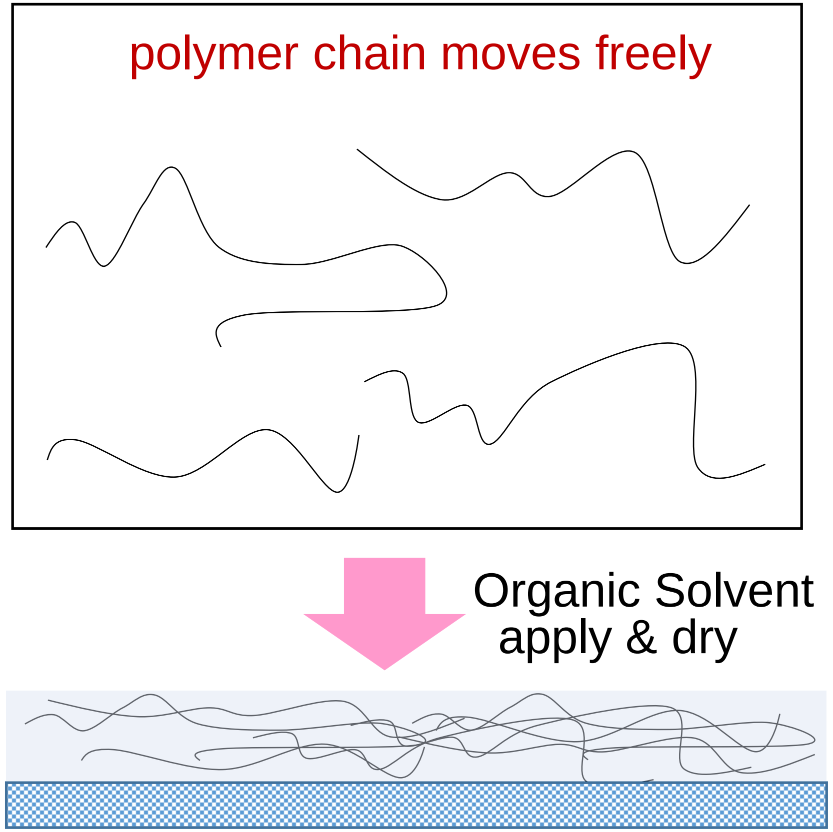
A Cost-Effective Approach to Formulate Emulsions Leading to Improved Colloidal Stability and Finished Coatings

Why Improve Coatings

1. Growing demand for higher-quality coatings
2. Need for increased durability
3. Improved adhesion
4. More robust and efficient manufacturing processes
5. Desire for greater transparency

Solvent-borne Coating (Homogeneous System)

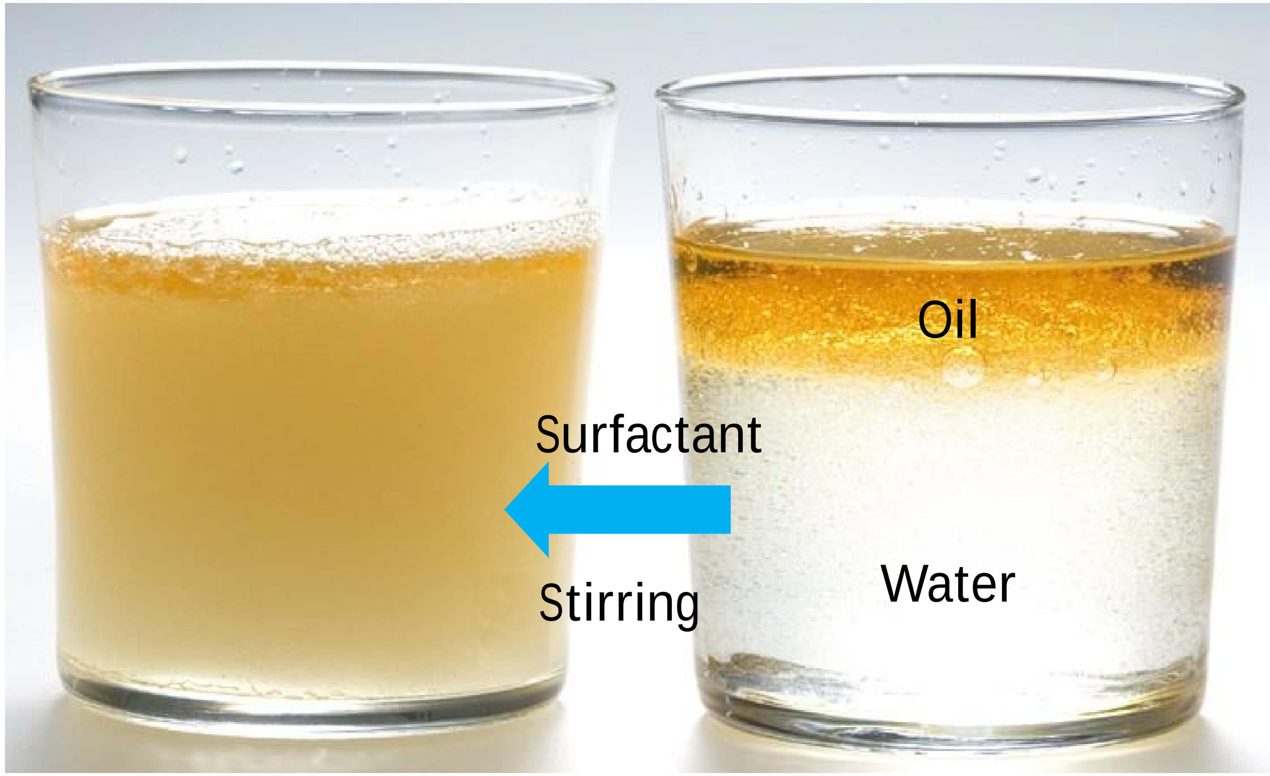


any Tg is possible
due to solvent as
plasticizer

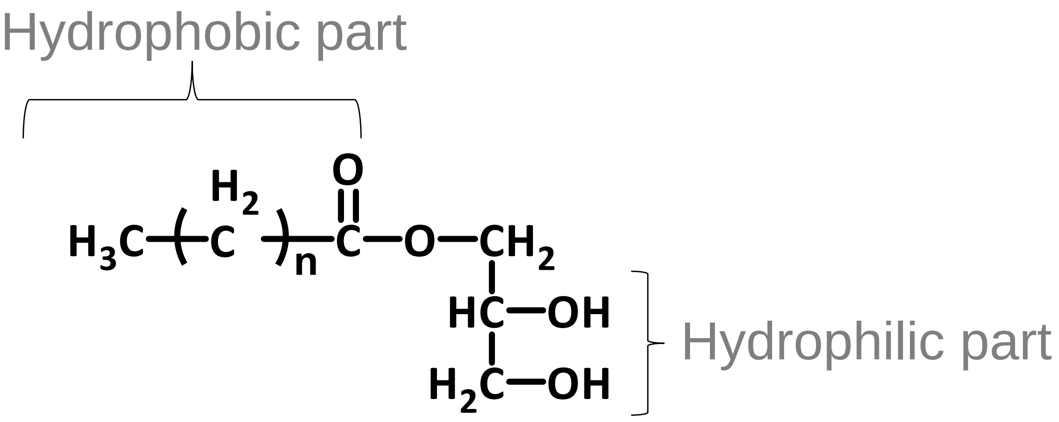
homogeneous film
substrate

Sufficient entanglement (→ good strength) | Easy to cure by various systems | No hydrophilic impurities

The Function of a Surfactant



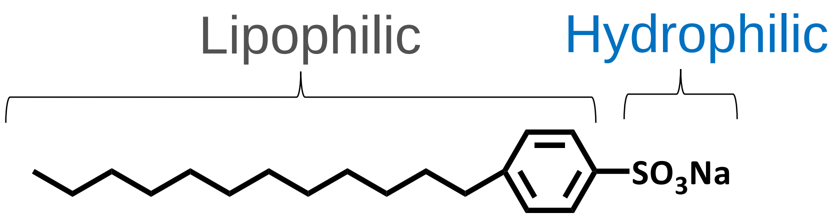
Absorbs at water/oil interface and stabilizes oil droplets in water

