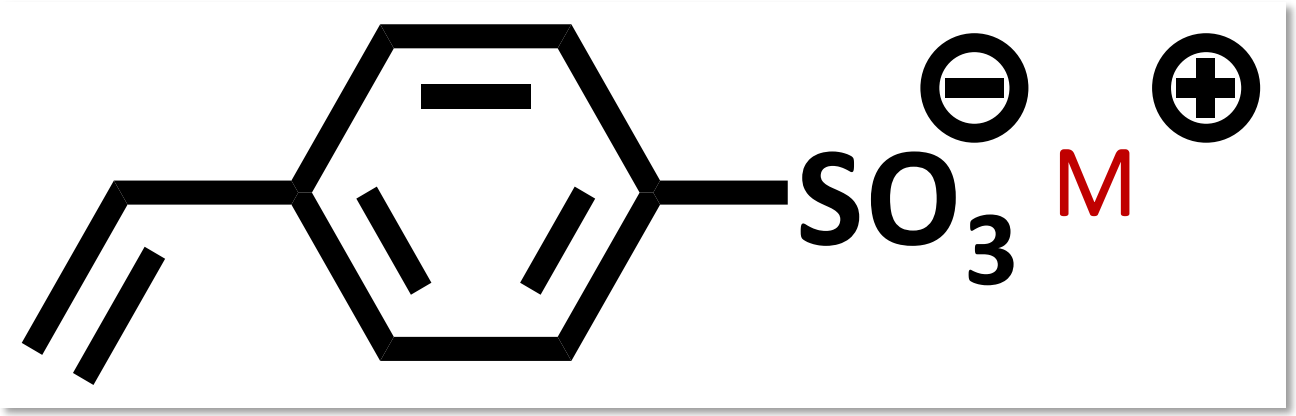
Coatings Trends & Technologies SUMMIT

Characteristics of Styrene Sulfonates and their Application to Coatings

Michael East, Ph.D.

Styrene Sulfonates



- **NaSS** （M=Na）

  Sodium Styrene Sulfonates

- **AmSS** （$M=NH_4$）

  Ammonium Styrene Sulfonates

Agenda

1. Brief history
2. Unique properties of NaSS
3. Application & Usage Examples of NaSS
4. Introduction of “AmSS”

Brief History

- NaSS was developed in the 1950's by Dow as a dye site for acrylic polymers. Since that time, NaSS has been used in styrene-acrylate polymers, water-based acrylic coating, water-based adhesives, descaling polymers for industrial boilers (heat resistance), anti-static coatings, clear coating for drinks containers (heat resistance for printing), oil drilling both as an emulsifier for specialized cement and as a gel breaker for fracking, dispersant for pigments/carbon and carbon nanotubes and a number of other applications.

Agenda

2. Unique properties of NaSS

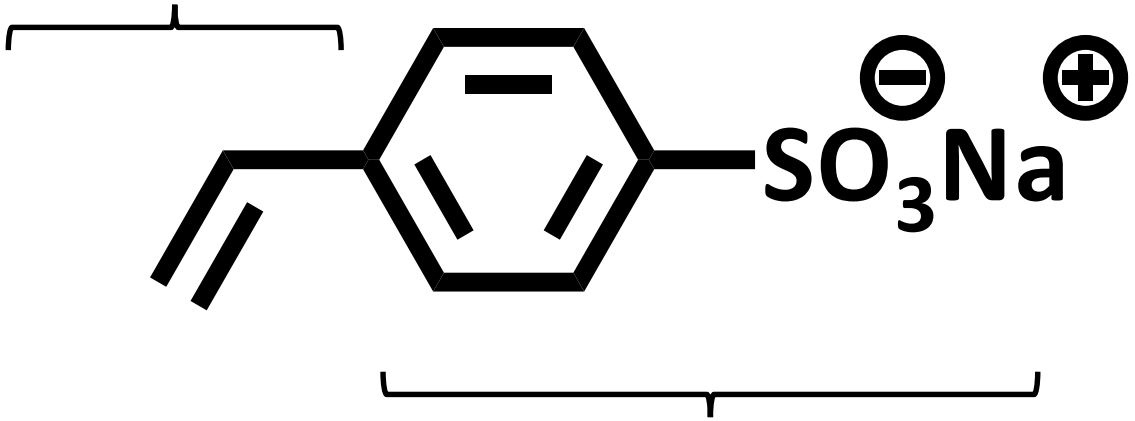
3. Application & Usage Examples of NaSS

4. Introduction of “AmSS”

What is NaSS ?

