TOSOH FINECHEM CORPORATION

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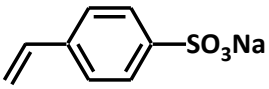
SPINOMAR® NaSS

Properties



Sodium p-styrene sulfonate

CAS No.	2695-37-6
MITI	(3)-1903
TSCA	Listed
REACH	Registered
ECL	KE-13273
Mol .Weight	206.2
Non-Toxic	
Non-Combustible	

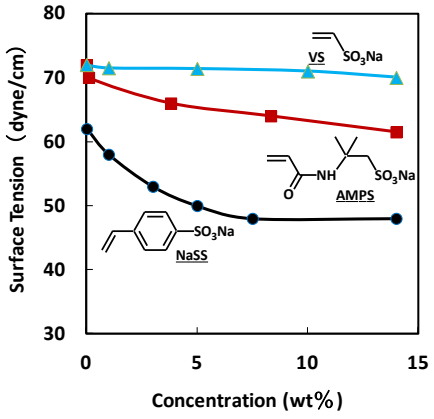
[Specification]

		Representative Value[1)]	Specification[1)]
NaSS[2)]	%	88.6[3)]	84～92
NaBr	%	2.2	≦4
Na_2SO_4	%	0.5	≦1
NaOH	%	≦0.1	≦1
Water	%	8.0	-

1) Wet basis
2) Vinyl activity by redox titration
3) 96% in dry basis

- Good Surface Activity
- Excellent Radical Reactivity
- Good Thermal/Chemical Stability
- Low Toxicity

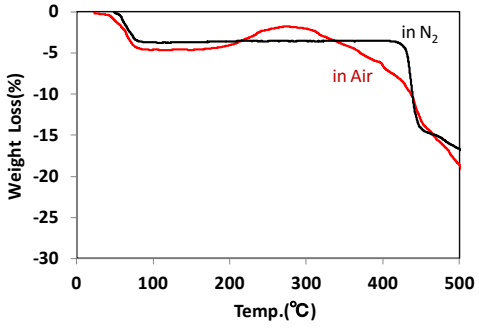
[Surface Tension of aq. Solution]



[Q-e value]

Monomer	Q	e
NaSS	2.49	-0.59
AMPS･Na	0.39	0.22
VS･Na	0.064	0.41
Styrene	1.00	-0.80

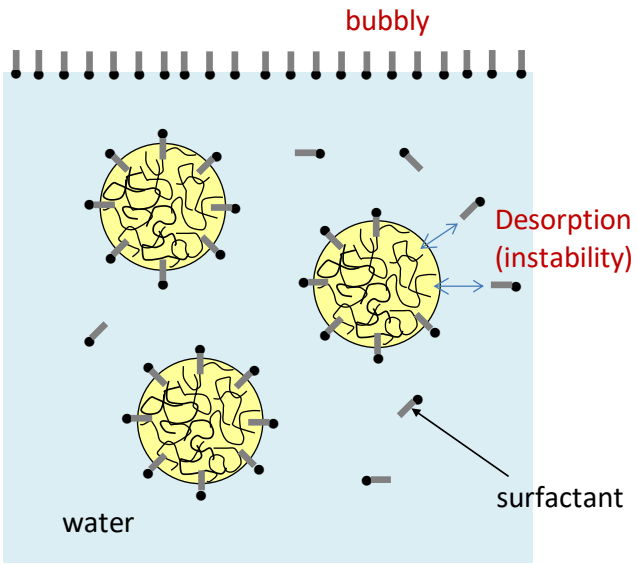
[TG-DTA Curves]

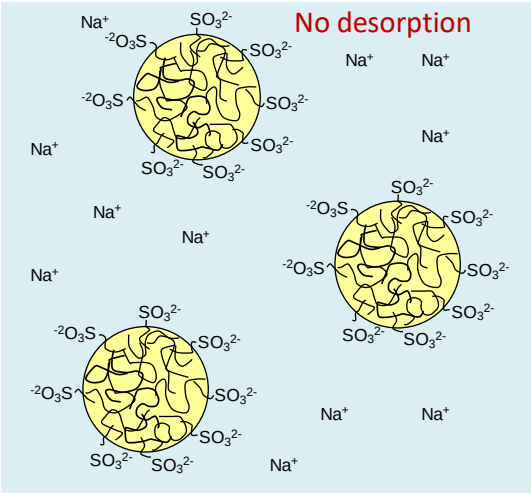


Application

- Emulsion Polymerization
  - ･Water-born paint/Adhesive
  - ･Acrylic Fiber
- Others
  - ･Water Treatment
  - ･Detergent (Dispersant)
  - ･Cation Exchange Membrane

