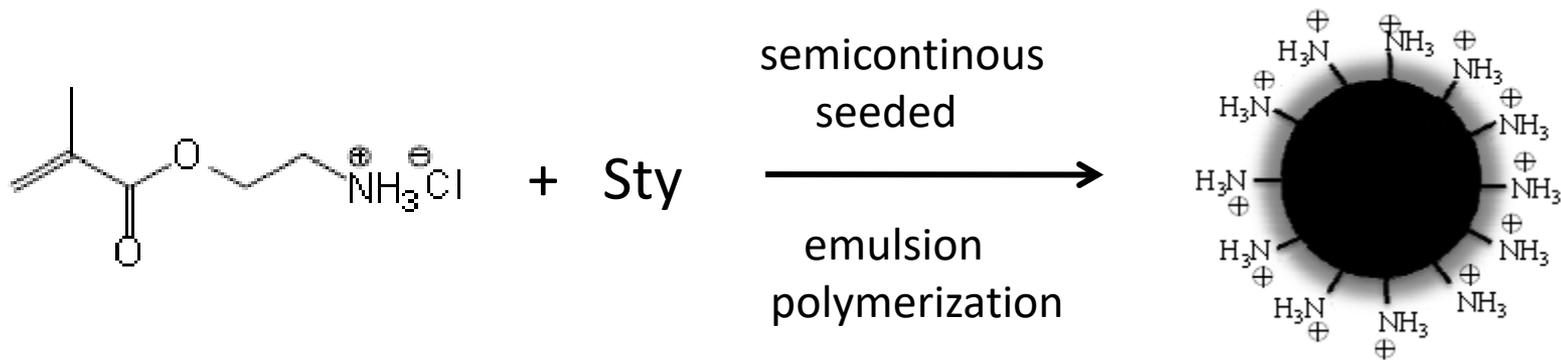
(b)

Kits para diagnósticos (imunoensaio)

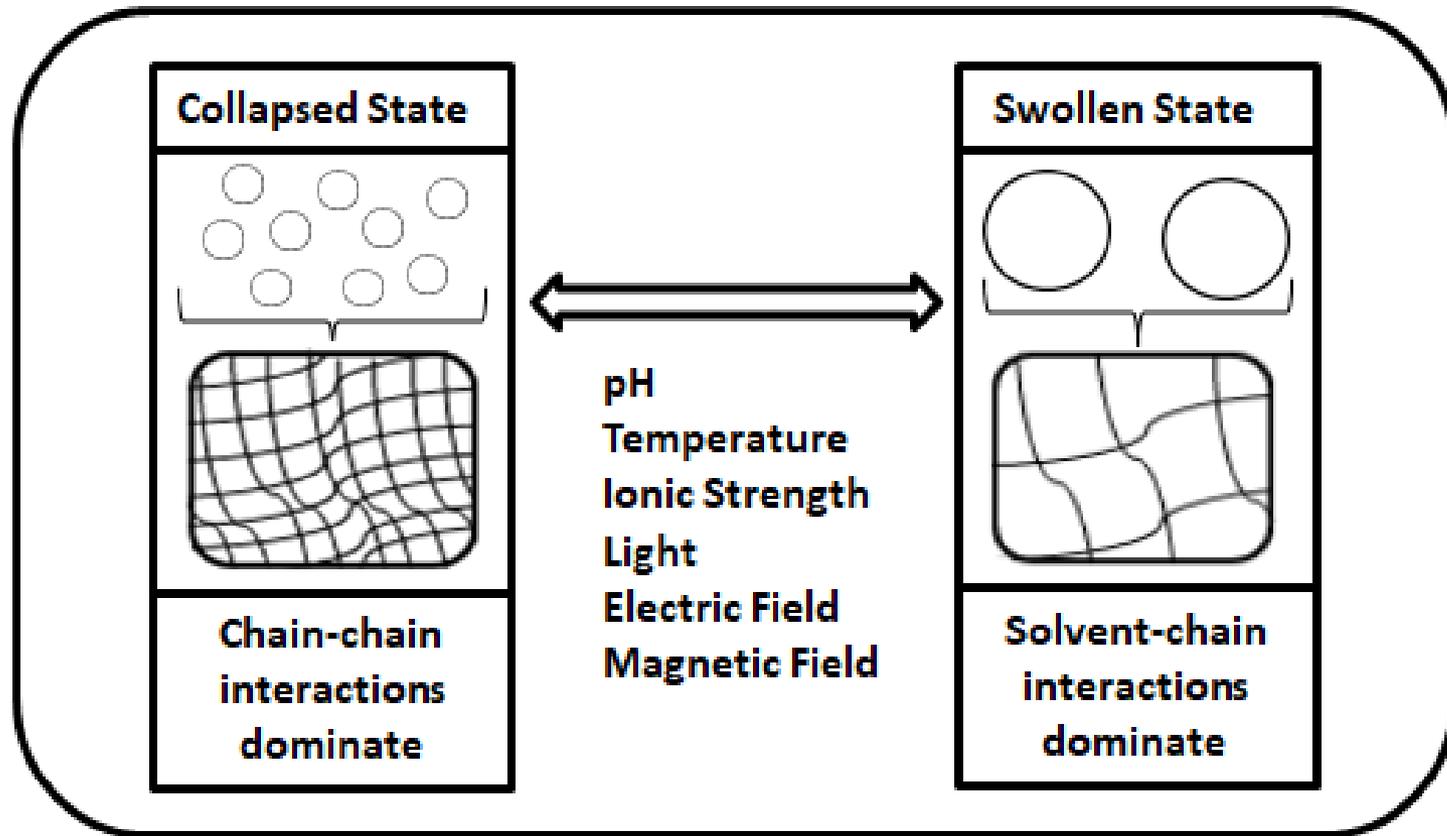
(ELISA - Enzyme-Linked Immunosorbent Assay)

50 – 500 nm
PSD Monodispersa
estabilidade coloidal
superfície funcionalizada



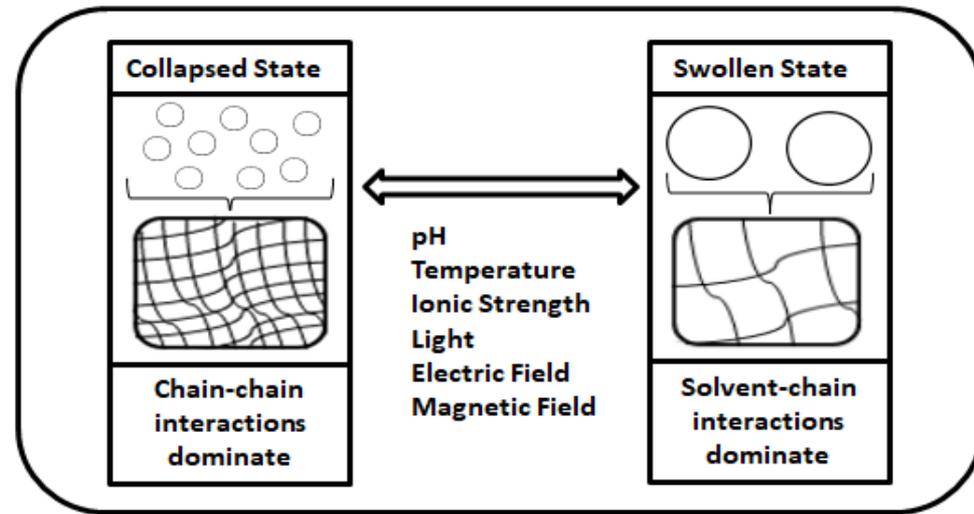


Polímeros responsivos a estímulos externos



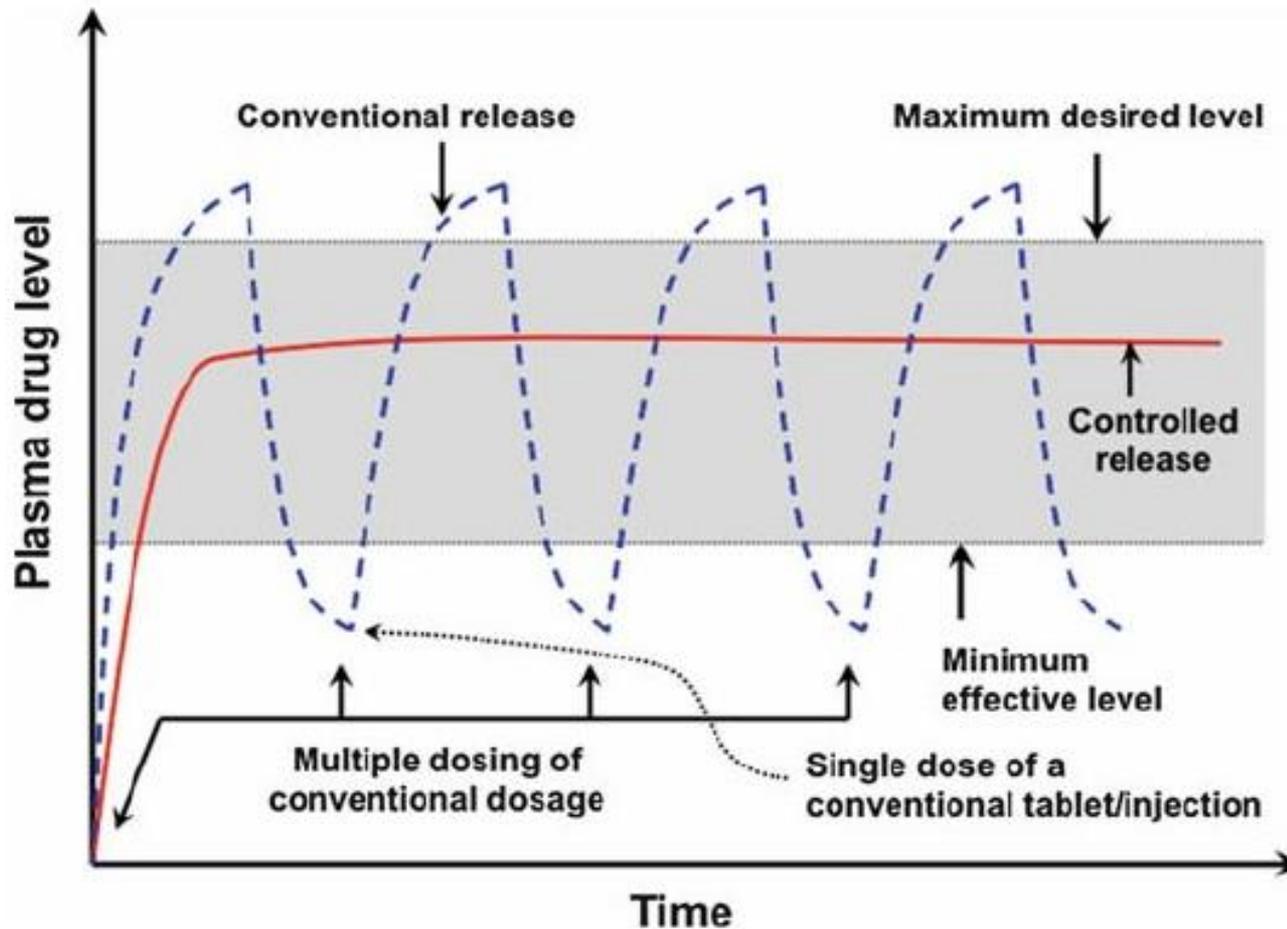
Natural polymers and synthetic monomers most often used in the synthesis of microgels.