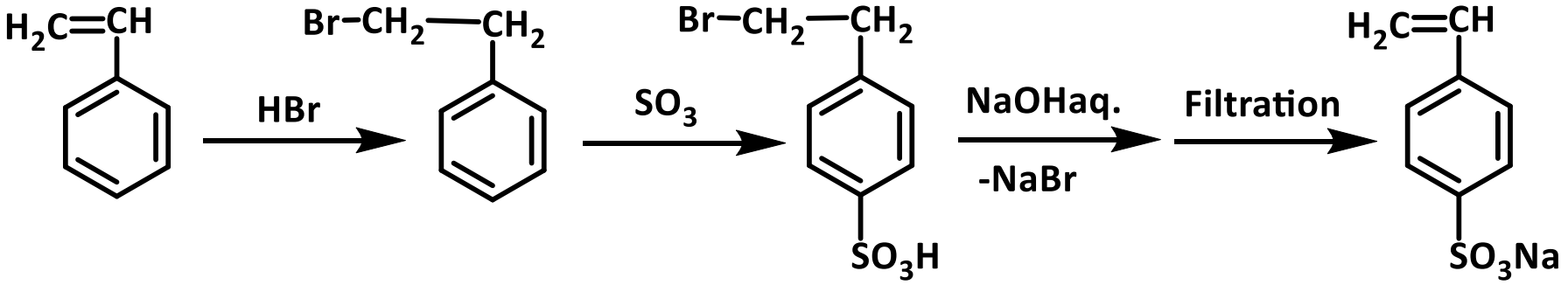
(1) Good Surface Activity

(2) High Reactivity



(3) High Thermal Stability

What is NaSS ?