Emulsion Stabilizing System

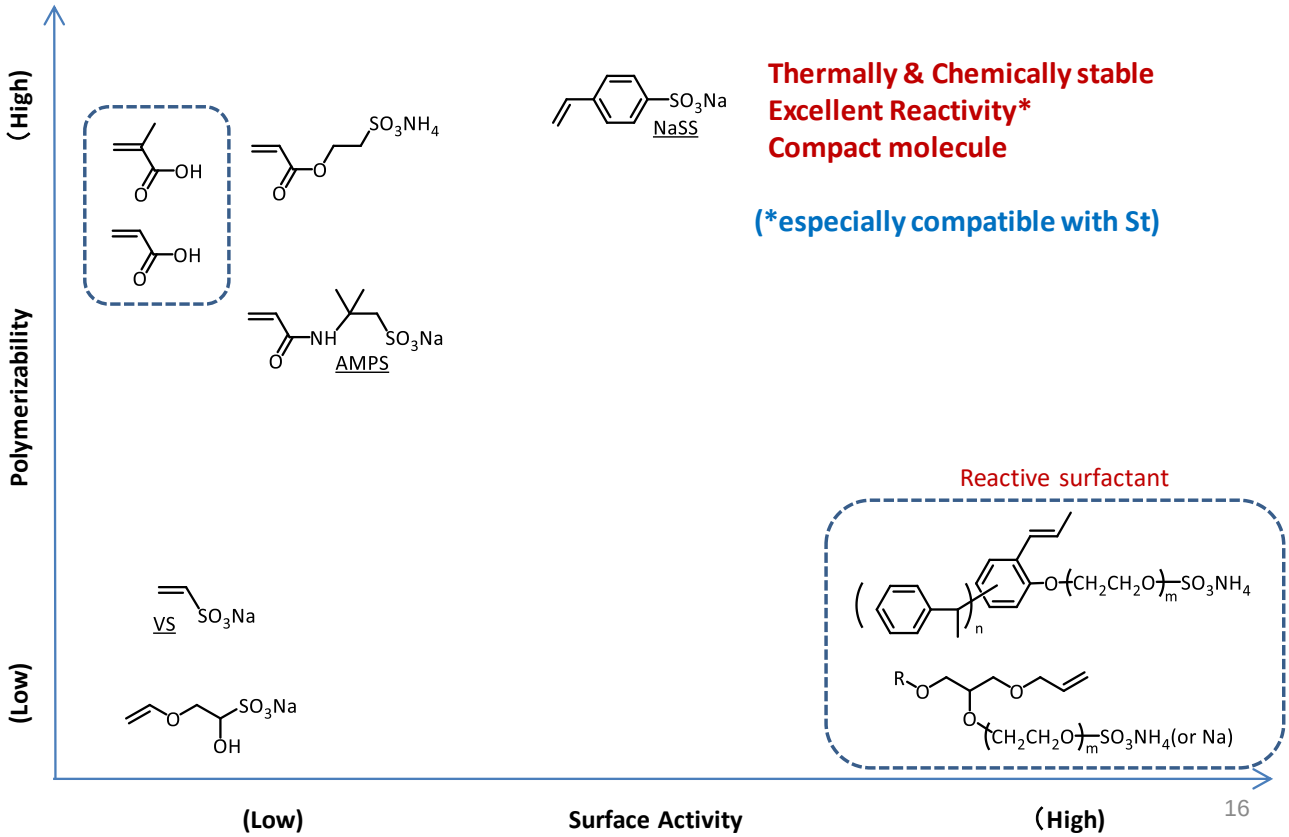




Stabilized with conventional soap

Stabilized with NaSS or reactive soap

Position of NaSS



Ex.of Soapless St/n-BA Em.Polym (1)

Preparation

Recipe	(phm)
Emulsifier*	= 0～4.00
$NaHSO_3$	= 0.25
Water	= 47.31
St	= 50.00
n-BA	= 50.00
Comonomer**	= 2.00
Water	= 46.86
APS	= 0.50
Water	= 43.80

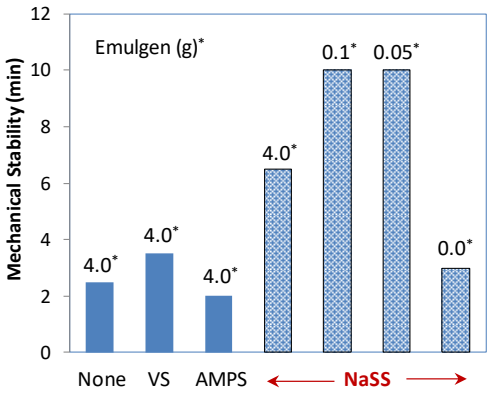
Reactor → 40℃ × 3h → 40℃ × 2h → Emulsion

Emulsion
Solid = 40.8%
Total Conv. = 97.3%
Viscosity = 10.5cps
Particle Size =160nm

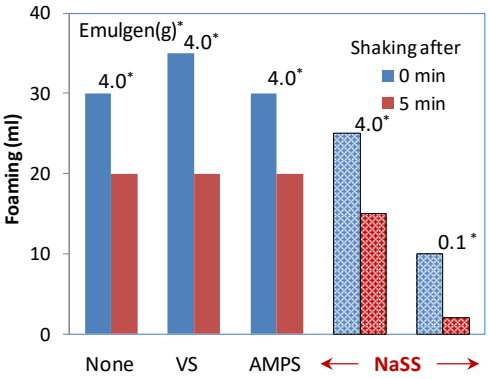
*Nonionic type made by KAO Corp.
**NaSS,AMPS,VS