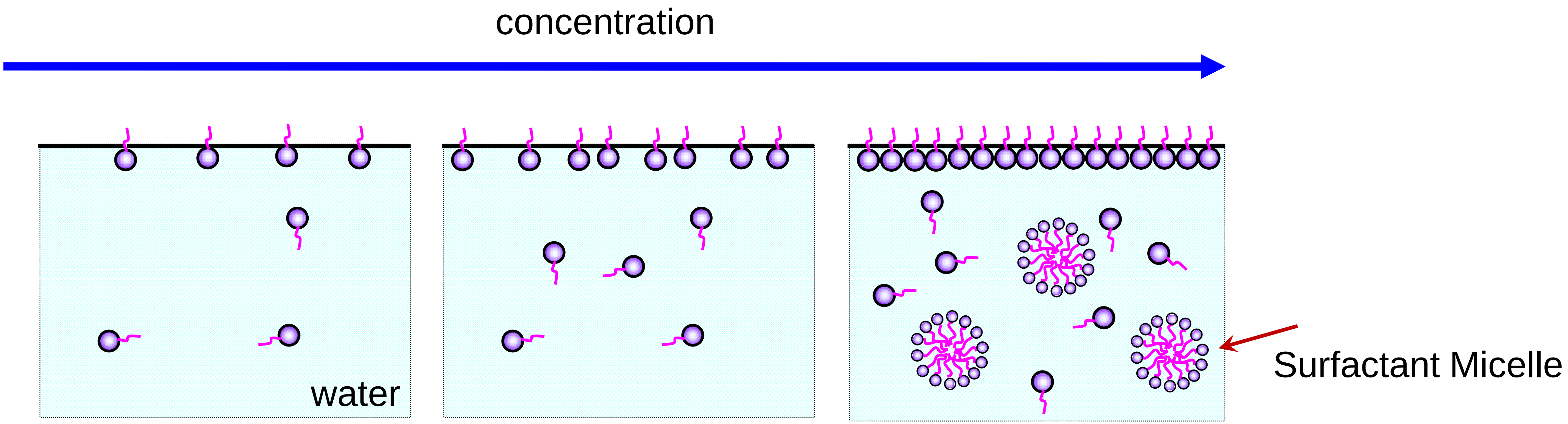


Typical Surfactant only Emulsion Polymerization

Limited solubility to both water and oil (Styrene,acrylate etc)

→ Localizes at their interface or forms micelle

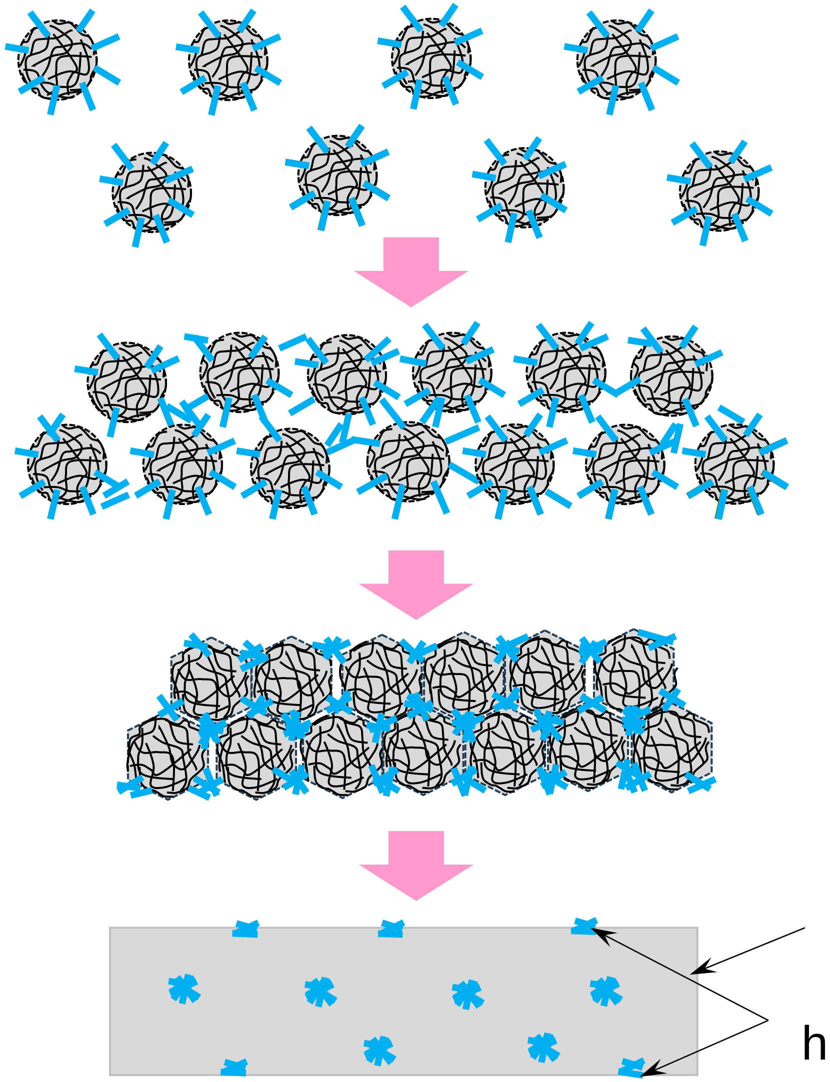




Water-borne Coating（Heterogeneous System）

polymer particle
in water (2 phases)

colloidal stability is obtained by physically adsorbed surfactant



(2 → 1 phase)

surfactant gradually desorb

polymer chain can only diffuse over Tg

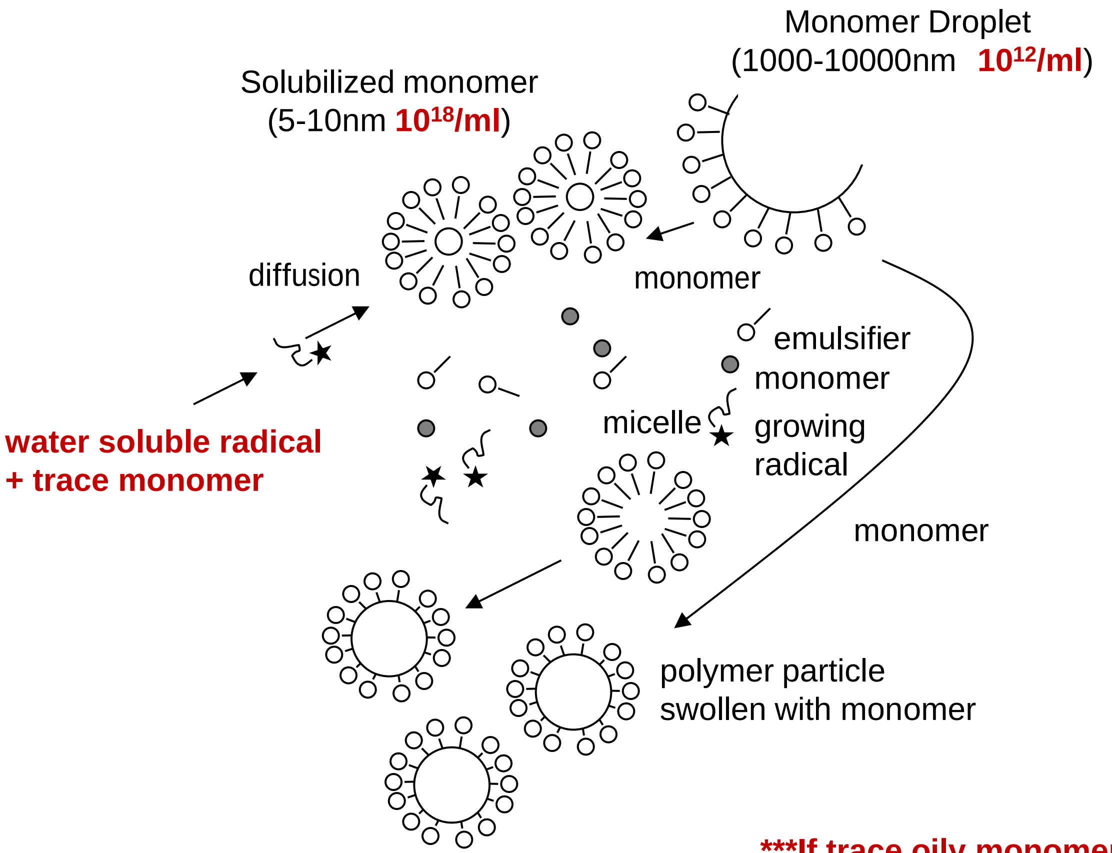
surfactant is a nuisance at this stage!
(no place to stay)

homogeneous film
is formed over Tg

absorbing water, causing blister & whitening

hindering adhesion

What is Emulsion Polymerization



Ingredients

oil-soluble monomer*
(*trace amount dissolves in water)
surfactant
water-soluble initiator**
water