Source: adapted from Lin and Metters (2006)



Synthetic monomers	Natural polymer
Hydroxyethyl methacrylate (HEMA)	Chitosan
N-(2-hydroxypropyl) methacrylate (HPMA)	Alginate
N-vinyl-2-pyrrolidone (NVP)	Fibrin
N-isopropylacrylamide (NIPAM)	Collagen
N-vinylcaprolactam (NVCL)	Gelatin
Vinyl acetate (VAc)	Hyaluronic acid
Acrylic Acid (AA)	Dextran
Methacrylic acid (MAA)	
Ethylene glycol acrylate/methacrylate (EGA/EGMA)	
Ethylene glycol diacrylate/dimethacrylate (PEGDA/PEGDMA)	

Esmar Faben Souza,
Tese de Doutorado,
USP, 2019.



Partículas de polímero
hidrogel (sensível a pH)
para liberação controlada de fármacos

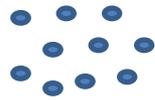
(insulina via oral)



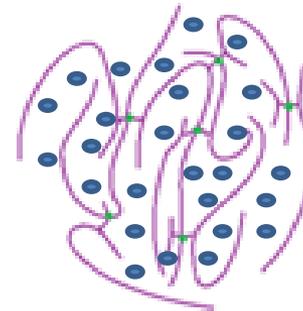
Polímero reticulado
(ligações cruzadas)



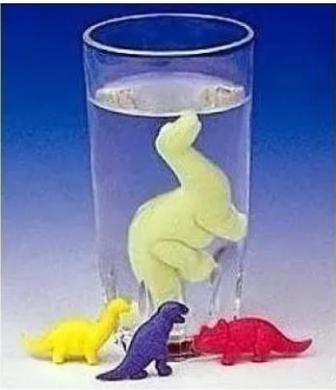
gel



solvente

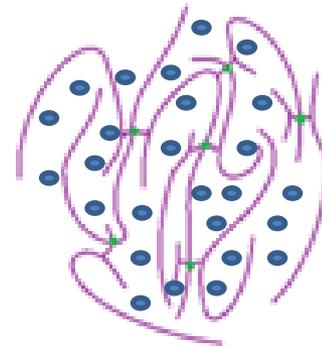
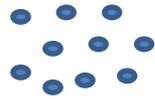


gel "inchado" (intumescido)





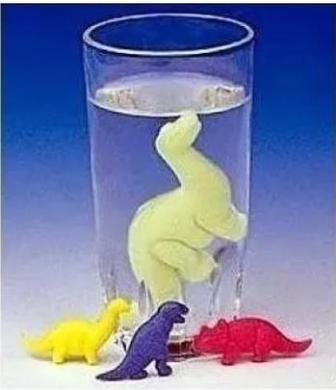
+



gel

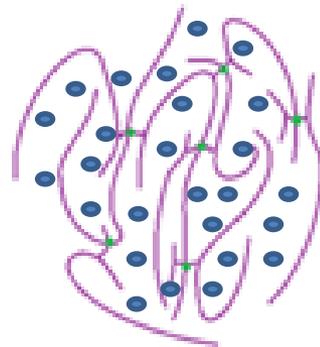
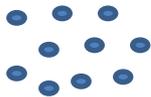
solvente

gel "inchado" (intumescido)





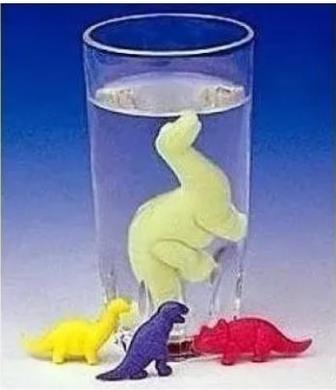
+



gel

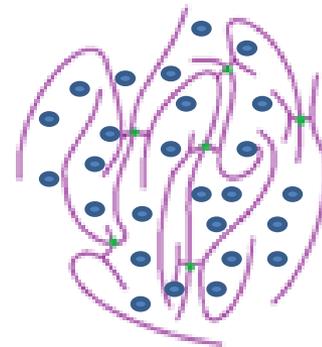
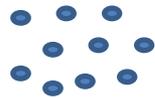
solvente

gel "inchado" (intumescido)





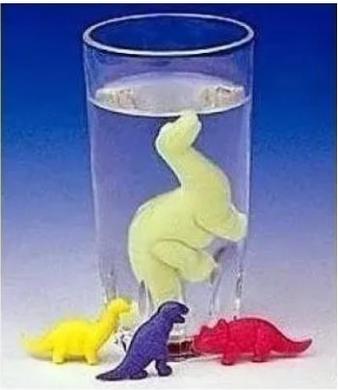
+



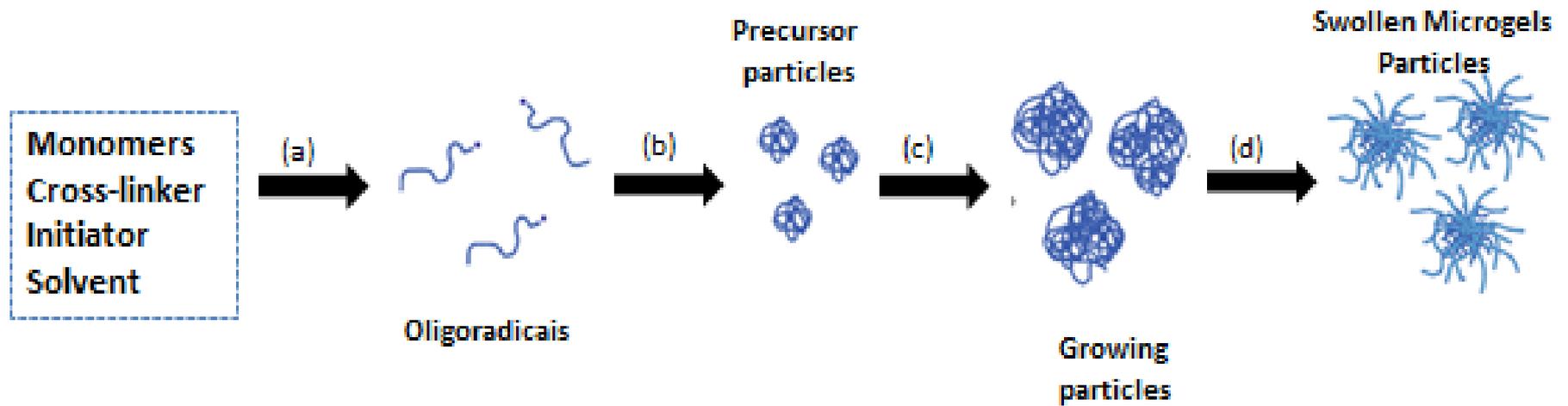
gel

solvente

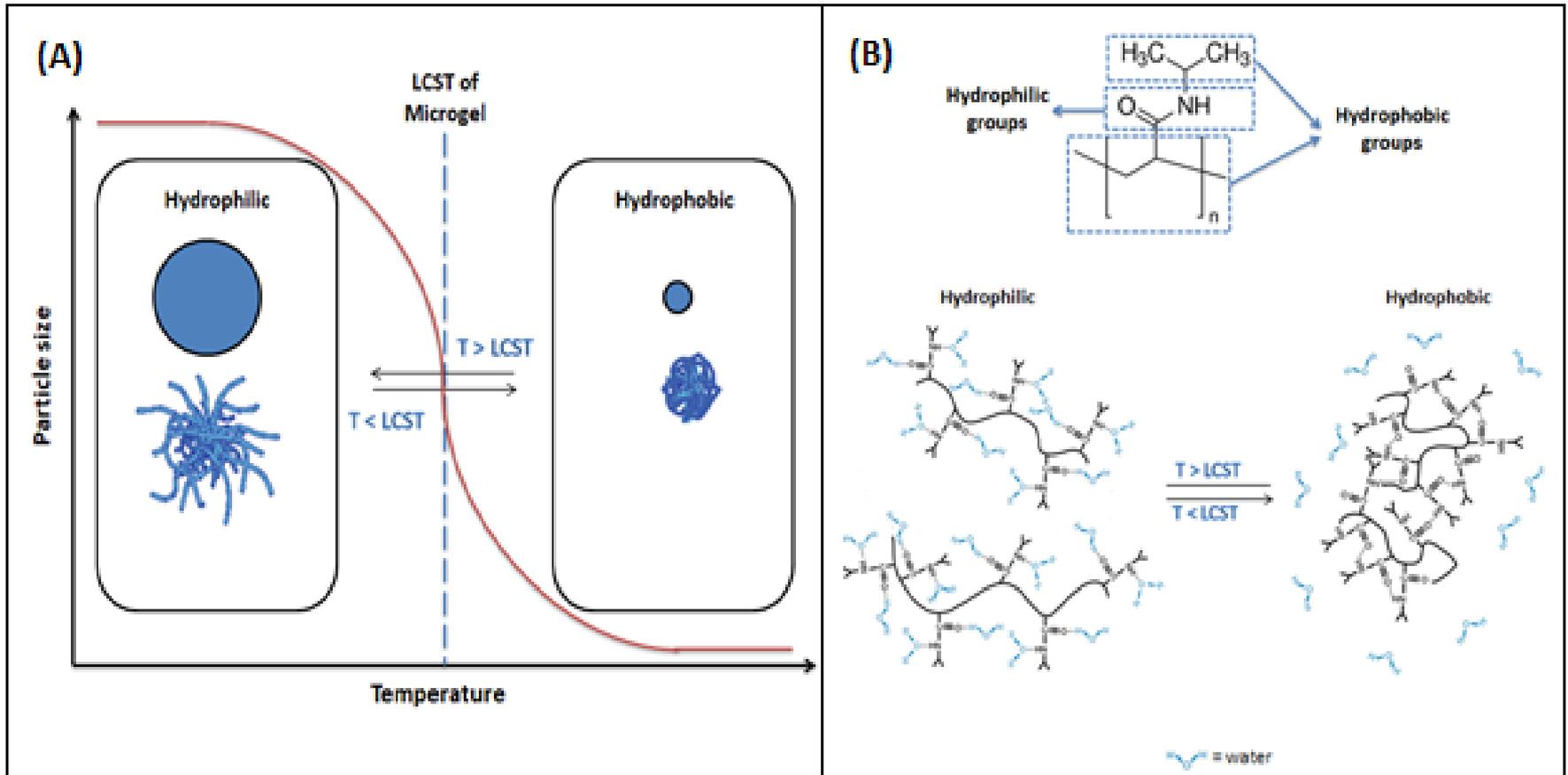
gel "inchado" (intumescido)