Benefits of NaSS

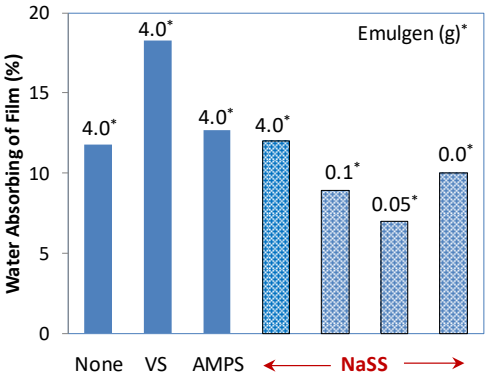
- Reduce conventional soap used
- High Mechanical Stability
- Low Water Absorption
- Low Foaming



(coagulation time by agitation at 5000rpm)



(30ml emulsion diluted 3% solid was put into 100ml cylinder and shaked violently ten times)



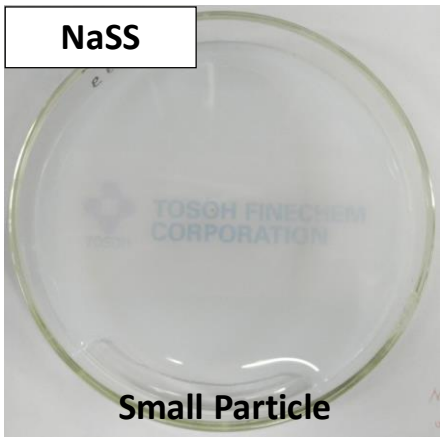
(dried film was immersed in water for 48h at RT)

Ex.of Soapless St(/n-BA) Em.Polym (2)

Styrene	= 33.00	wt%
NaSS or AMPS	= 1.00	mol% (1.76phm)
DBS	= 0.02	mol% (0.05phm)
KPS	= 0.10	mol% (0.14phm)
Water	～ 66	wt%

65℃ × 3h → Polystyrene Emulsion

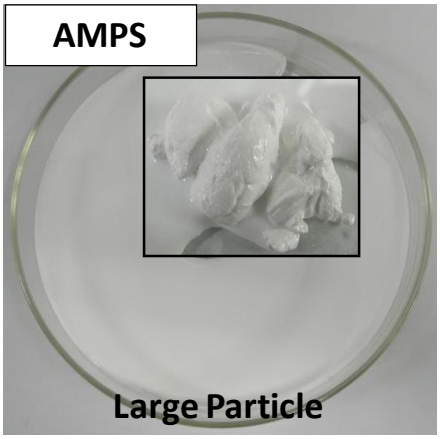
NaSS



Small Particle

Conv.～98%/3h
（Aggregates < 1%）

AMPS



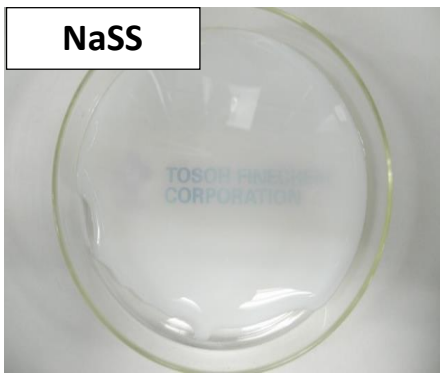
Large Particle

Conv.～24%/1h
（Aggregates～65%）

St/n-BA(=1/1)	= 33.00	wt%
NaSS or AMPS	= 1.00	mol%
DBS	= 0.02	mol%
KPS	= 0.10	mol%
Water	～ 66	wt%

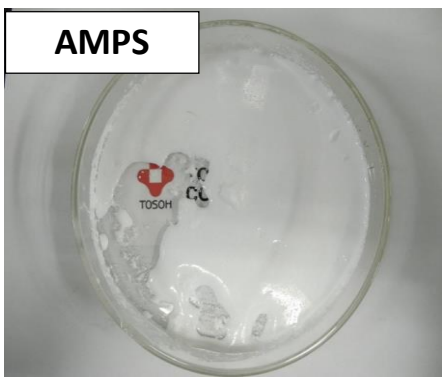
65℃ × 3h → Copolymer Emulsion

NaSS



Conv. : 93%
Aggregates : <1 %

AMPS



Conv. : 70%*
Aggregates : ～20%
(*Plaster-like)