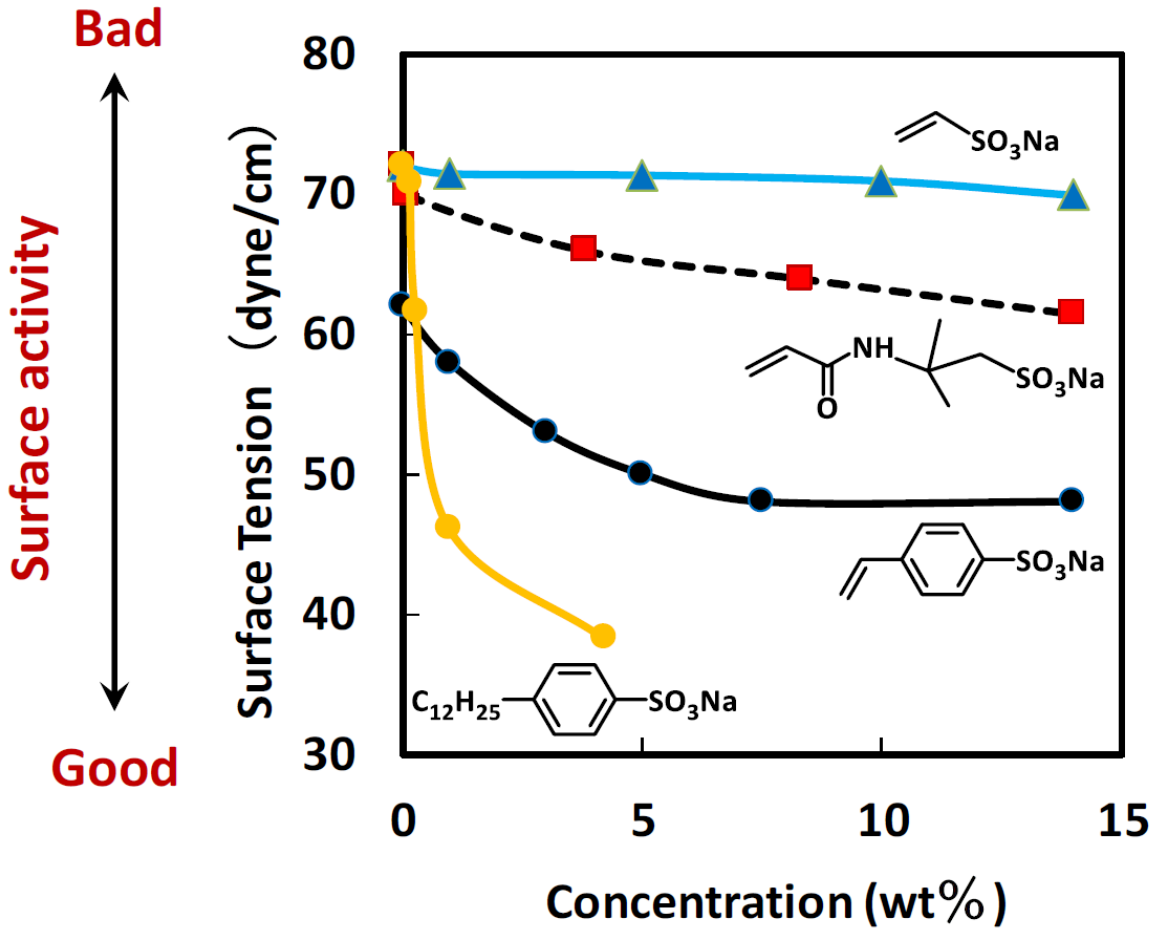
Item		Representative Value[1)]	Specification[1)]
NaSS[2)]	%	88.4[3)]	84～92
NaBr	%	2.2	≦4
Na_2SO_4	%	0.5	≦1
NaOH	%	0.27	≦1
Water	%	8.0	-

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

JP5946094B (filed Oct.16, 2012)
JP5930307B (filed Oct.15, 2012)
US9,505,713B2 (filed Sep.2, 2013)
TWI579261B (filed Nov.15,2012)