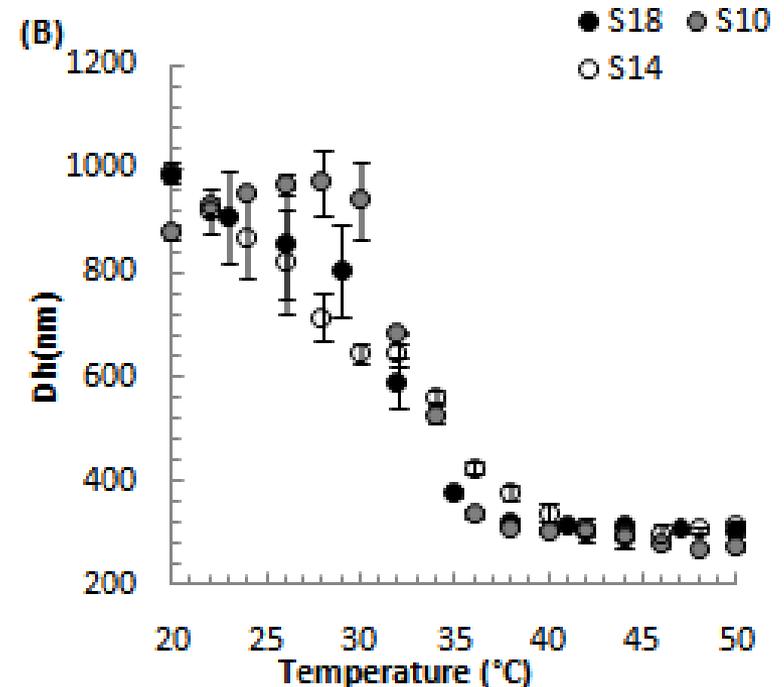
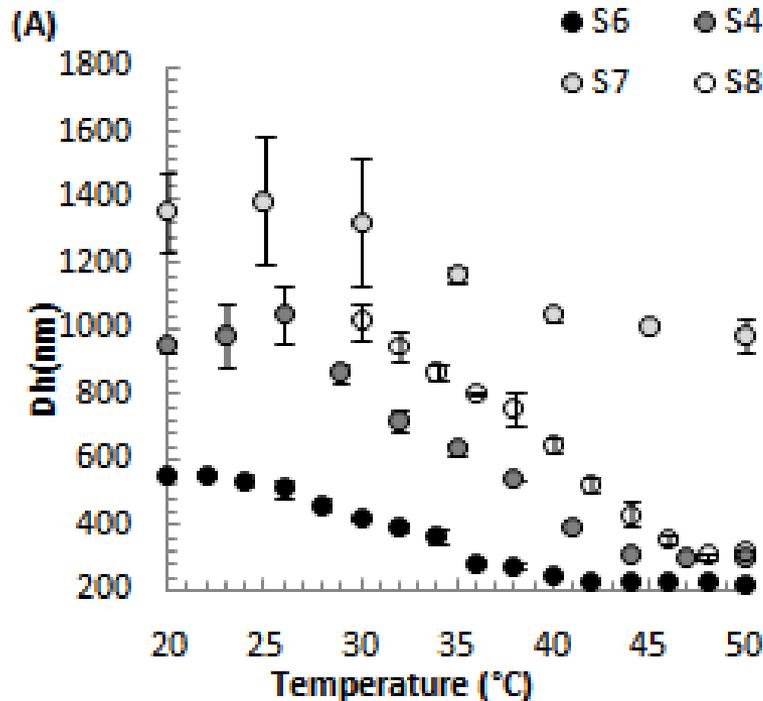
Precipitation polymerization



Polímeros responsivos a T (microgéis com p-NIPAM)



p-NIPAM-co-AA (T-responsive)



Average particle size variation in water as a function of temperature and VPTT values.

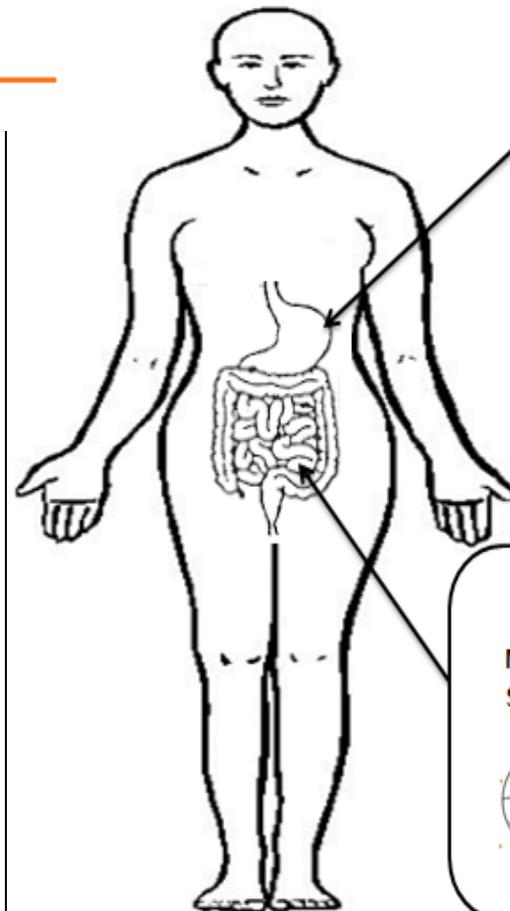
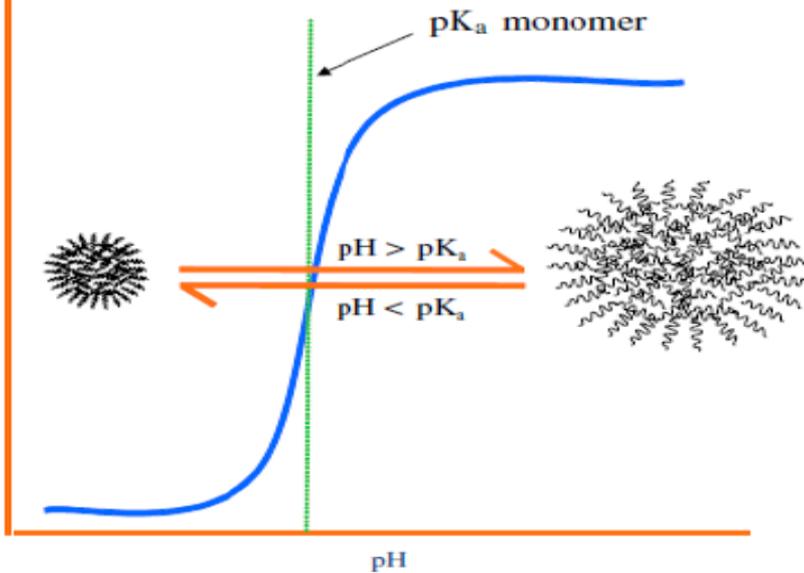
Samples with variation in AA concentration in mmol.L⁻¹:

(A) S6 (0), S4 (27), S7 (54) and S8 (108);

(B) S18 (10), S10 (20) and S14 (40).

Polímeros responsivos ao pH (microgeis com p-AA)

Particle size



Stomach (pH = 1-2.5)

Network Collapse



- Low drug release rate
- Drug protection against acid-catalysed hydrolysis

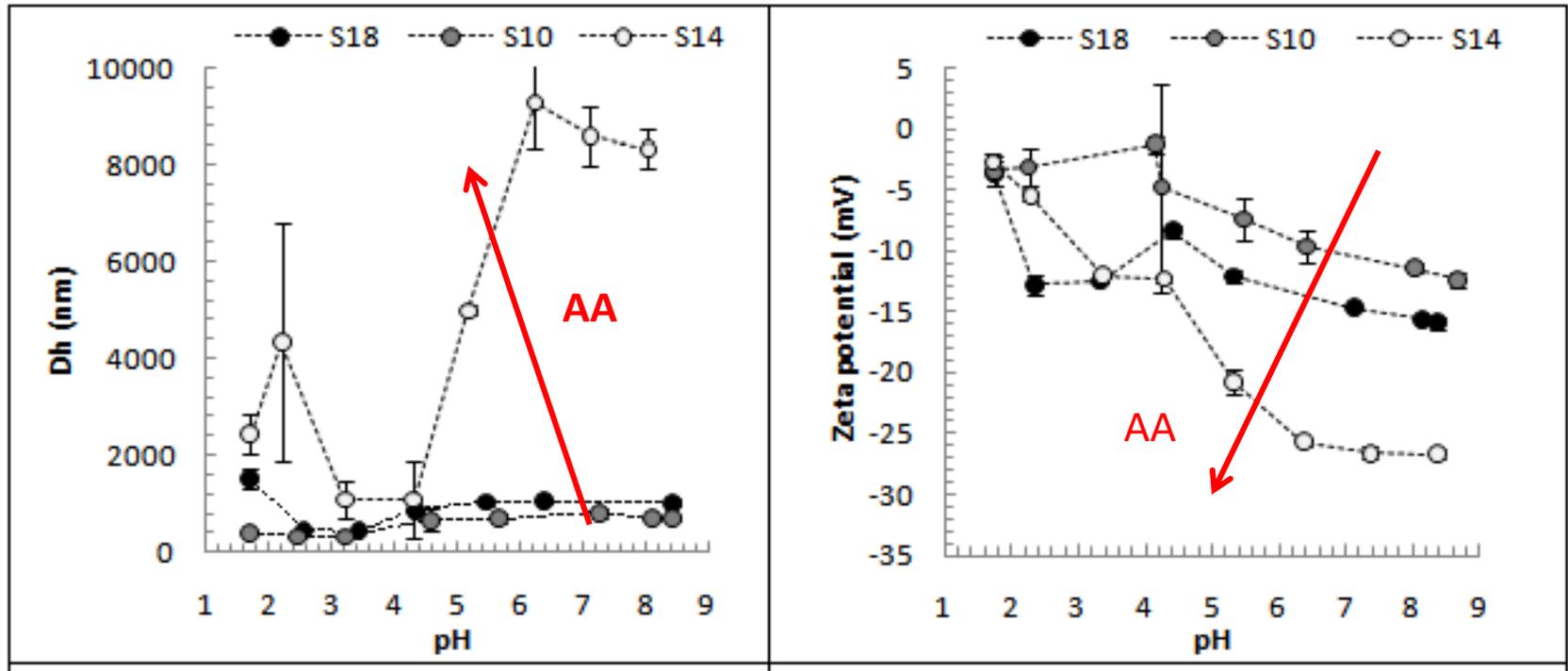
Small Intestine (pH = 6.6-7.5)

Network Swelling



- High drug release rate
- More effectively absorption
- More stable against hydrolytic degradation

p-NIPAM-co-AA (pH-responsive)



Evaluation of the influence of AA concentration in the average particle size and zeta potential of poly(NIPAM-co-AA) at different pHs.