Primary radical
generates
in water phase

Where primary radical go ?
to monomer micelle or
trace monomer in water phase***

Because total surface area
micelle >>> monomer droplet

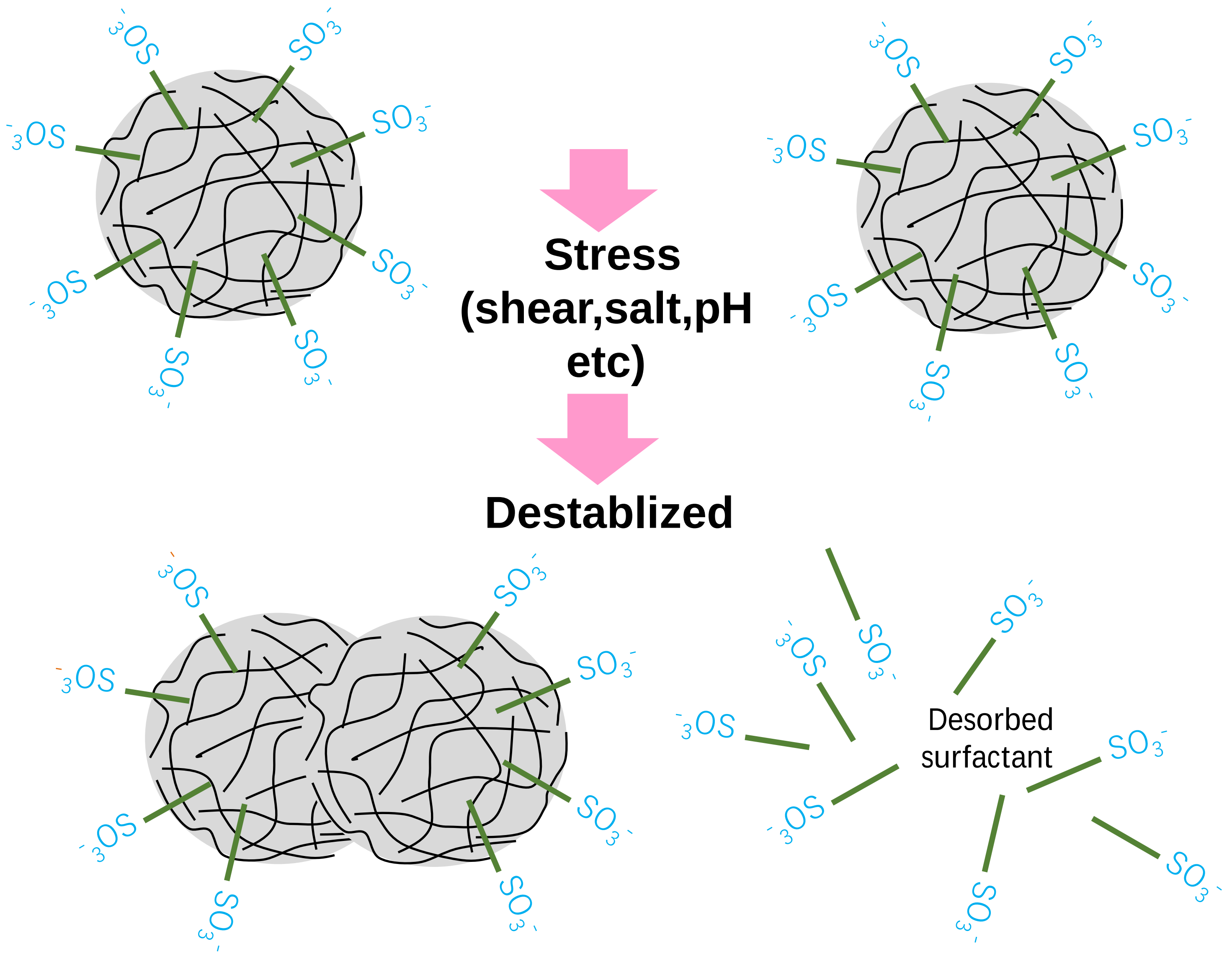
****If oil-soluble initiator is used,**
polymerization proceeds in large droplet and then these aggregate

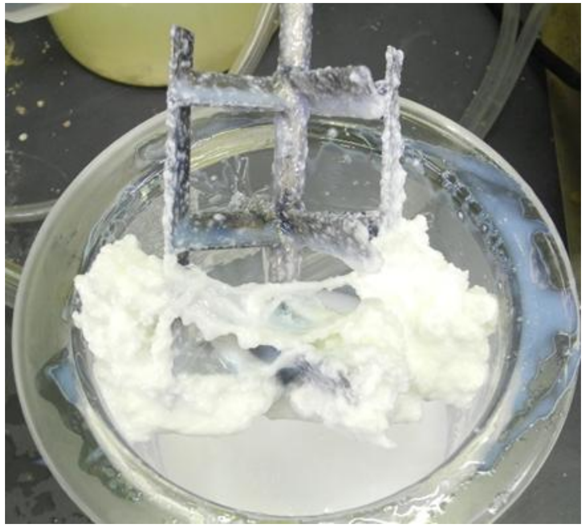
*****If trace oily monomer exists in water ,**
oily oligomer generates and enter into micelle. No problem!

*****If water-soluble monomer exists in water,**
water-soluble polymer generates.****
These polymer gives bad affect to emulsion and film property.

******How to prevent this is critical !**

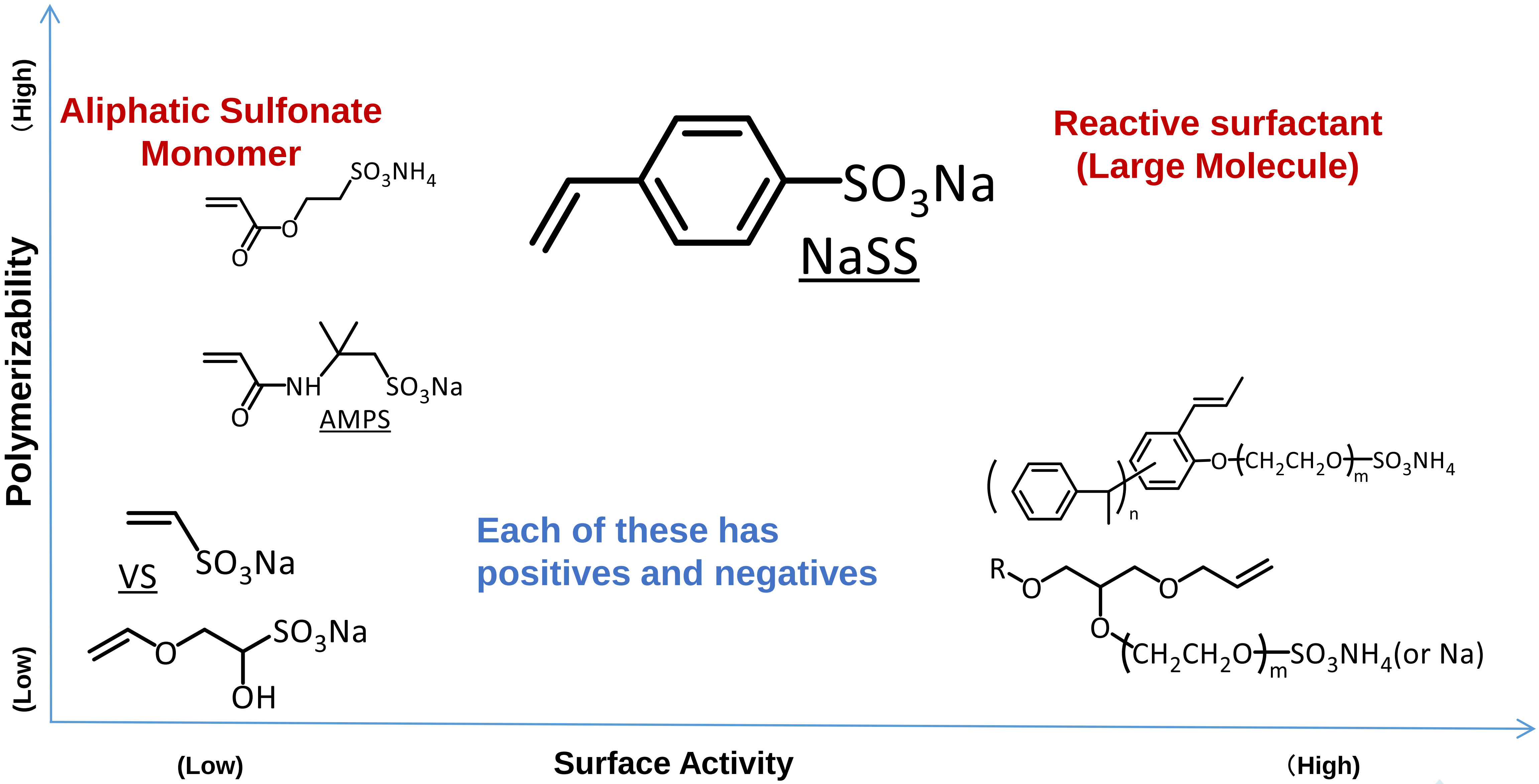
Emulsion Stabilized by Conventional Surfactant