CN1047365216B (filed Sep.2, 2013)
MY-186412-A (filed Sep.2, 2013)
JP7365444B2 (filed Mar.9, 2022)

Good Surface Activity

Well suited for emulsion polymerization, dispersant



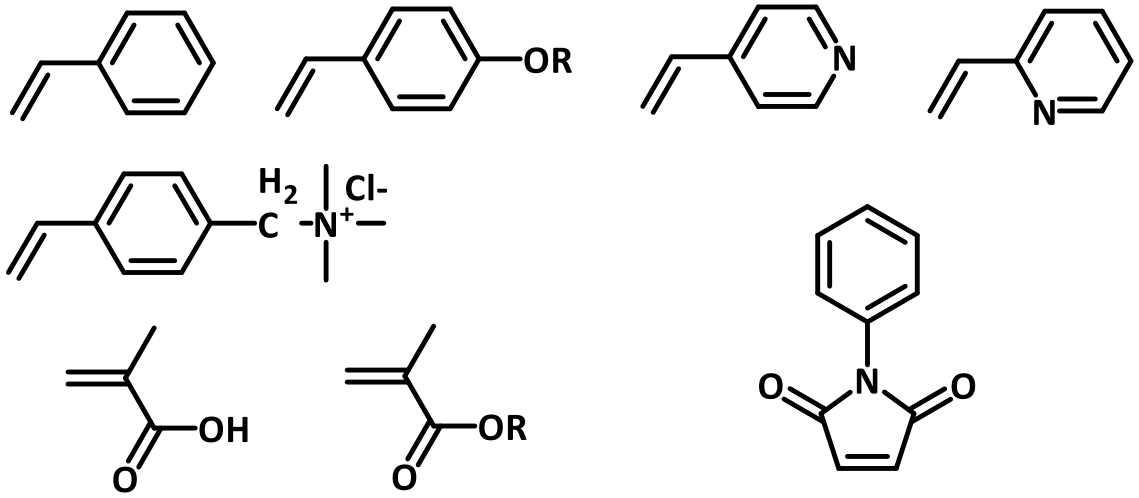
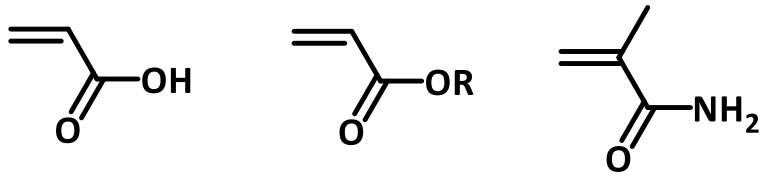
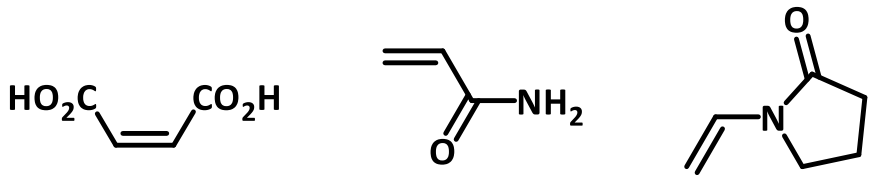
Wilhelmy method
(Pt plate, 25℃, solution in water)