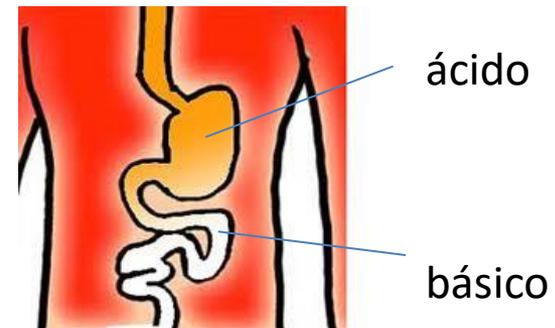
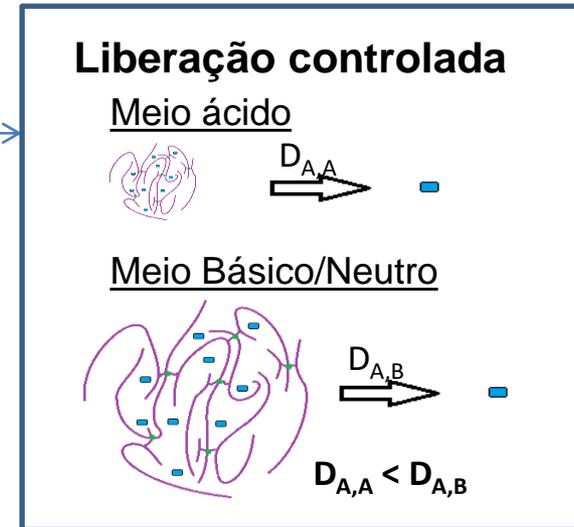
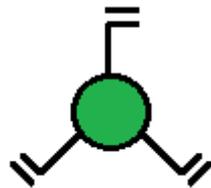
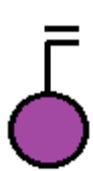
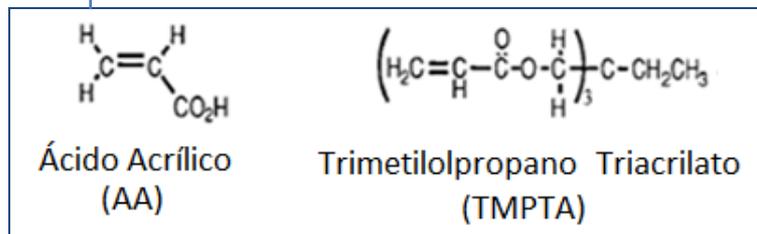
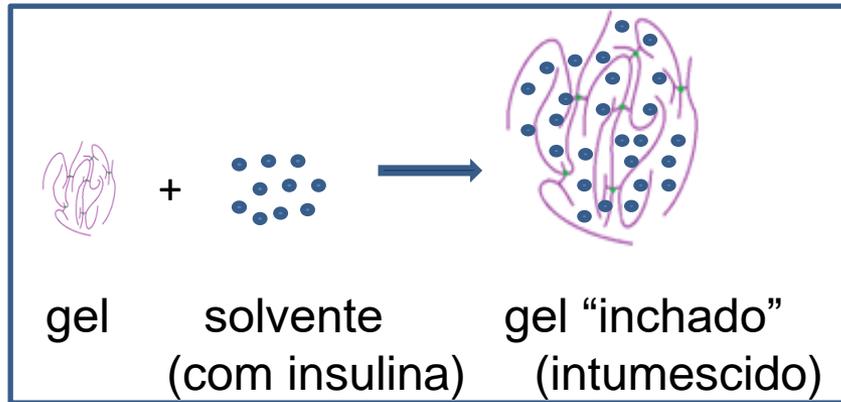
Samples formulation:

S18, S10 and S14 have the AA concentration 10, 20, 40 mmol.L⁻¹, respectively.

All the samples have MBA and KPS concentration equal to 2 and 5 mmol.L⁻¹, respectively.

POLIMERIZAÇÃO EM MINIEMULSÃO

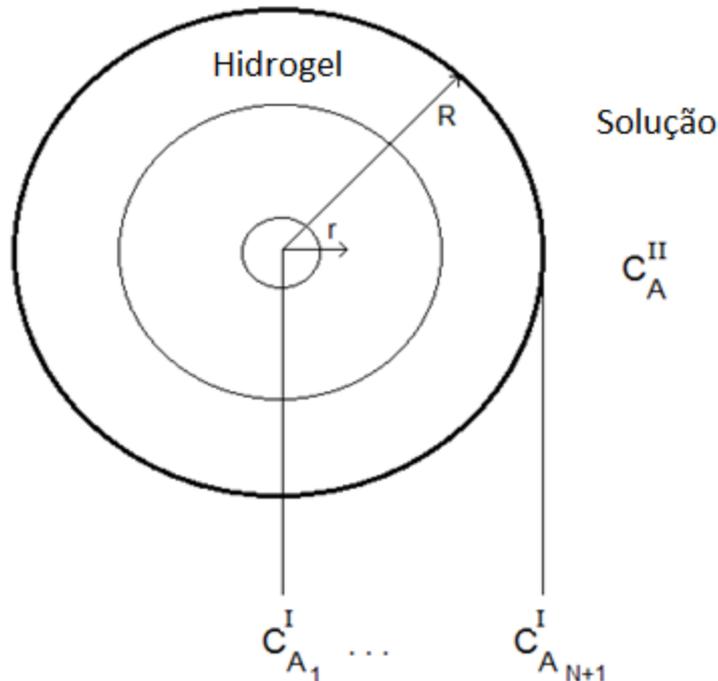
Gel de poli-(AA-co-TMPTA) sensível a pH para liberação controlada de insulina



Raymundi, Aguiar, Souza, Sato, & Giudici (2016). Controlled release of insulin through hydrogels of (acrylic acid)/trimethylolpropane triacrylate. *Heat and Mass Transfer*, 52(10), 2193-2201.

Modelagem Matemática

Modelo para a liberação controlada de insulina:



Balço diferencial de massa

Dentro do hidrogel (Fase I)

$$\frac{\partial C_A^I}{\partial t} = D_A \left[\frac{\partial^2 C_A^I}{\partial r^2} + \frac{1}{r} \frac{\partial C_A^I}{\partial r} \right]$$

$$\left. \frac{\partial C_A^I}{\partial r} \right|_{r=0} = 0$$

$$-D_A \left. \frac{\partial C_A^I}{\partial r} \right|_{r=R} = k_c \left(\frac{C_A^I|_{r=R}}{K_p} - C_A^{II} \right)$$

Solução pelo método das linhas

Fora do hidrogel (Fase II)

$$\frac{dC_A^{II}}{dt} = k_c \left(\frac{C_{A,N+1}^I}{K_p} - C_A^{II} \right) a_v \frac{V^I}{V^{II}}$$

Hipóteses:

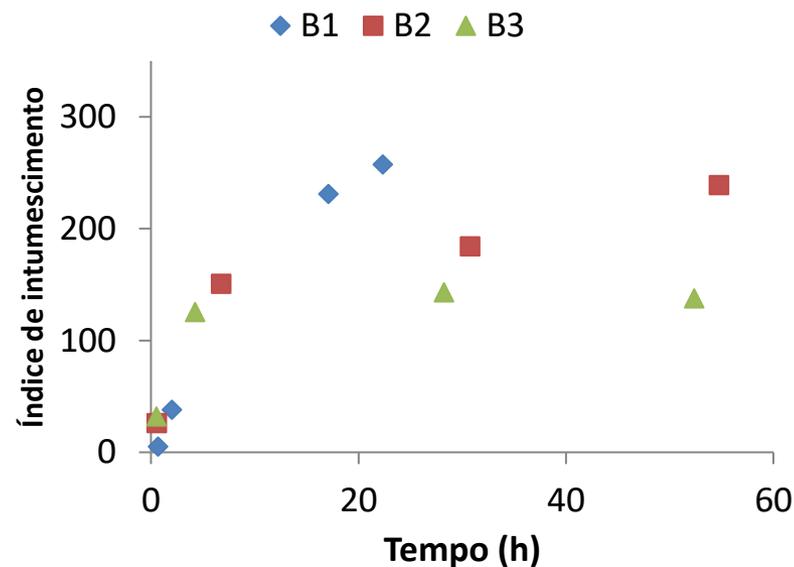
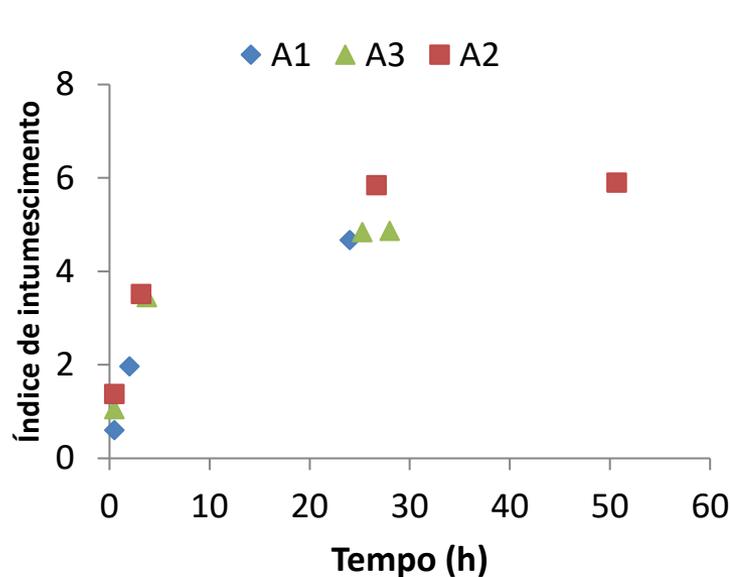
- Partícula esférica;
- Não há reação química;
- Densidades e difusividades constantes.

Resultados

Ensaio realizados

Hidrogel	Y_C (%)	Ensaio em solução	
		ácida	básica
HG1	0,01	A1	B1
HG2	0,15	A2	B2
HG3	0,30	A3	B3

Y_C : Teor de TMPTA usado na polimerização.



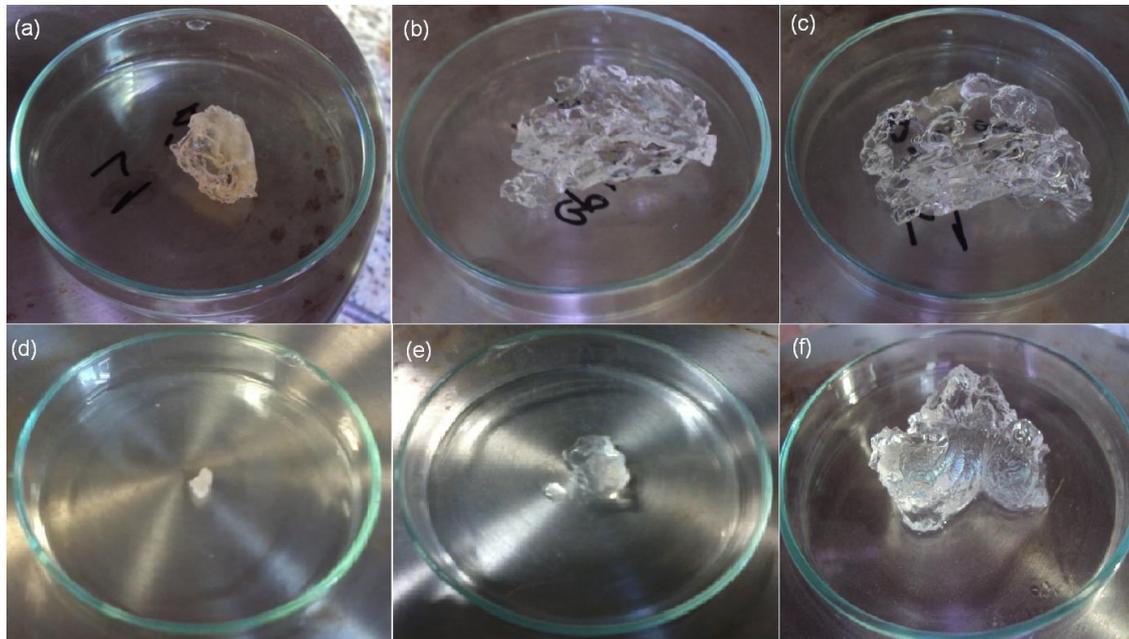
Curvas de índice de intumescimento.