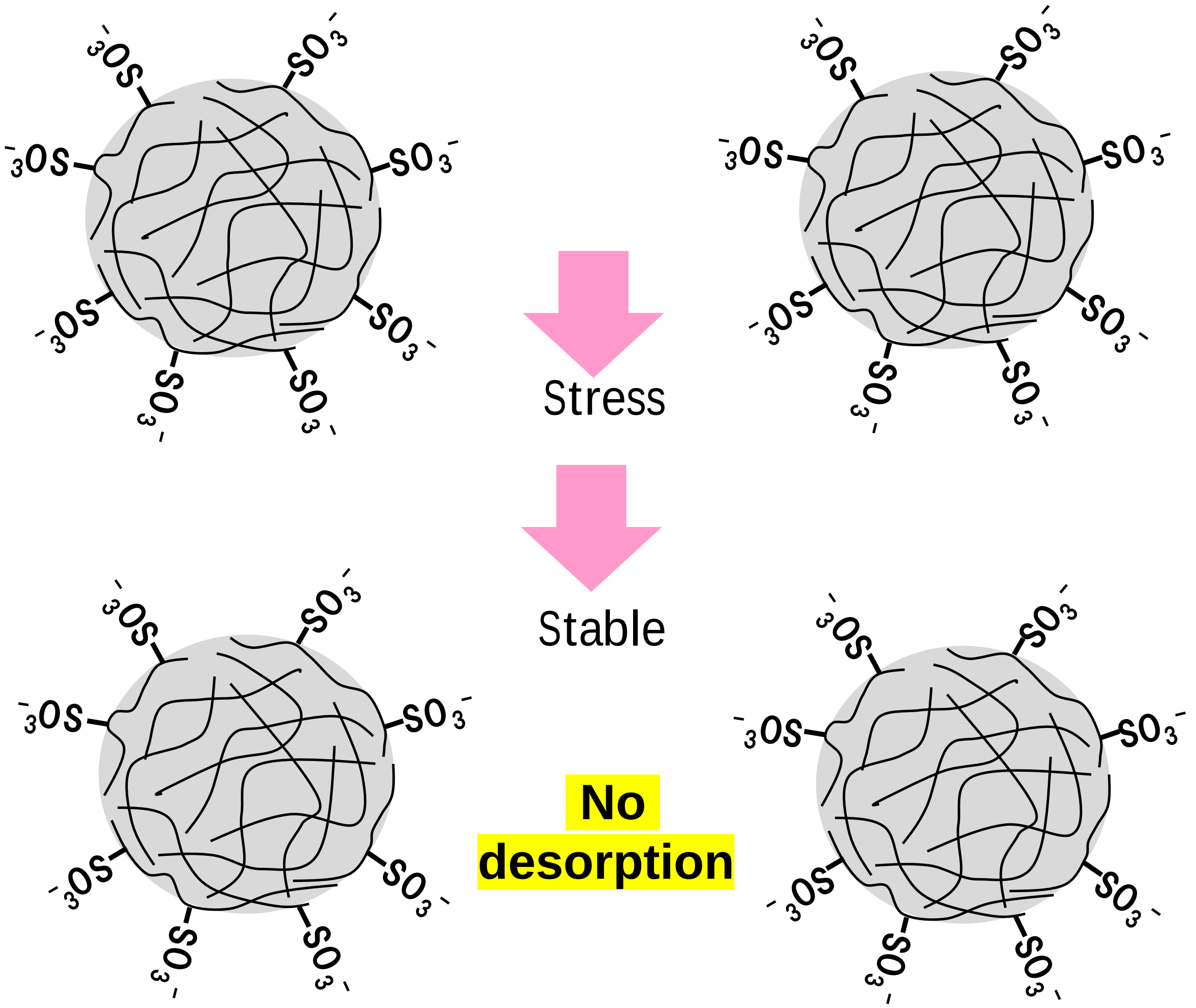


Aggregation

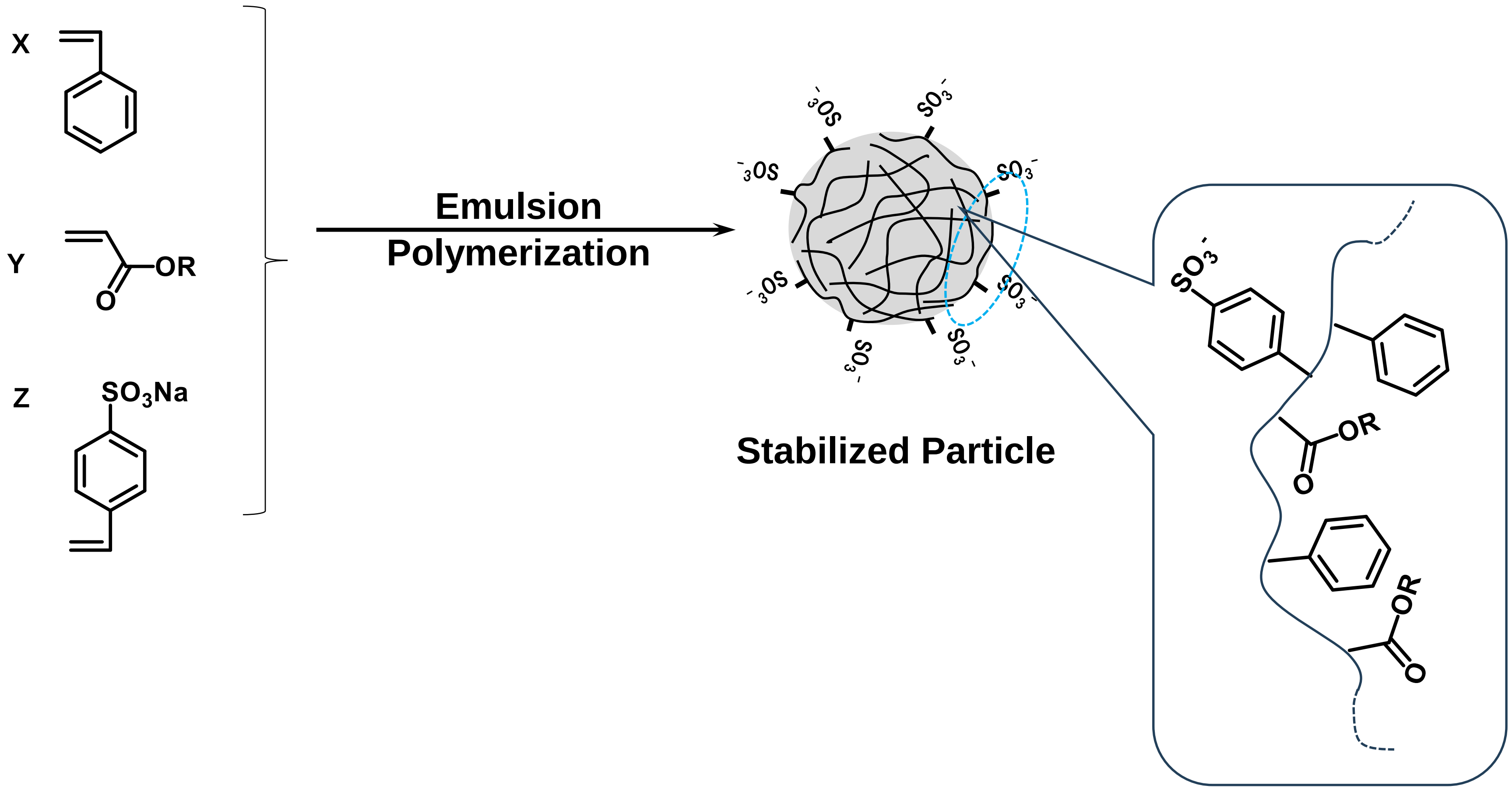
Reactive Emulsifiers



Emulsion Stabilized by NaSS (ideal image)