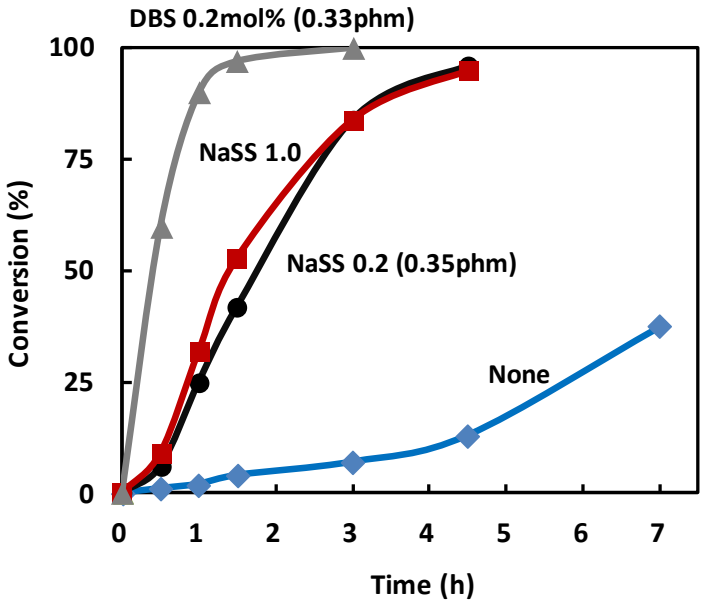
Ex.of Soap-Free Em.Polym.of St/n-BA

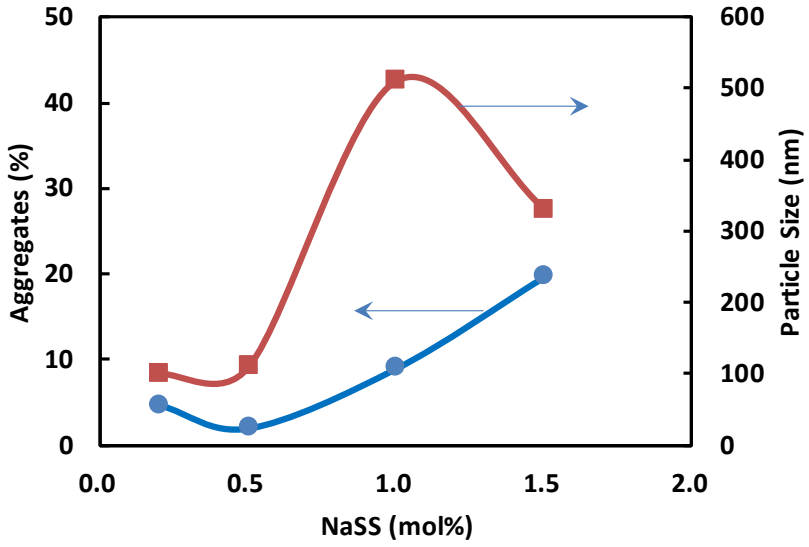
[Quoted from M.Okubo : J. Adhe.Soc.Jap. Vol.18(12),1982,530-535] (joint research)

Recipe

St/n-BA = 1/1 wt.r
NaSS or DBS = variable
KPS = 0.2 mol%/MM
Water (Total monomer=20wt%)

→ 70℃ × 5h





Alkaline buffer increases water absorption of film

Recipe

- St/n-BA = 1/1 wt.r
- NaSS = 0.25 mol%
- KPS = 0.2 mol%/MM
- Buffer A～C = 0.02 mol/L
- Water (Total monomer=33wt%)

↓

70℃ × 5h

↓

Cast Film

A : $Na_2CO_3/NaHCO_3$=1/1mol.r (pH=8.7)
B : KOH/KH_2PO_4=1/2mol.r (pH=6.5)
C : None (pH=10.8 → 2.8)

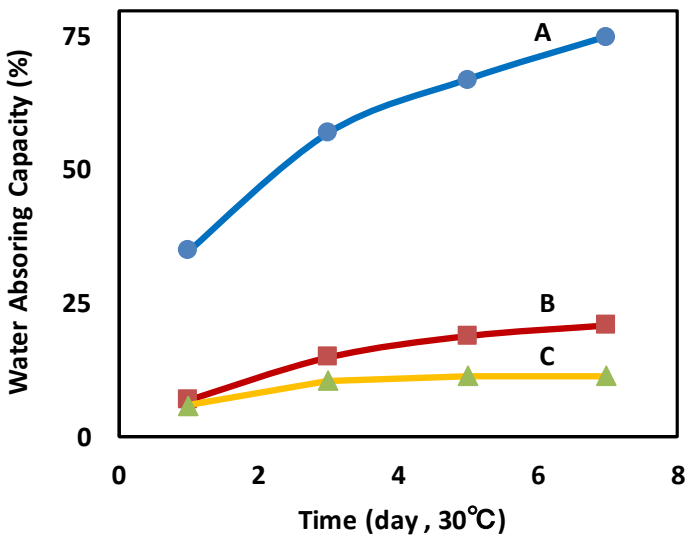
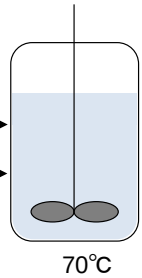


Fig. Effect of Buffer on Water Absorbing Capacity of Film

NaSS dosing condition impacts water absorption

Initial Dose

St/n-BA=1/1 wt.r
(A) NaSS=1mol% × 100～0%
KPS=0.2mol%/MM
Water
(total MM = 16.8wt%)