Resultados

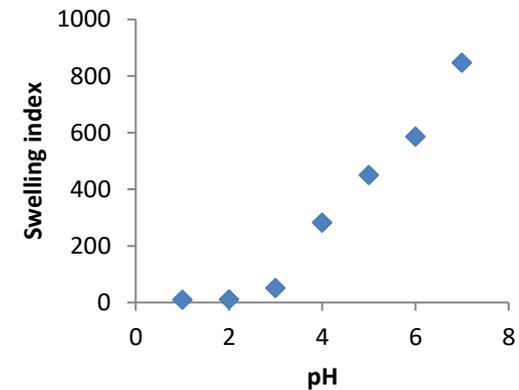
Experimentos de intumescimento.

Pictures of HG1 swollen in acid and basic media at different swelling times.
The times and weights are the following:

for acid medium (a) 0h (1.33g), (b) 24h (7.59g), (c) 72h (9.93g);



for basic medium: (d) 0h (0.0264g), (e) 2h (1.03g), (f) 24h (6.83g).

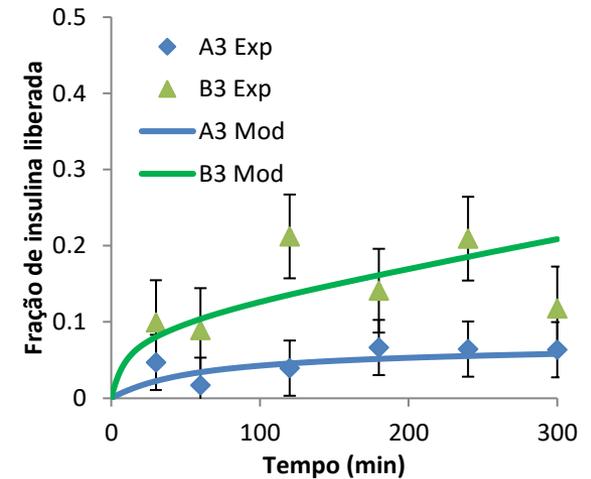
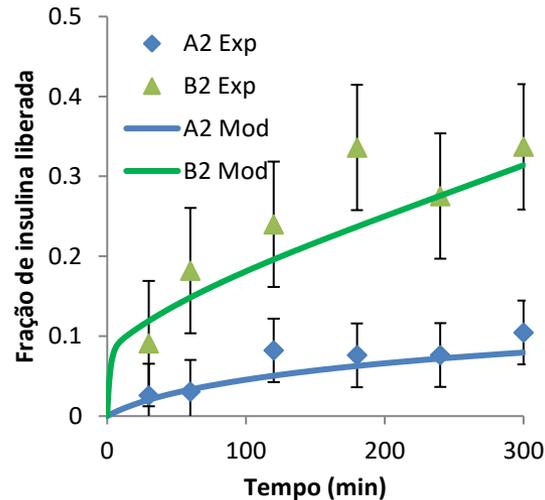
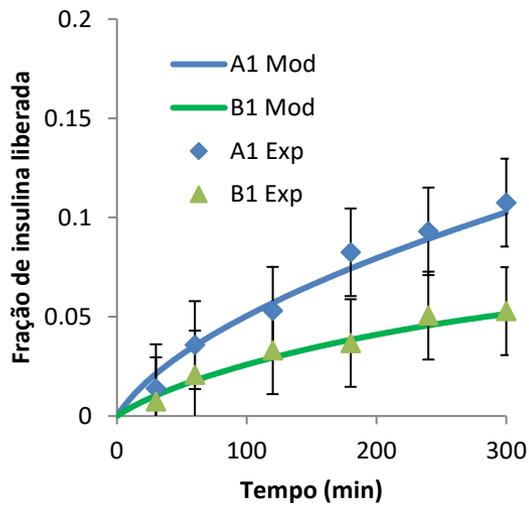


Resultados

Ensaio realizados

Hidrogel	Y_C (%)	em solução ácida	em solução básica
HG1	0,01	A1	B1
HG2	0,15	A2	B2
HG3	0,30	A3	B3

Y_C : Teor de TMPTA usado na polimerização.



Resultados experimentais e de simulação dos ensaios de liberação controlada

Parâmetros ajustados

	A1	A2	A3	B1	B2	B3
D_A (cm ² /s)	$1,0 \times 10^{-6}$	$7,0 \times 10^{-7}$	$6,0 \times 10^{-7}$	$1,3 \times 10^{-6}$	$9,0 \times 10^{-7}$	$8,0 \times 10^{-7}$
Kp		43,5			26,5	
k_c (cm/s)		$2,0 \times 10^{-4}$			$2,0 \times 10^{-4}$	

Redução do teor de
monômero residual
e VOCs
de polímeros

(“tinta sem cheiro”)

Redução de monômero residual e VOCs de polímeros

- **Desvolatilização/stripping**

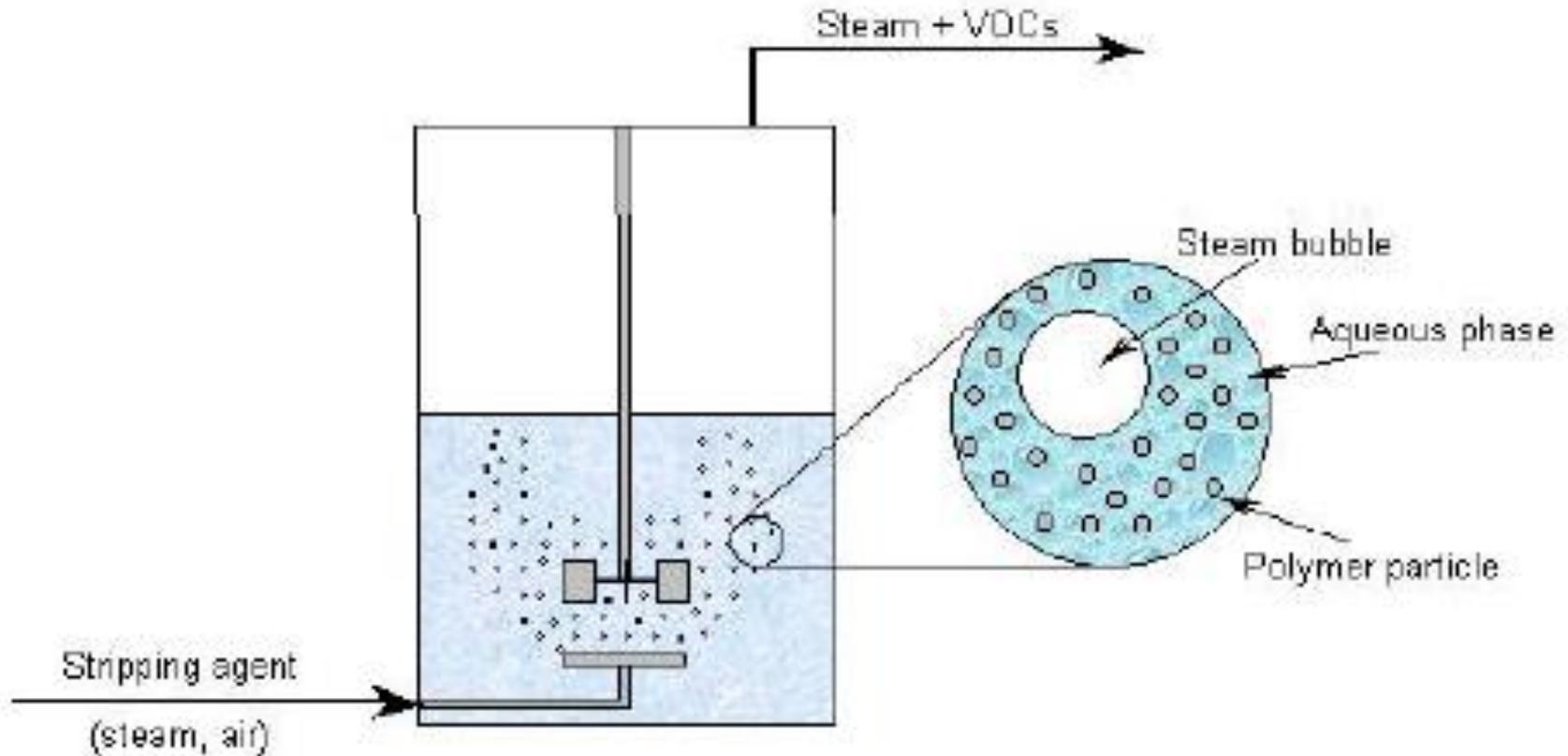
- separação física
- borbulhamento de vapor ou ar quente

- **Pós-polimerização**

- reação química
- adição de mais iniciador, aumento de temperatura

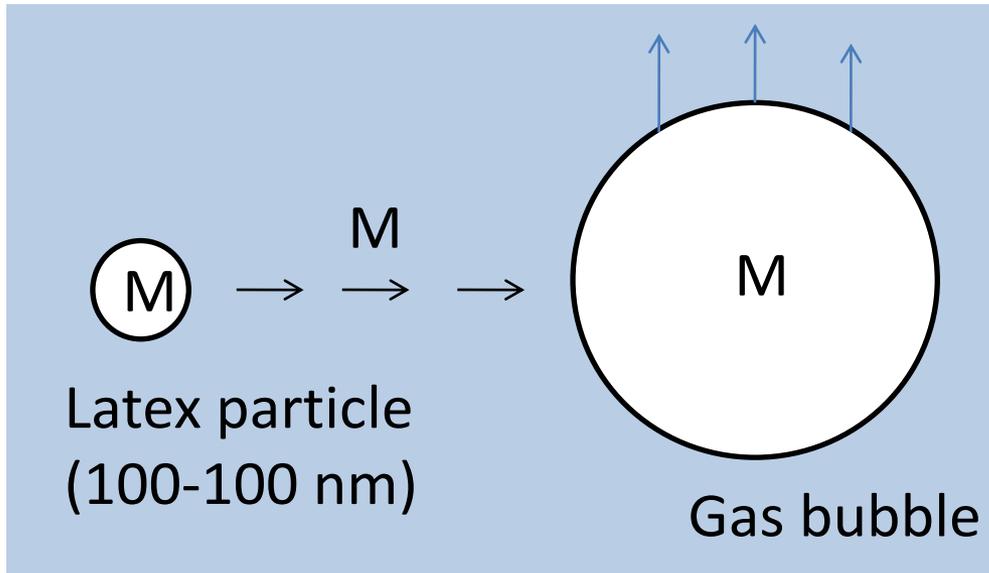
Redução de monômero residual e VOCs de polímeros