Emulsion Stabilized by NaSS (closer look)



NaSS copolymer

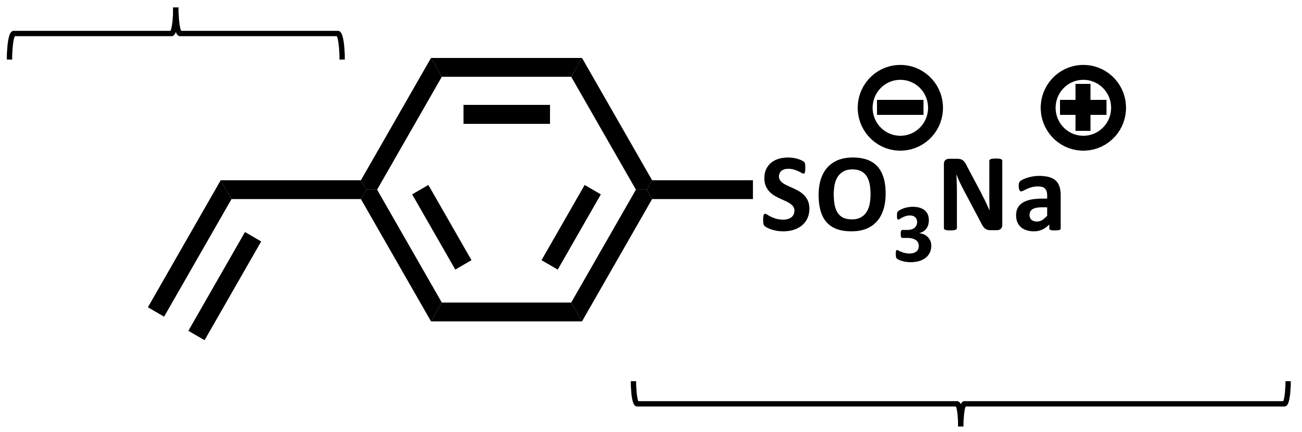
Major Advantages/Disadvantages

1. Small RE molecules (AMPS, SVS) lack emulsification
2. Large RE molecules have a higher molecular weight and usage and cost/kg
3. Large RE molecules can also act as a defect similar to emulsifiers
4. While NaSS isn't a 'Superman' solution, it does offer significant advantages

Sodium Styrene Sulfonate

(1) Good Surface Activity

(2) High Reactivity



(3) High Thermal Stability

Surfactant-free Emulsion Polymerization by NaSS

Polymerization proceeds by small dosage of NaSS

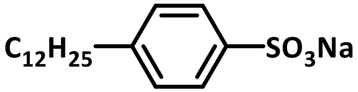
Ingredients

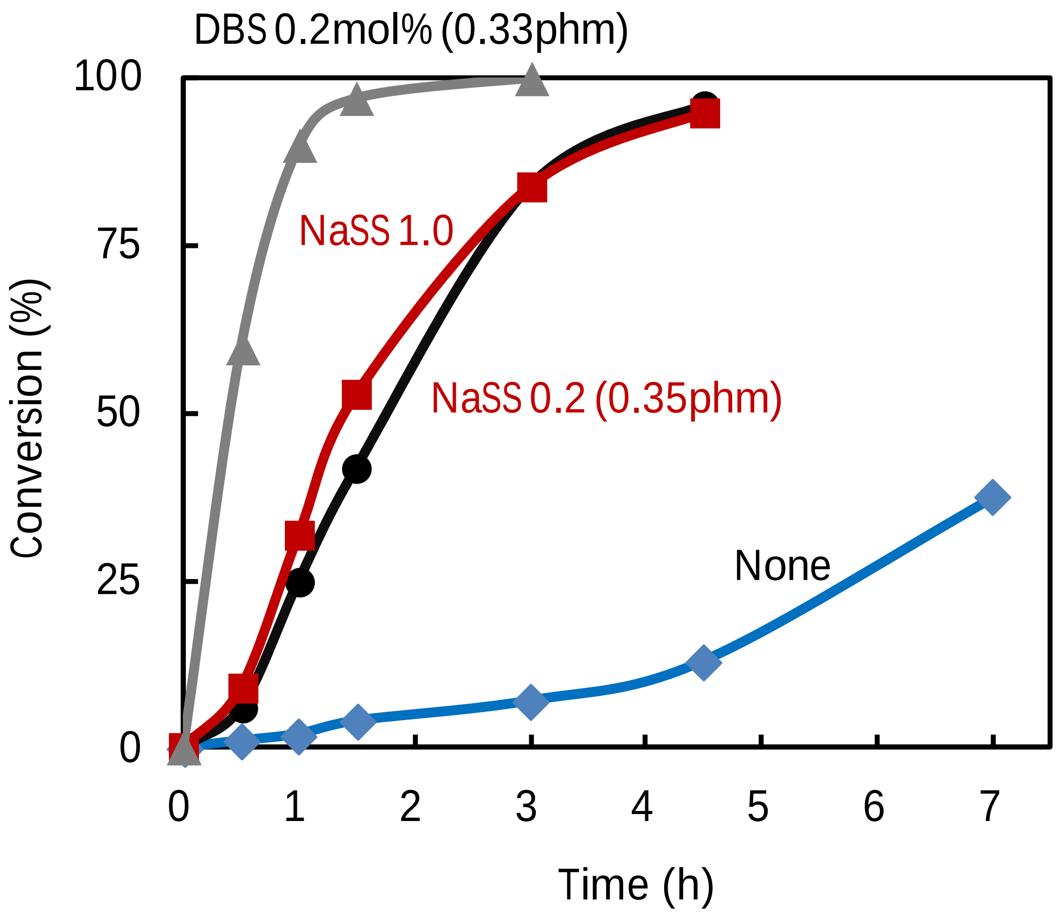
Styrene/n-Butylacrylate = 1/1 wt.r
NaSS or DBS* = variable
Potassium Persulfate = 0.2 mol%/MM
Water (Total MM=20wt%)

Dosed all at once

70℃×5h

***DBS**





Polymerization time vs. conversion

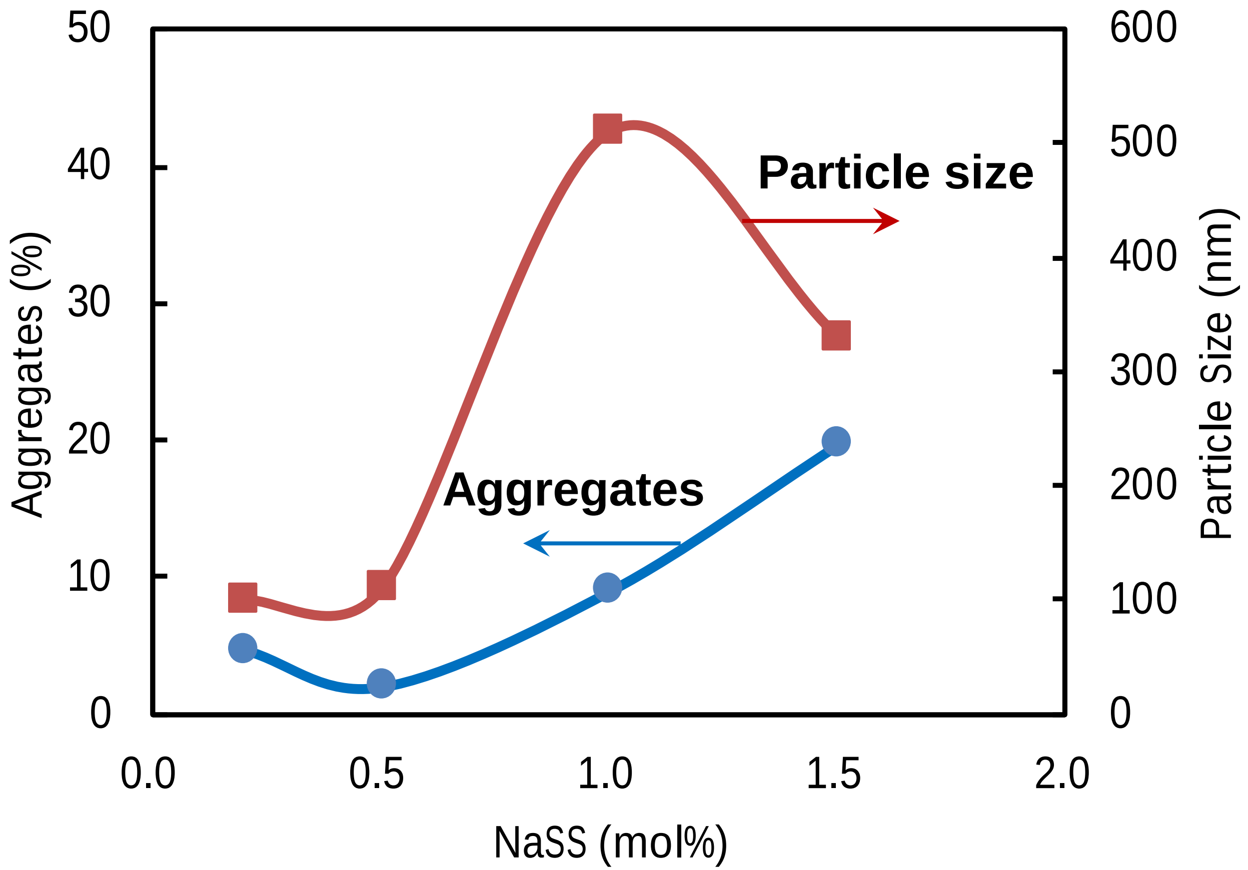
Surfactant-free Emulsion Polymerization by NaSS