2nd (Stepwise) Dose

(B) NaSS=1mol% × 0～100%

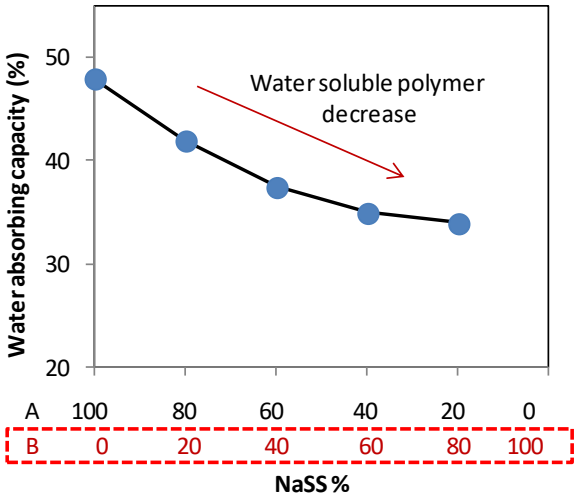
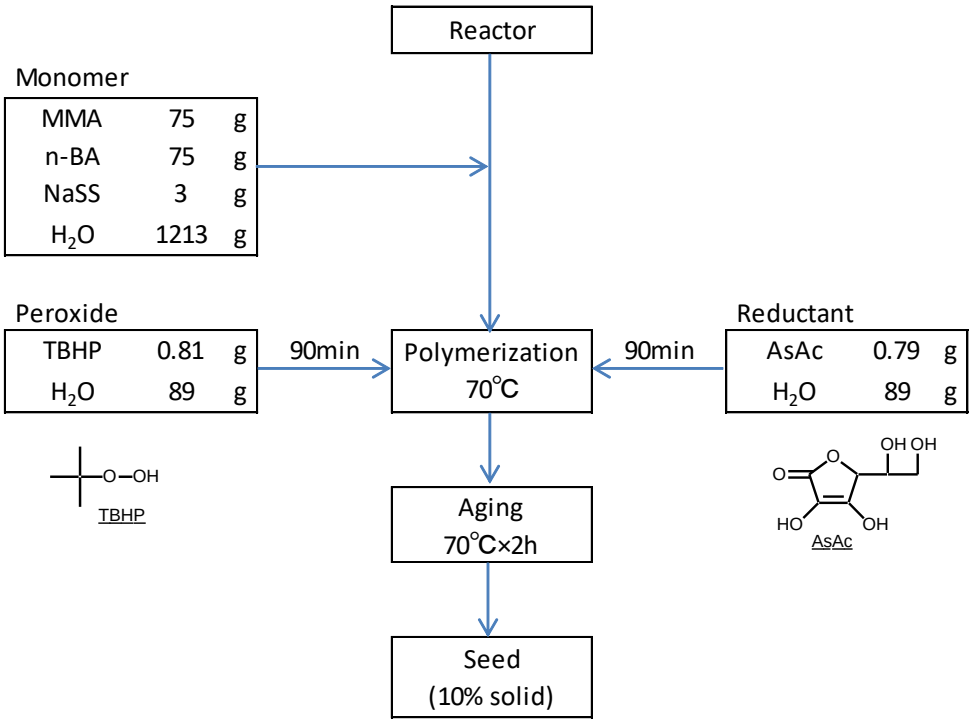


Fig. Effect of NaSS dosing condition on the water absorbing capacity of film (30℃ × 72h)

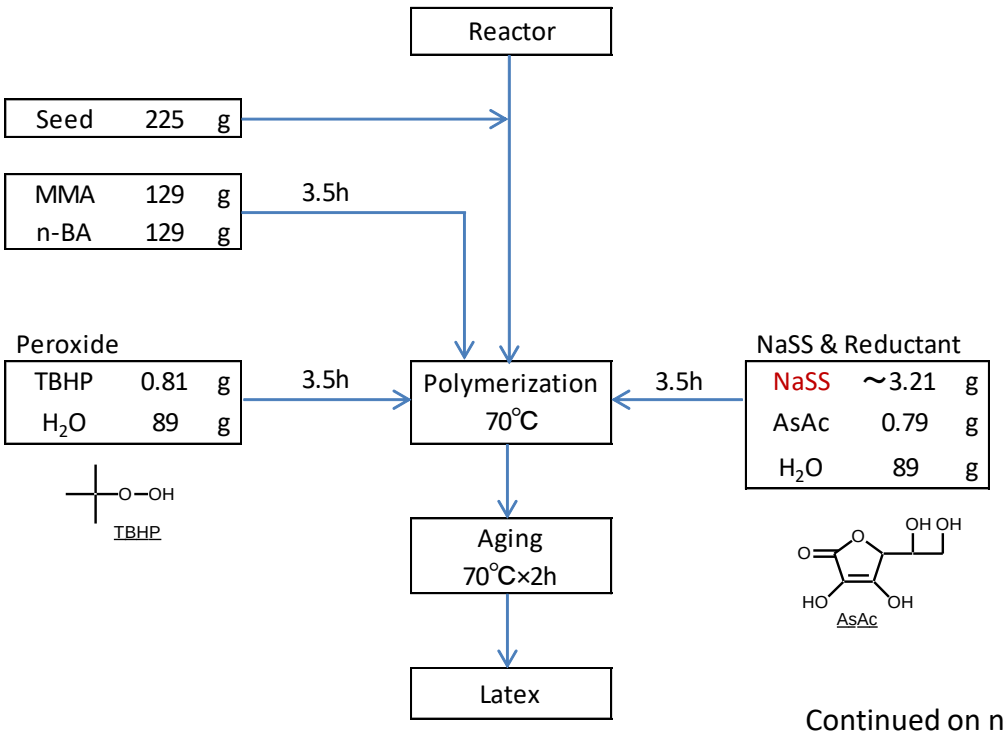
Ex.of Soap-free Seed Em.Polym. of MMA/n-BA (1)