Desvolatilização (Stripping)



Redução de monômero residual e VOCs de polímeros

Desvolatilização (Stripping)



Menos eficiente para
monômeros
hidrofóbicos
e/ou
pouco voláteis

- (1) Difusão na partícula
- (2) Transf. massa partícula-água
- (3) Difusão/TM na fase aquosa
- (4) Transf. massa água-bolha

Tamanho das partículas

Agitação

Tamanho da bolha

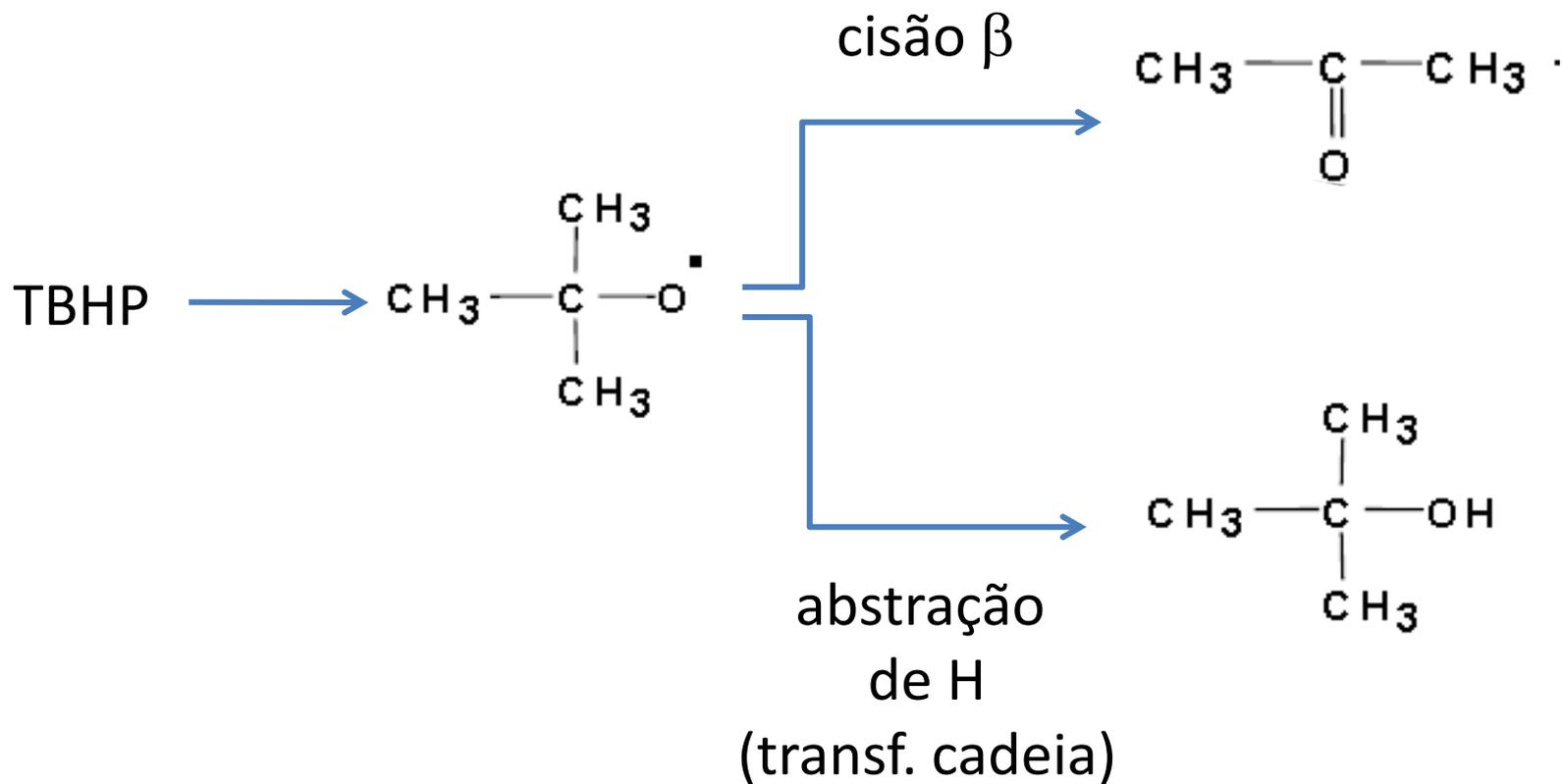
Redução de monômero residual e VOCs de polímeros

Pós-polimerização (cooking)

- **Iniciadores**

- **Orgânicos (geram radicais dentro das partículas, mas podem gerar outros VOCs)**
- **Solúveis em água (pares redox, geração de radicais bem rápida)**
 - **Oxidante**
 - radicais hidrofóbicos TBHP
 - radicais hidrofílicos KPS, H_2O_2
 - **Redutor**
 - Ácido ascórbico, açúcares, metabissulfito, ácido tartárico
- **Radicais devem ser gerados onde está o monômero**
hidrofobicidade TBHP > H_2O_2 > KPS

Formação de novos VOCs (exemplo)



Redução de monômero residual e VOCs de polímeros

- **Desvolatilização/stripping (separação física)**
 - Todos VOCs são reduzidos
 - Desestabilização da emulsão (coagulação, espuma)
 - Necessário equipamento adicional
 - Tratamento do efluente gasoso
- **Pós-polimerização (reação química)**
 - Não precisa de equipamento adicional
 - Apenas reduz monômero residual (não outros VOCs)
 - Pode produzir outros VOCs
 - Pode desestabilizar a emulsão
 - Pode alterar as características do polímero

Redução do teor de monômero residual de polímeros em emulsões (“tinta sem cheiro”)

via intensificação da reação ao seu final

aumento de T

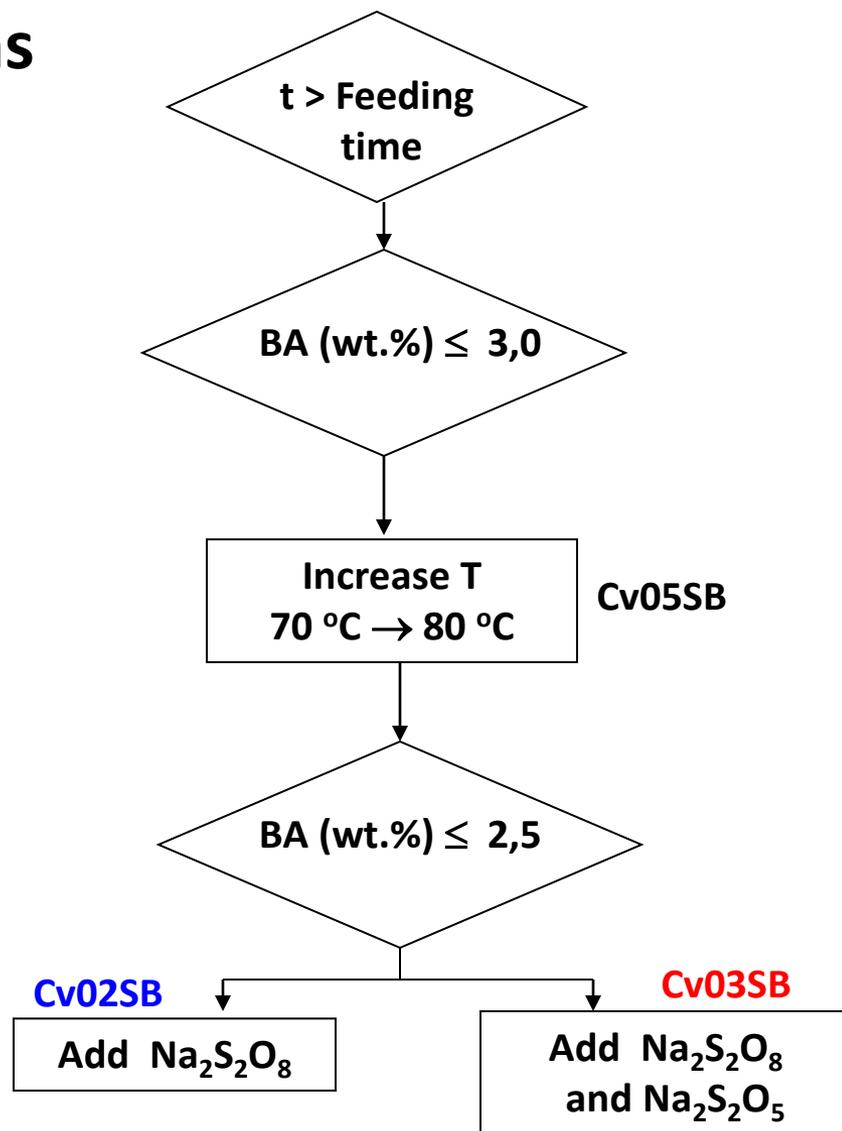
adição de carga adicional de iniciadores

Reduction of Residual Monomer in Emulsion Copolymerizations

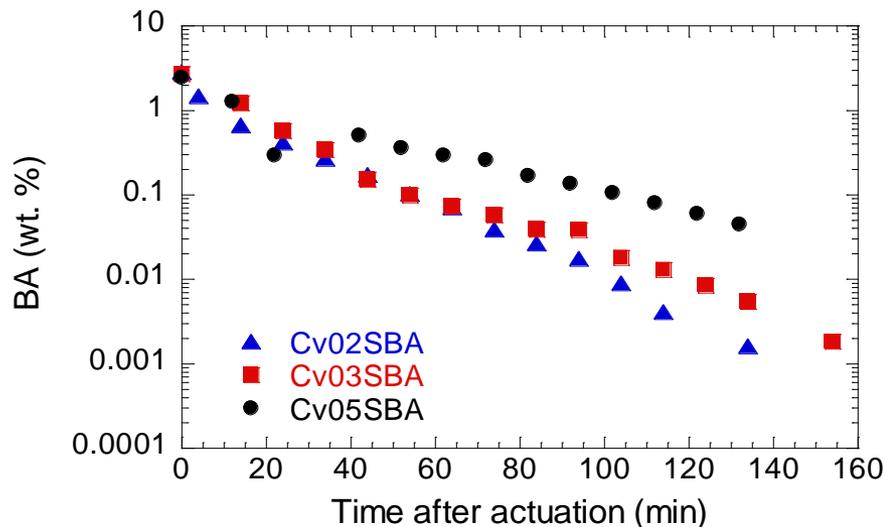
Semicontinuous styrene/butyl acrylate reactions.