Optimal NaSS dosage ~ 0.5 mol%

Ingredients	
Styrene/n-Butylacrylate	**= 1/1 wt.r**
NaSS	**= variable**
Potassium Persulfate	**= 0.2 mol%/MM**
Water	**(Total MM=20wt%)**

Dosed all at once

70℃×5h



NaSS dosage vs. aggregates and particle size

Practical Example of Emulsion Polymerization

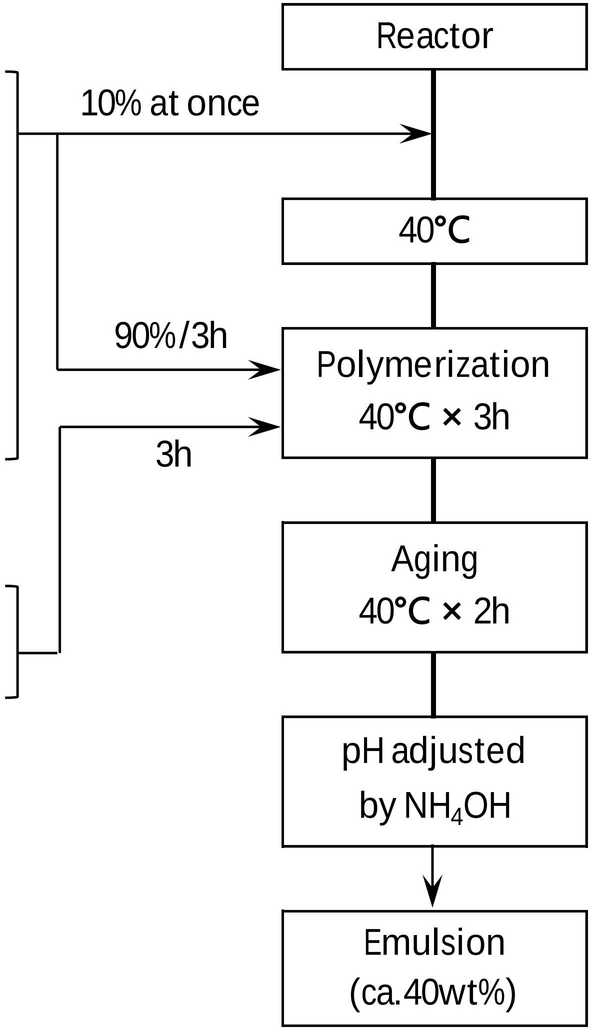
Condition

Pre-emulsified monomer was continuously dosed

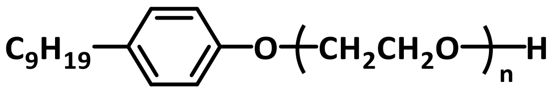
Nonionic surfactants were used to emulsify monomer

Monomer Emulsion		
Styrene	50.5	g
n-Butylacrylate	51.0	g
Sulfonate monomer*	2.0	phm
Surfactant**	0～4	phm
Sodium bisulfite	0.25	phm
Water	94.0	g

Initiator		
Ammonium persulfate	0.5	phm
Water	48.0	g

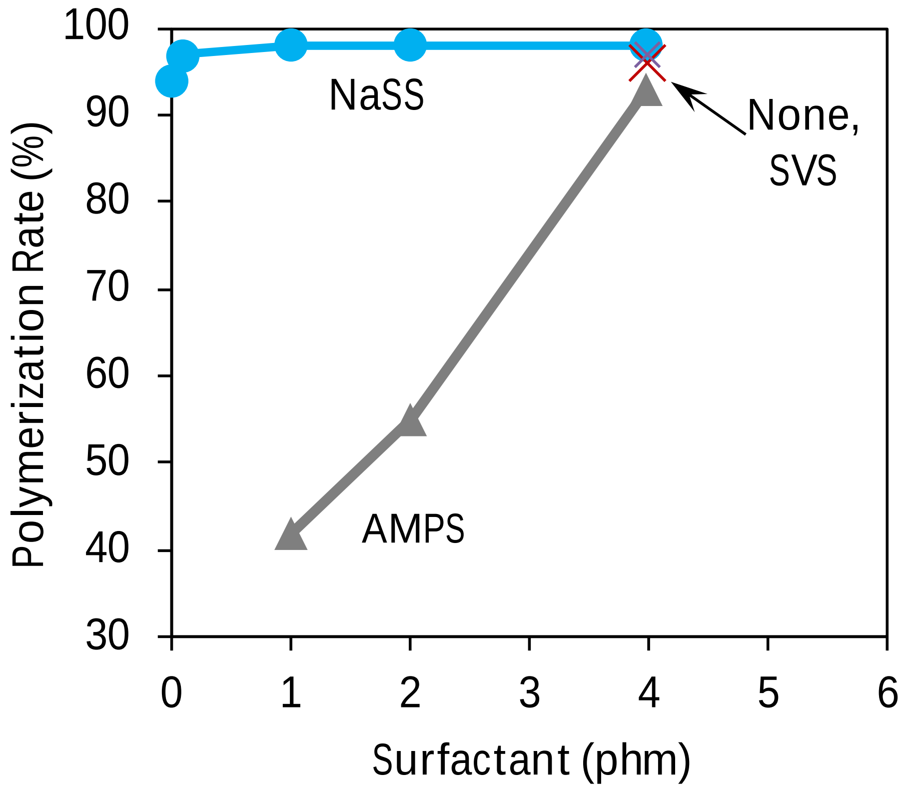


**Surfactant



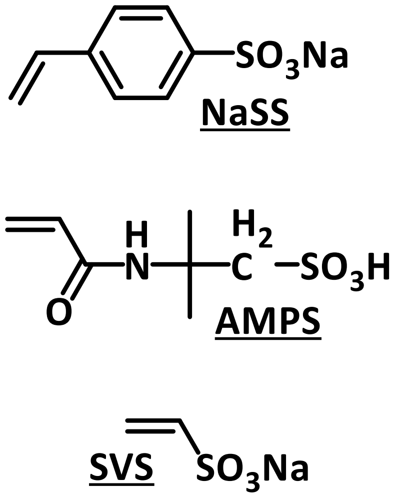
Benefits of NaSS : Polymerization Rate

Emulsion polymerization proceeds up to high conversion with less surfactant



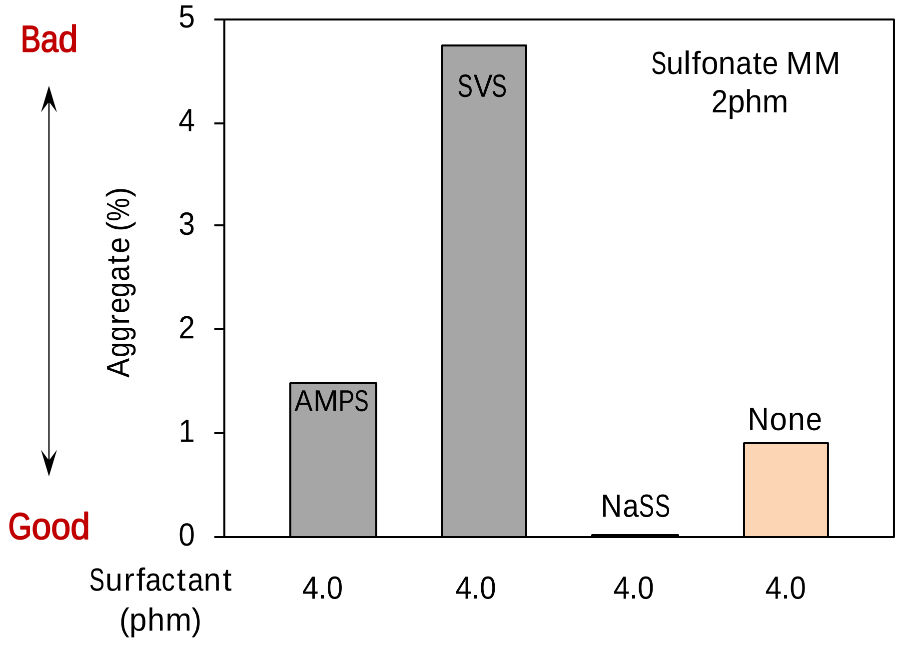
Surfactant dosage vs. conversion

*Sulfonate monomer
(2phm ≒ 0.9～1.7mol%)