[Quoted from Jose M.Asua : European Polymer Journal 93 (2017) 480-494]

[Seed preparation]



[Seeded emulsion polymerization]



Continued on next page

NaSS gives excellent colloidal stability and clean surface

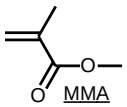
	Basic Characteristics of Latex				Salt Tolerance [Coagulation(%)]			Freeze Thaw Stability [Z-ave change(%)]	
NaSS (wt%/MM)	-SO_3Na (mmol/kg)	Surface Tension (mN/m)	ζ-potential (mV)	Z-$_{ave}$ (nm)	0.02M $CaCl_2$	0.05M $CaCl_2$	1M NaCl	1st cycle	3rd cycle
3.6	86	51.8	58.4	281	<6	<6	<6	<6	
1.3	31	54.8	52.8	241	<6	massive coagulation			
1.0	24	58.1	52.6	251	<6				
0.5	12	63.3	51.0	250	<6			massive coagulation	
SDS=1.2	21	40.9	46.6	255	19				

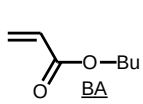
$C_{12}H_{25}$—O—SO_3Na
SDS

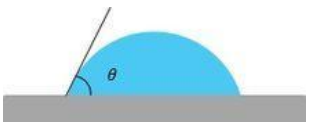
	Contact Angles			Moisture Permeability ($g \cdot mm/m^2$)
NaSS (wt%/MM)	Before Washing	After Washing	Gloss at 20°	
3.6	32.5	–*	66.4	-
1.3	68.4	69.4	64.3	59
1.0	71.1	69.7	69.1	14
0.5	69.8	69.9	66.1	10
SDS=1.2	52.4	68.3	56.3	11

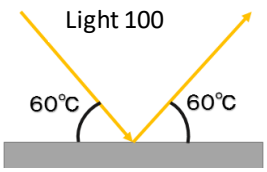
* Integrity lost

$C_{12}H_{25}$—O—SO_3Na
SDS

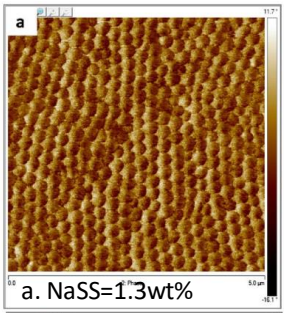


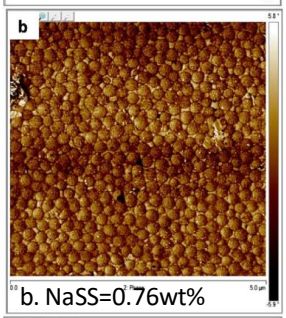


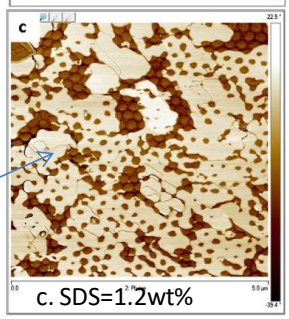




Gross







Surface is covered with SDS
(=white area)

Fig. AFM phase images of film-air interface

Ex.of Soap-free Seed Em.Polym. of MMA/n-BA (2)