(T = 70 °C and 200 rpm)

Reagents	Initial Charge	Feed Stream 1	Feed Stream 2
Sty (g)	-	447,00	-
BA (g)	-	447,00	-
AA (g)	-	4,47	-
Water (g)	1700,00	-	114,80
SLS (g)	9,443	-	-
Na ₂ S ₂ O ₈ (g)	-	-	4,940
Na ₂ CO ₃ (g)	4,512	-	-



Reduction of Residual Monomer in Emulsion Copolymerizations



Strategies for monomer reduction

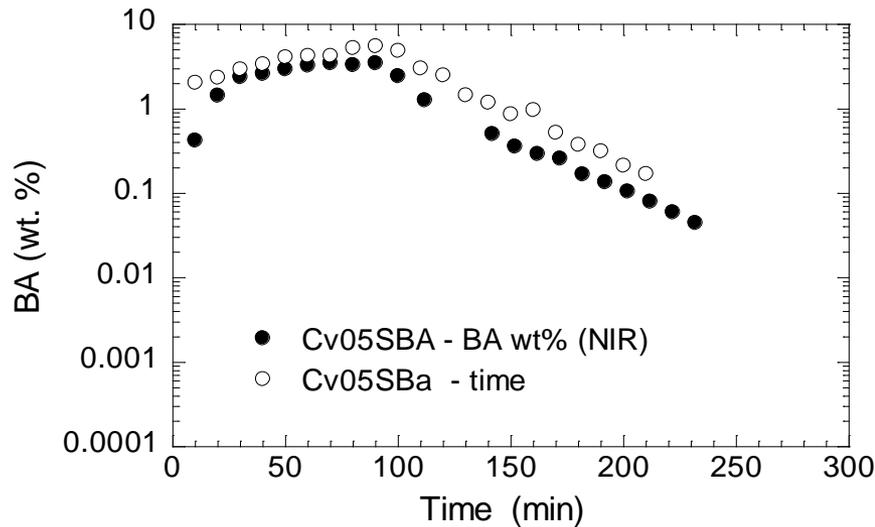
Reaction	BA (%)	T (°C)	Na ₂ S ₂ O ₈ (g)	Na ₂ S ₂ O ₅ (g)
Cv02SB	3.0	70 → 80	-	-
	2.5	-	3.21 ^a	-
Cv03SB	3.0	70 → 80	-	-
	2.5	-	3.24 ^b	5.73 ^c
Cv05SB	3.0	70 → 80	-	-
	2.5	-	-	-

Hirota et al., *Polímeros*, 14(1), 51-56 (2004)

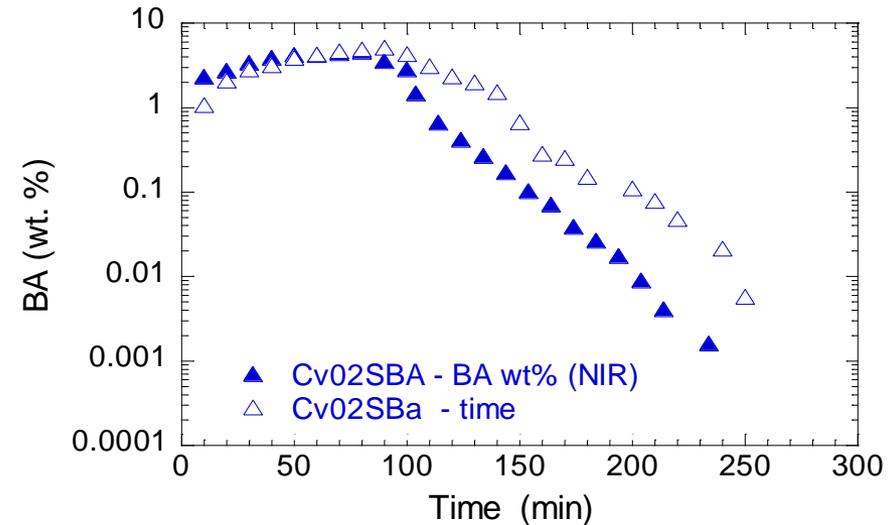
Reaction	[BA] (ppm)	[Sty] (ppm)
Cv02SB	266	nd
	176	nd
	89	nd
	41	nd
	16	nd
Cv03SB	179	6
	129	4
	85	4
	54	2
	18	nd
Cv05SB	1049	21
	797	21
	597	nd
	447	nd
	350	nd

Reduction of Residual Monomer in Emulsion Copolymerizations

Temperature increase 70 → 80



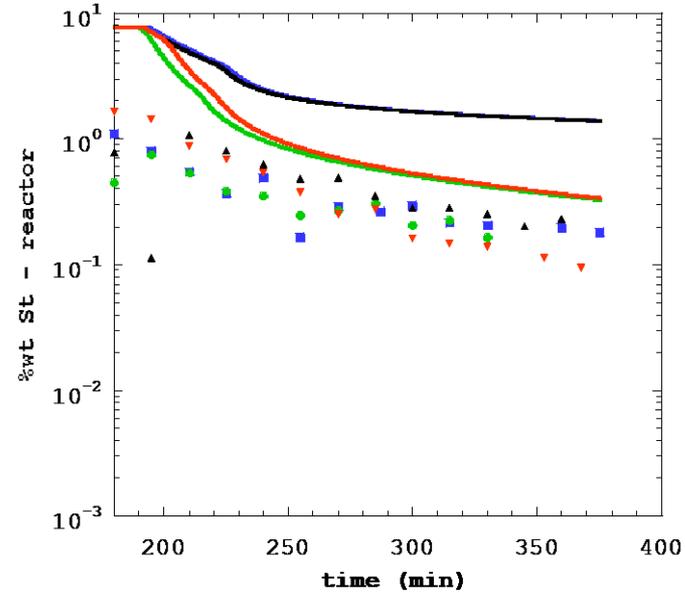
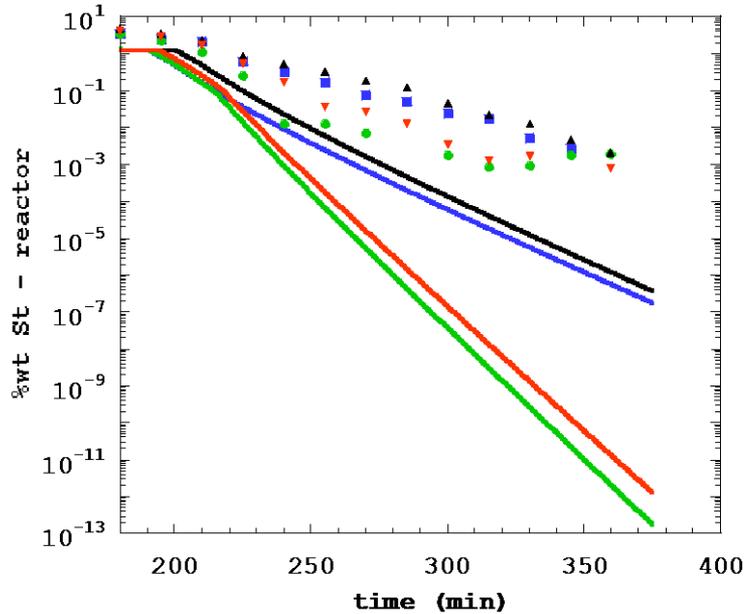
Temperature increase 70 → 80
and addition of $\text{Na}_2\text{S}_2\text{O}_8$



Hirota et al., *Polímeros*, 14(1), 51-56 (2004)

Reduction of Residual Monomer in Emulsion Copolymerizations

Evolution of residual St contents after the end of the monomer feeding time



- S %wt pred-base
- S %wt gc + grav-base
- S %wt pred-T
- S %wt gc + grav-T

- S %wt pred-I
- ▲ S %wt gc + grav-I
- S %wt pred-T+I
- ▼ S %wt gc + grav-T+I

Araújo, Sayer, Giudici & Poco, *Polym.Eng. Sci.* 42(7), 1442-1468 (2002)

Hirota, Reis, Sayer, Giudici & Araújo. *Polímeros: Ciência e Tecnologia*, 14(1), 51-56 (2004).

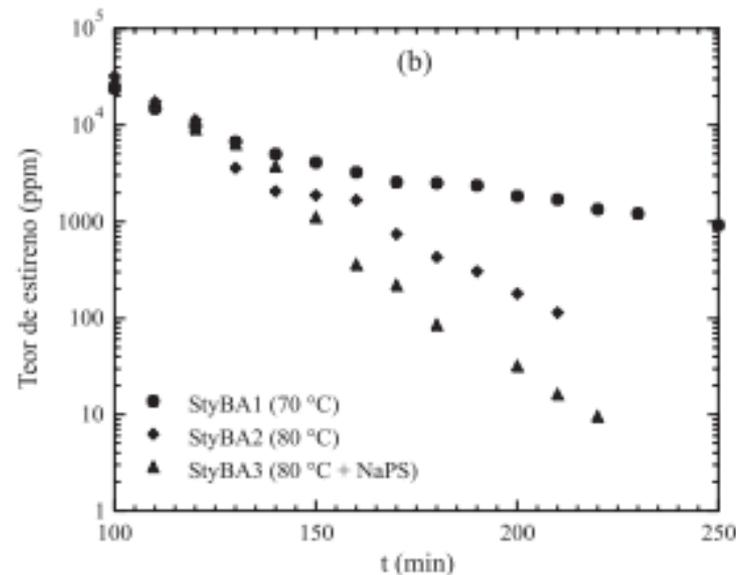
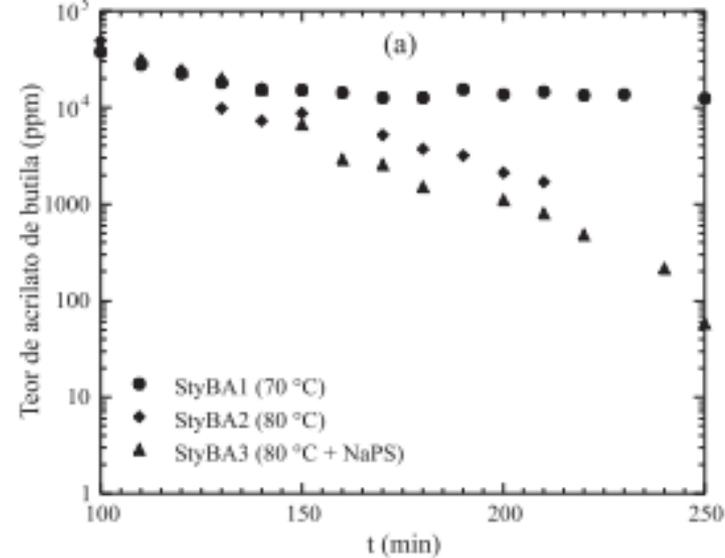
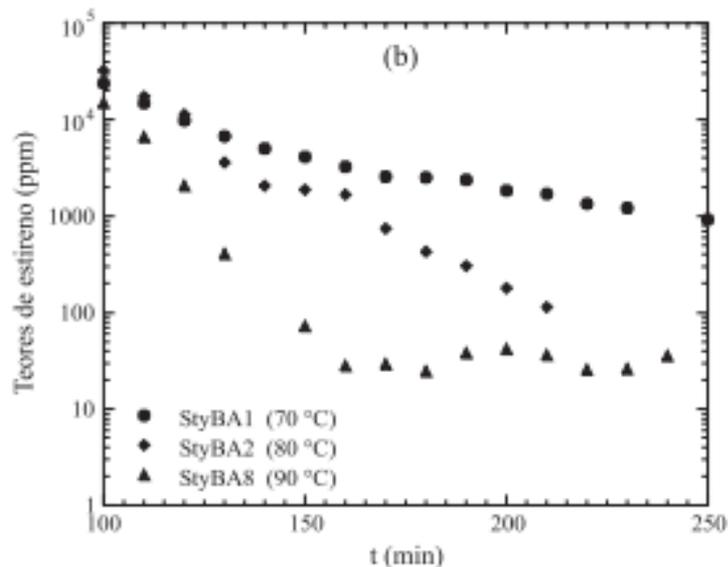
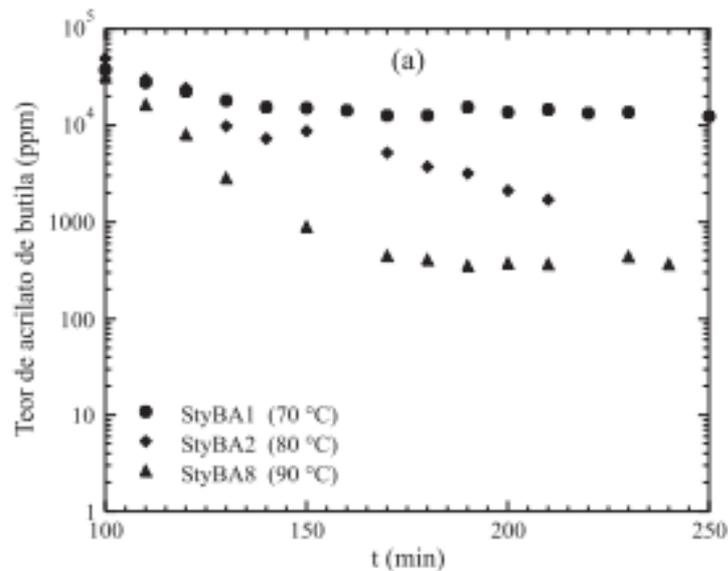