Excellent Radical Reactivity

Good compatibility with conjugated monomers such as Styrene, Methacrylate

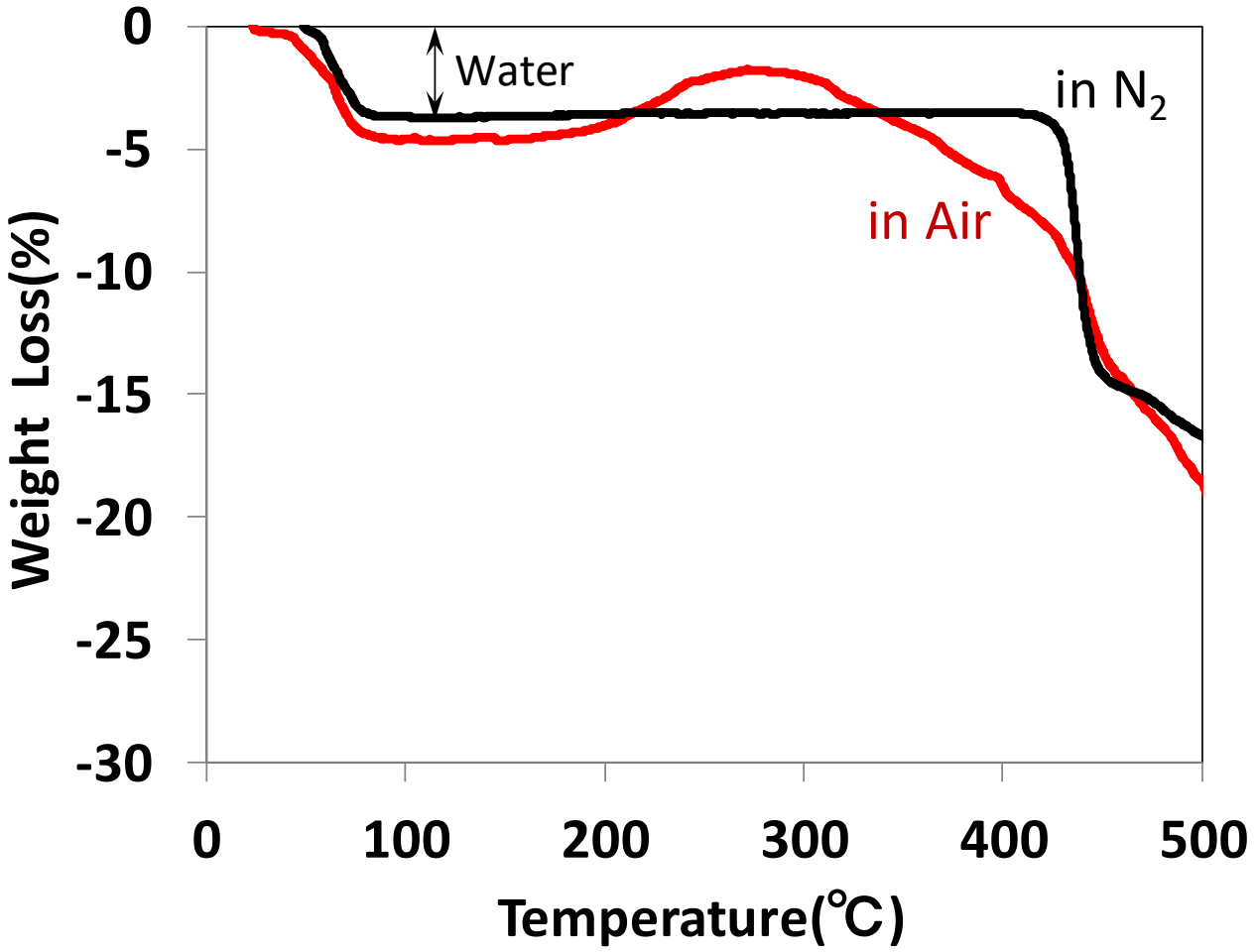
Monomer	Q	e
NaSS	2.49	-0.59
2-Acrylamid-2-methylpropane sulfonic acid	0.39	0.22
Sodium methalyl sulfonate	0.23	0.28
Sodium vinyl sulfonate	0.06	0.41
Sodium allyl sulfonate	0.15	-0.24
Methacrylic acid	2.34	0.65
Sodium methacrylate	1.36	-1.18
Acrylamide	1.15	1.30
Methacrylamide	1.46	1.24
N-Vinylpyrrolidone	0.14	-1.14
Maleic acid	0.75	1.50