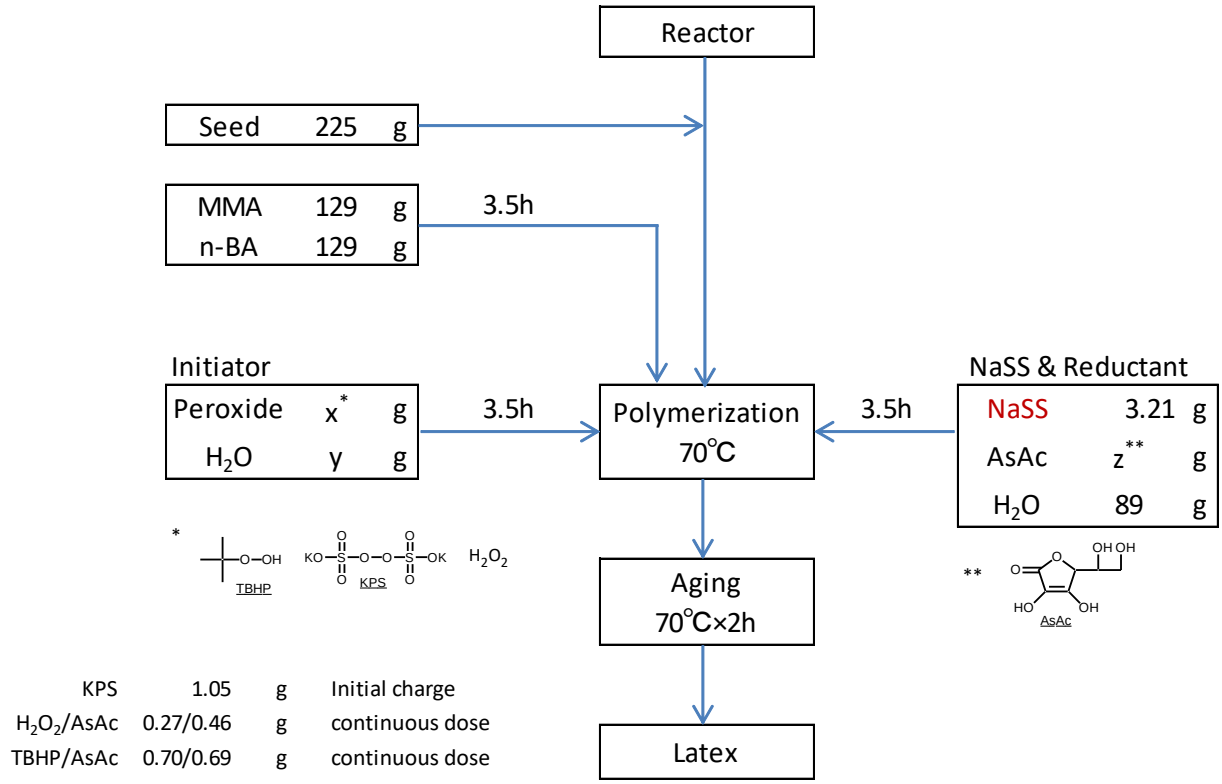
Initiator system impacts on NaSS incorporation

[Quoted from Jose M.Asua : Polymer 117 (2017) 64-75]

[Seed preparation]

- same as page 7

[Seeded emulsion polymerization]



	Basic Characteristics of Latex			Salt Stability [Coagulation(%)]		Freeze Thaw Stability [Z-ave change(%)]	
Initiator System	NaSS Incorporation (%)	Particle Size(nm)	Coagulation (wt%)	0.02M $CaCl_2$	0.5M NaCl	1st cycle	3rd cycle
KPS	60.7	265	1.9	Good	NG	<6	<6
H_2O_2/AsAc	64.1	250	0.7	NG		NG	NG
TBHP/AsAc	72.5	240	0.7	<6	<6	<6	<6