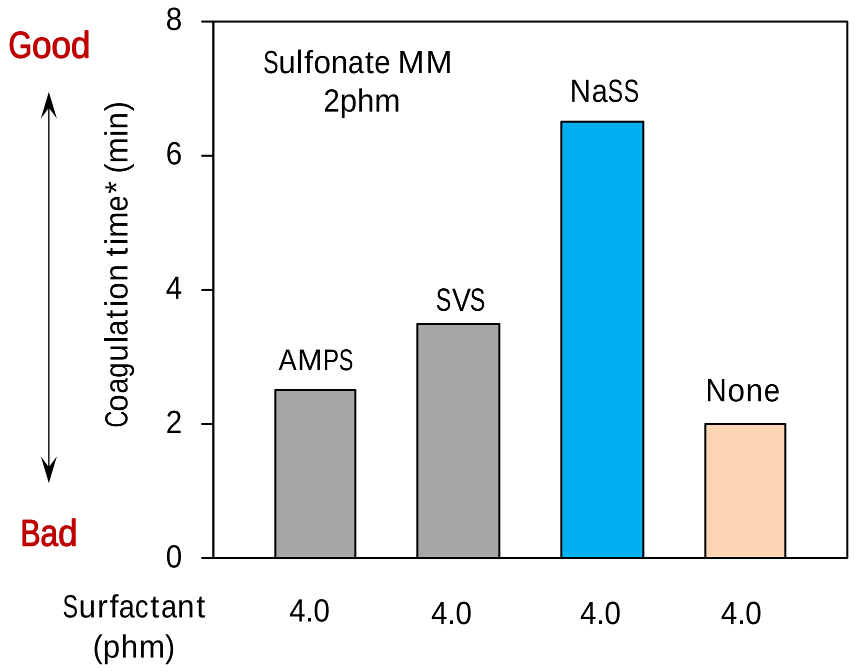


Benefits of NaSS : Emulsion Stability

NaSS gives excellent colloidal stability



Aggregation during polymerization



Mechanical stability of emulsion

***by agitation at 5,000rpm (Maron test)**

Benefits of NaSS : Emulsion Properties

NaSS gives good film-forming property

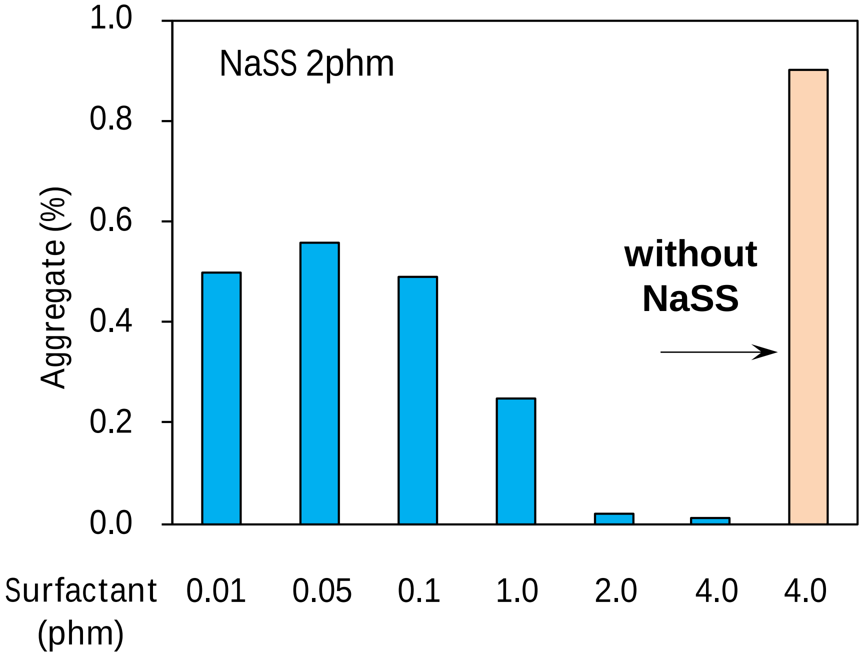
Sulfonate monomer (phm)		Emulsifier (phm)	Aggregate (%)	Particle diameter (µm)	Mechanical* Stability (min)	Appearance of dry film	Water absorption of film (%)**
None	0.0	4.0	0.90	0.19	2.0	translucent	12.7
NaSS	2.0	4.0	0.01	0.09	6.5	transparent	12.0
AMPS	2.0	4.0	1.48	0.19	2.5	opaque	11.8
SVS	2.0	4.0	4.74	0.20	3.5	translucent	18.3

* Coagulation time by agitation at 5,000rpm (Maron test)

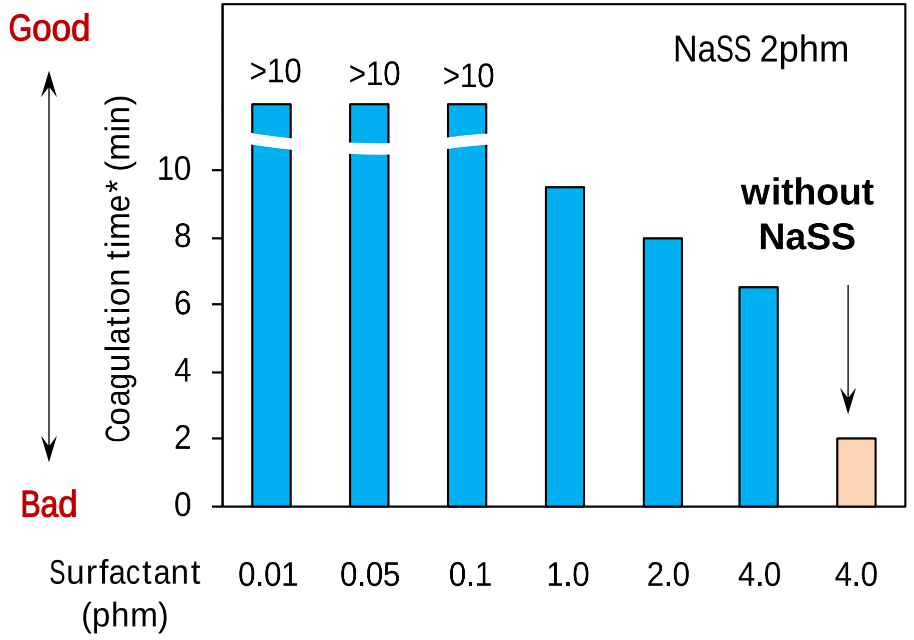
**Immersion of dried-film in water for 48h at RT, film thickness ～0.5mm

Benefits of NaSS : Reduction of Surfactant

Excellent colloidal stability is obtained with less surfactant.