Copolymerizability with NaSS

Compatibility	Comonomer
Excellent	
Fair	
Poor	

High Thermal Stability

Well suited to applications that involves high temp. condition



Agenda

3. Application & Usage Examples of NaSS

4. Introduction of “AmSS”

Applications

Emulsion polymerization

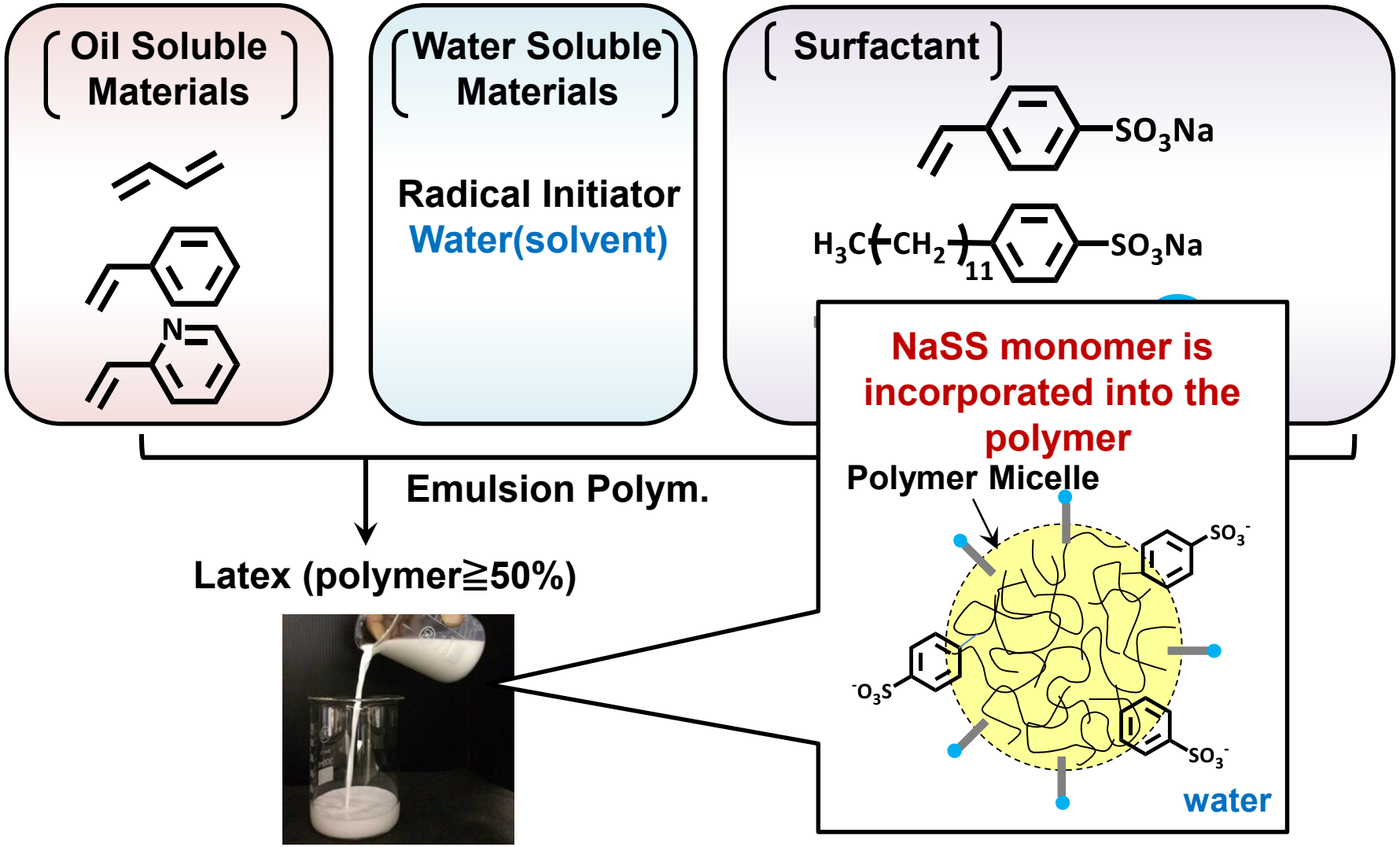
- Water-based acrylic paint
- Drink container coating
- Water-based adhesives
- Acrylic fiber

Solution polymerization

- Anti-static Coating
- Pigment dispersion
- Anti-scaling agent
- Oil drilling (gel breaker)

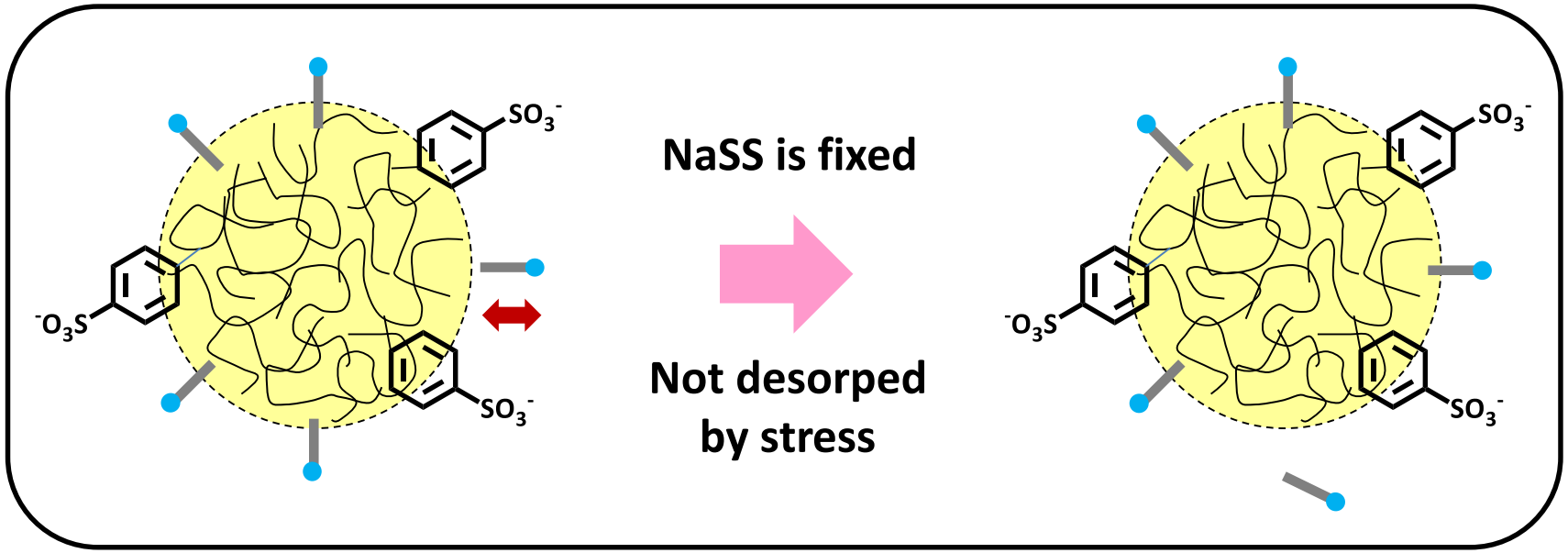
※Numerous other applications are possible.