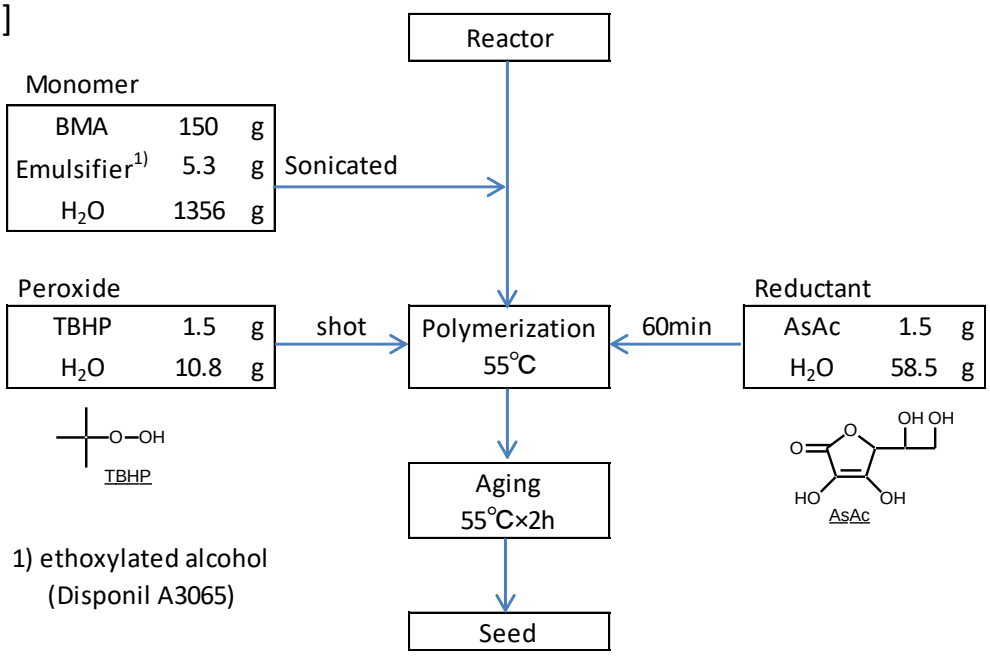
NaSS=1.3wt%/total monomer

Ex.of Soap-free Seed Em.Polym. of n-BMA

Comonomer hydrophilicity impacts on NaSS incorporation

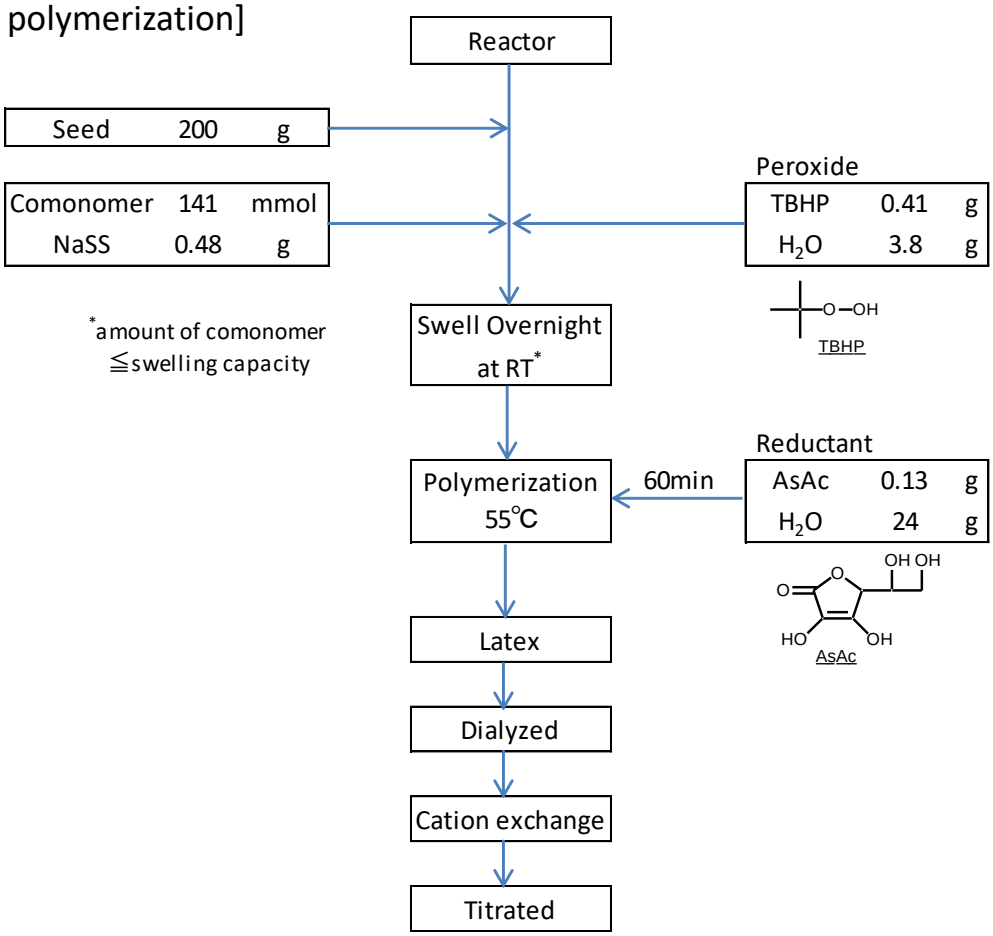
[Quoted from Jose M.Asua : RSC Advances 2016,6,63754-63760]

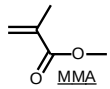
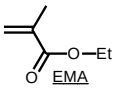
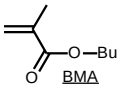
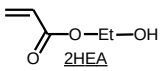
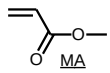
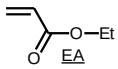
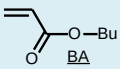
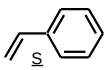
[Seed preparation]



1) ethoxylated alcohol
(Disponil A3065)

[Seeded emulsion polymerization]



Monomer	Solubility in Water (mM) at 25℃	Particle Size (nm)	NaSS incorporation(%)
 MMA	150	188	75.5
 EMA	45	196	57.2
 BMA	4	201	53.8
 2HEA	∞	476	99.7
 MA	650	193	86.9
 EA	150	194	77.6
 BA	11	211	48.7
BA/2HEA=95/5mol%		193	78.9
 S	3.5	197	42.3

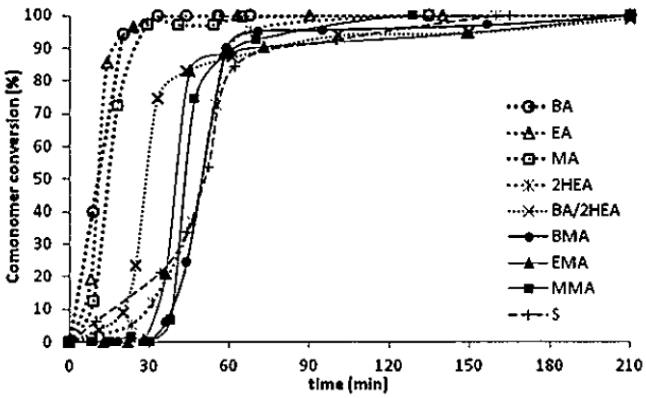


Fig. Time vs Monomer Conversion