Figura 3. Comparação entre as diferentes estratégias usadas para a redução do teor de monômero residual durante reações semi-contínuas de copolimerização de estireno e acrilato de butila em emulsão. Efeito do aumento da temperatura na etapa final da reação. a) Acrilato de butila; b) Estireno.

Figura 4. Comparação entre as diferentes estratégias usadas para a redução do teor de monômero residual durante reações semi-contínuas de copolimerização de estireno e acrilato de butila em emulsão. Efeito do aumento da temperatura e da adição de iniciador (NaPS) na etapa final da reação. a) Acrilato de butila; b) Estireno.

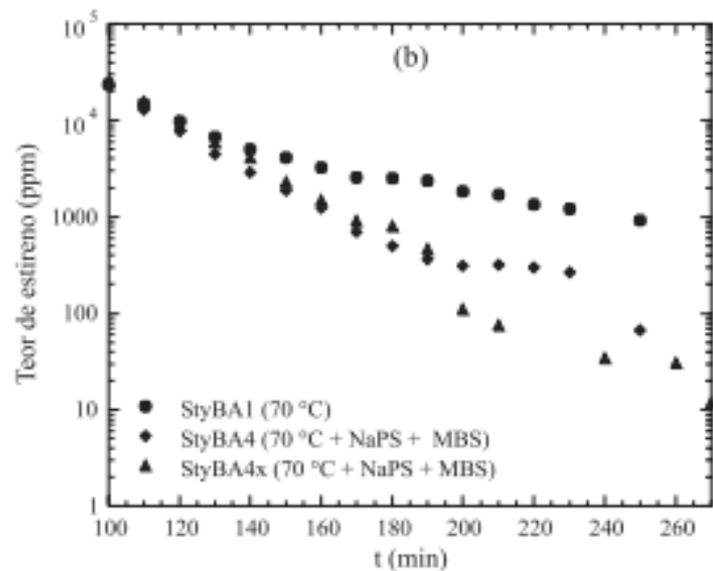
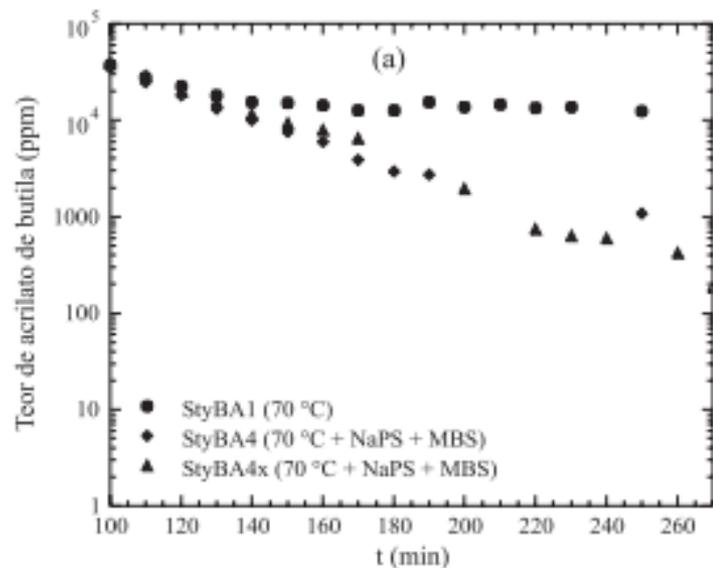


Figura 5. Comparação entre as diferentes estratégias usadas para a redução do teor de monômero residual durante reações semi-contínuas de copolimerização de estireno e acrilato de butila em emulsão. Efeito da adição de iniciador (NaPS + MBS) na etapa final da reação. a) Acrilato de butila; b) Estireno.

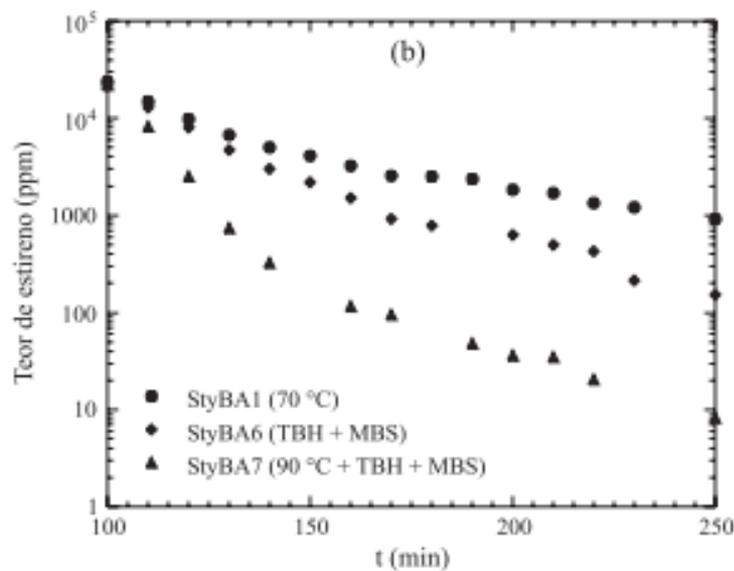
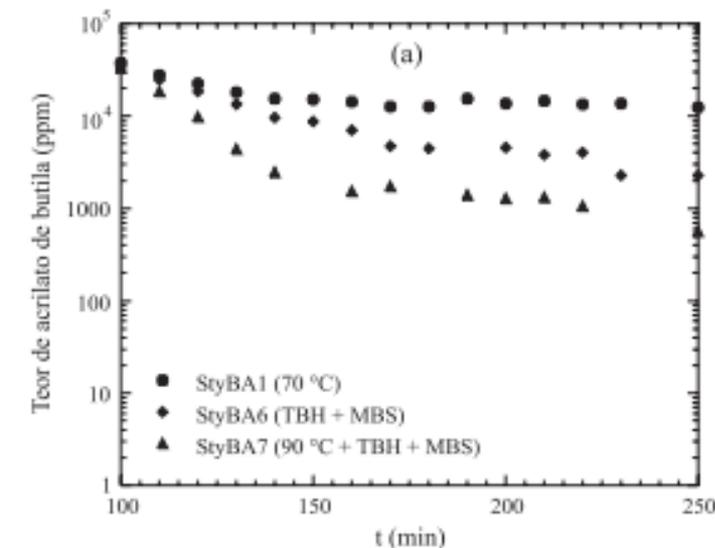


Figura 6. Comparação entre as diferentes estratégias usadas para a redução do teor de monômero residual durante reações semi-contínuas de copolimerização de estireno e acrilato de butila em emulsão. Efeito do aumento da temperatura e da adição de iniciador (TBH + MBS) na etapa final da reação. a) Acrilato de butila; b) Estireno.

Efeitos da Temperatura e do Tipo de Iniciador na Redução do Teor de Monômero Residual Durante Reações de Copolimerização de S/BA em Emulsão

Redução de ordem de grandeza no teor final de monômero livre

Tabela 3. Teores de monômero finais após aplicação das estratégias para sua redução.

Reação	Teor final de acrilato de butila (ppm)	Teor final de estireno (ppm)	Estratégia
StyBA1	~ 10000 ~1%	~ 1000 ~0,1%	—
StyBA3	~ 100	~ 10	T = 80 °C + NaPS
StyBA4x	~ 200	~ 10	NaPS + MBS
StyBA7	~ 500	~ 10	T = 90 °C + TBH + MBS
StyBA8	~ 300	~ 25	T = 90 °C

T - temperatura; NaPS - persulfato de sódio; TBH - terc-butil-hidroperóxido; MBS - metabissulfito de sódio.

Techniques for Reducing Residual Monomer Content in Polymers: A Review

P. H. H. ARAÚJO¹, C. SAYER¹, J. G. R. POÇO², and R. GIUDICI^{1,*}

¹USP – Universidade de São Paulo
Escola Politécnica
Departamento de Engenharia Química
Av. Prof. Luciano Gualberto, trav. 3, n. 380, 05508-900,
São Paulo, SP, Brazil

²IPT – Instituto de Pesquisas Tecnológicas do Estado de São Paulo
Av. Prof. Almeida Prado, n. 532, 05508-901, São Paulo, Brazil

Reducing the residual monomer content is a desire of every polymer producer, as a product with no or very low levels of residual monomer would have a different commercial appeal. The presence of residual monomer may create hazards to workers as a result of long-term exposure during polymer processing and sometimes even to customers. There are several techniques for reducing residual monomer content and the industrial importance that has been given to the presence of residual monomers in polymeric products is reflected in the number of patents involving residual monomer reduction techniques. Nevertheless, choosing the best, or the most adequate, technique is not always an easy task, and one still observes a relative lack of scientific literature on this subject. The technique to be employed will depend upon polymer application, which determines the grade of purity, and also on polymer quality, as some monomer reducing techniques might change polymer properties. The main objective of this review is to summarize and discuss the principal methods employed for reducing residual monomer content.

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