Latex stabilized by NaSS



Benefits of NaSS

- Improvement of colloidal stability by the fixed NaSS
- Adhesion increases by the reduction of surfactant



Usage Example：Soap-Less Emulsion Polymerization

Component A	(phm)
Emulsifier*	0～4.0
Sodium hydrogen sulfite	0.3
Water	47.3
Component B	**(phm)**
Styrene	50.0
Butyl acrylate	50.0
Component C	**(phm)**
Additive monomer**	2.0
Water	46.9
Component D	**(phm)**
Ammonium persulfate	0.5
Water	43.8

*Nonionic surfactant
**Additive monomer: NaSS, AMPS, VS

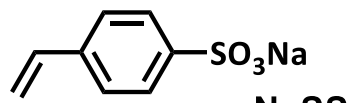
A additive

40°C × 3 hrs.

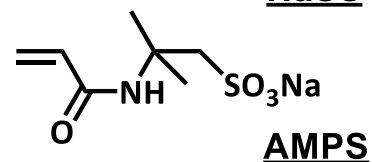
B, C, D Additives

40°C × 3 hrs.

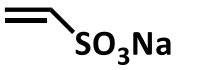
Additive monomer
NaSS, AMPS,VS



NaSS



AMPS



VS

Emulsion

Solid content = 40.8%
Conversion rate = 97.3%
Viscosity = 10.5cps
Grain diameter = 160nm

Properties of Emulsion : Benefits of NaSS

- Reduction of conventional soap
  - High Mechanical Stability
  - Low Water Absorption
  - Low Foaming

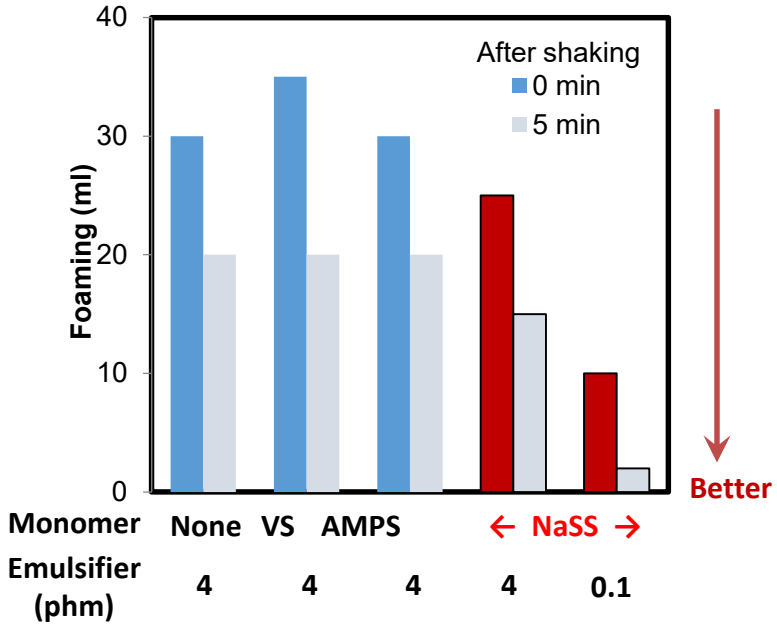


Fig.2 30ml emulsion diluted 3% solid was put into 100ml cylinder and shook violently ten times