Aggregation during polymerization



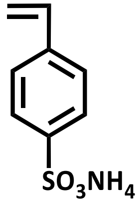
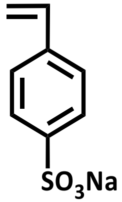
Mechanical stability of emulsion

***by agitation at 5,000rpm (Maron test)**

AmSS

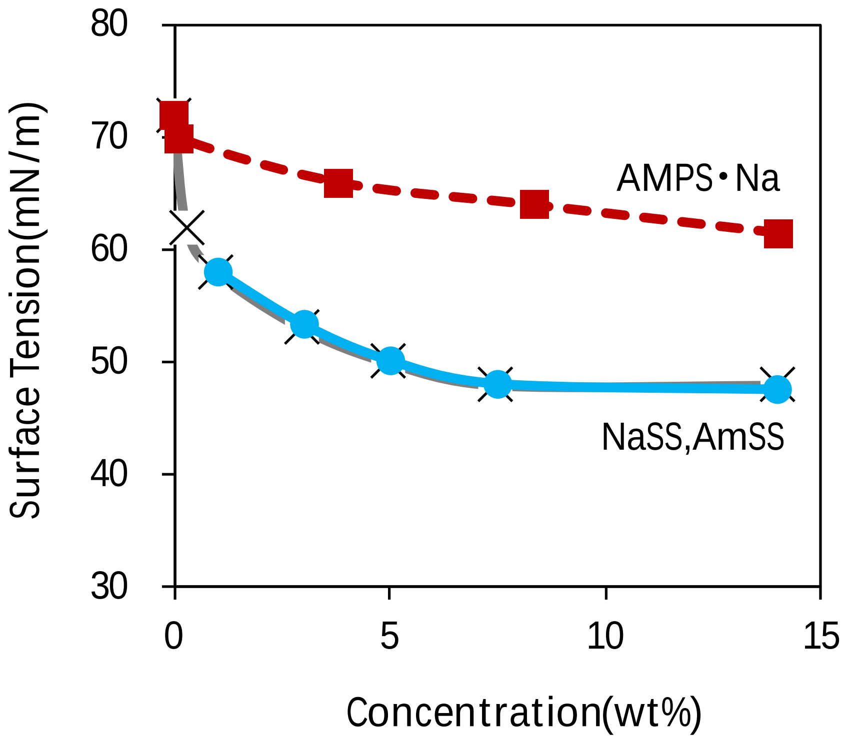
Ammonium Styrene Sulfonate

1. Metal-free
2. High surface activity
3. High reactivity
4. Organic solvent soluble
5. Higher corrosion resistance compared to NaSS

		 AmSS	 NaSS
Registrations			
CAS No.		19922-72-6	2695-37-6
MITI(JAPAN)		3-1948	3-1903
TSCA(USA)		-	Listed
REACH(EU)		-	Registered
ECL(KR)		-	KE-13273
Specification			
Purity	wt%	≧95	≧84
Metal	wt%	< 0.5	11～14
pH of 10wt%aq.		5～6	10～12
Solubility at 25℃	wt%		
H_2O		26.0	21.0
Methanol		13.2	4.4
DMSO		43.9	27.3
NMP		31.0	8.6

Surface Activity

Like NaSS, AmSS demonstrates good compatibility with emulsion polymerization processes



Aqueous solution conc. vs Surface tension

(Wilhelmy method,Pt plate at 25℃)

Surfactant-Less Emulsion Polymerization by AmSS

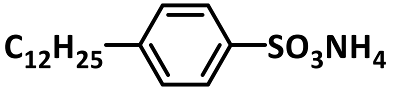
Polymerizes efficiently to high conversion levels.

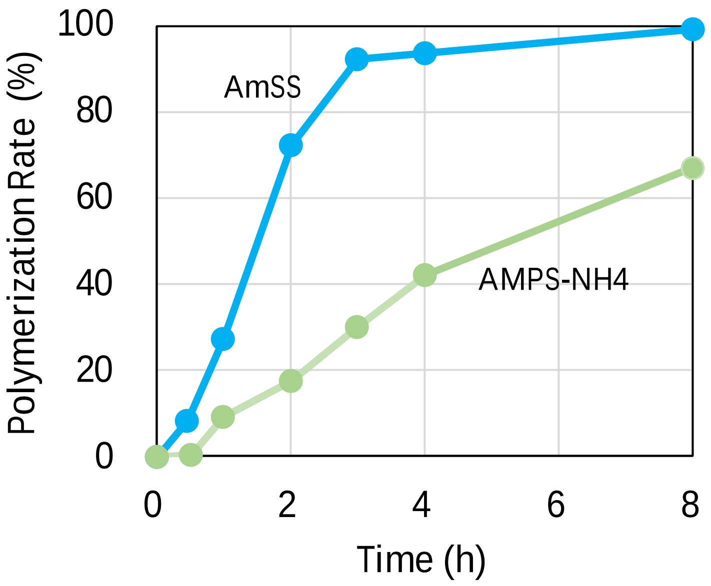
Ingredients	
Styrene/n-Butylacrylate	**= 1/1 wt.r**
AmSS or AMPS·NH_4	**= 1 mol%**
DBS·NH_4*	**= 0.02 mol%/MM**
Ammonium Persulfate	**= 0.10 mol%/MM**
Water	**(Total MM=34wt%)**

Dosed all at once

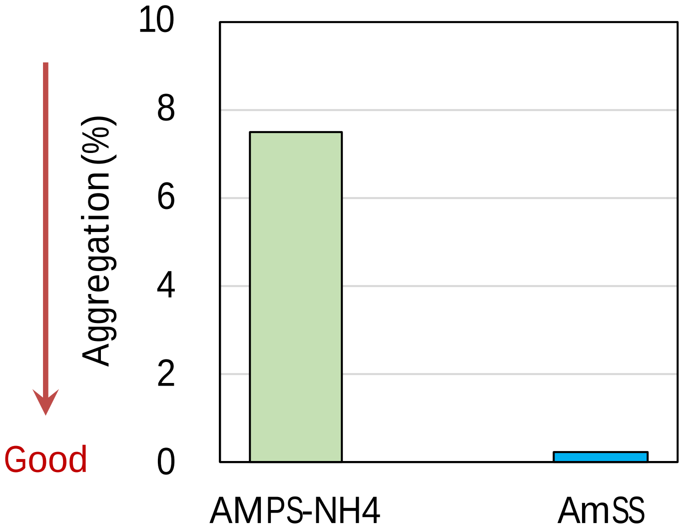
60℃

*DBS·NH_4





Time vs. conversion



Aggregation during polymerization

Advantages of Being Metal-free

AmSS enhances the water resistance properties of the coating

< Model Polymer Synthesis >

・Monomer
  St/n-BA : 50/50wt.r
  AmSS(NaSS) : 0.5 or 2 mol%
  Overall : 48wt%
・Initiator V-40 : 1mol%
・Solvent : N,N-Dimethylacetamide

Temp. : 90℃×46h
Overall conv. : >99%

< Film Preparation >

・Substrate : Slide Glass
・Dry : 100℃×24h,full vacuum
・Thickness : ca.0.15mm

< Water Resistance >

・Immersed in water at 40℃ for 25h

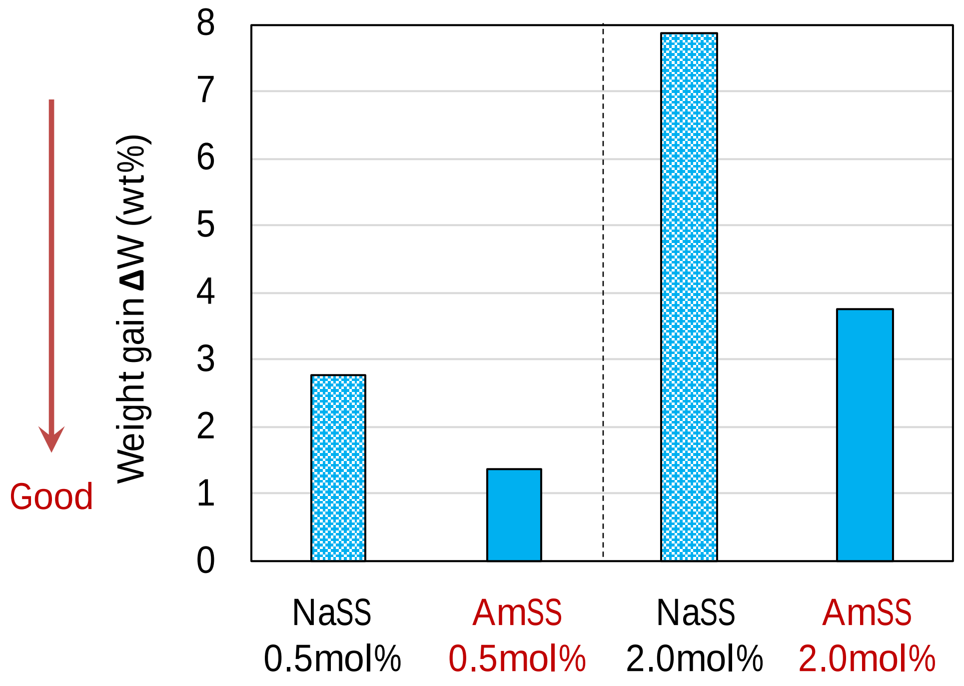


Fig.14 Water absorption of dry film

Contact

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