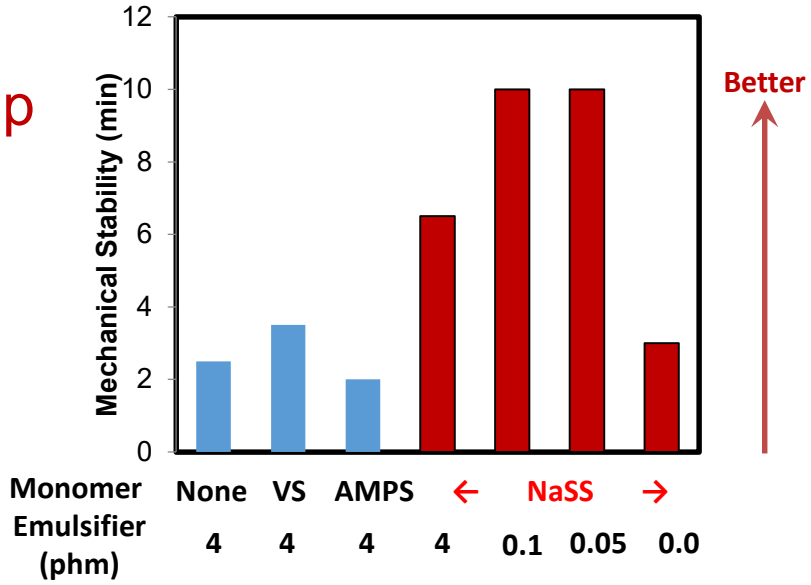


Fig.1 Coagulation time by agitation at 5000rpm

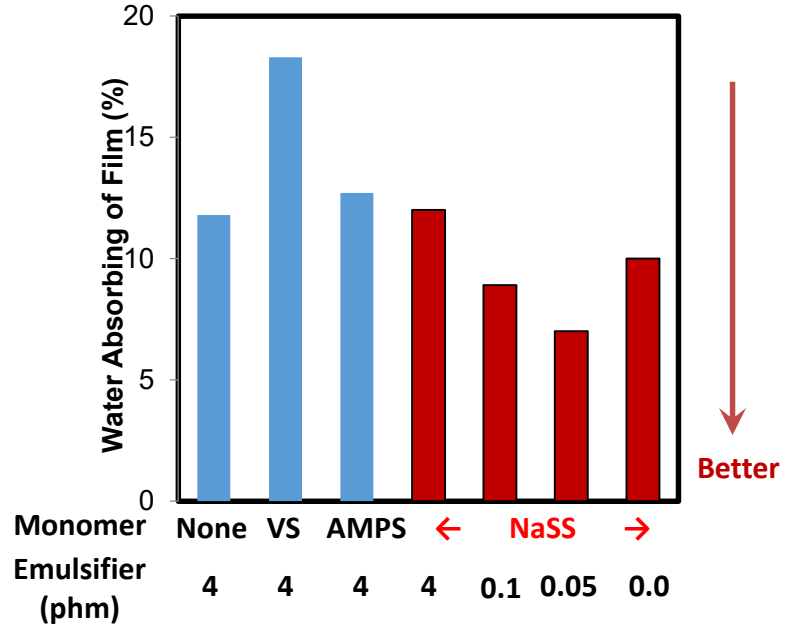
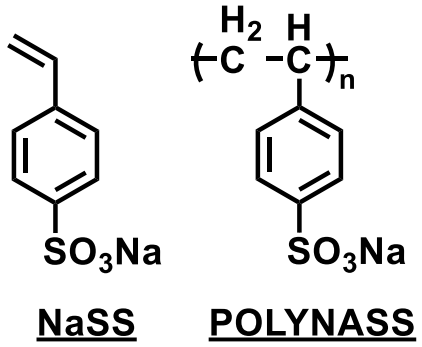


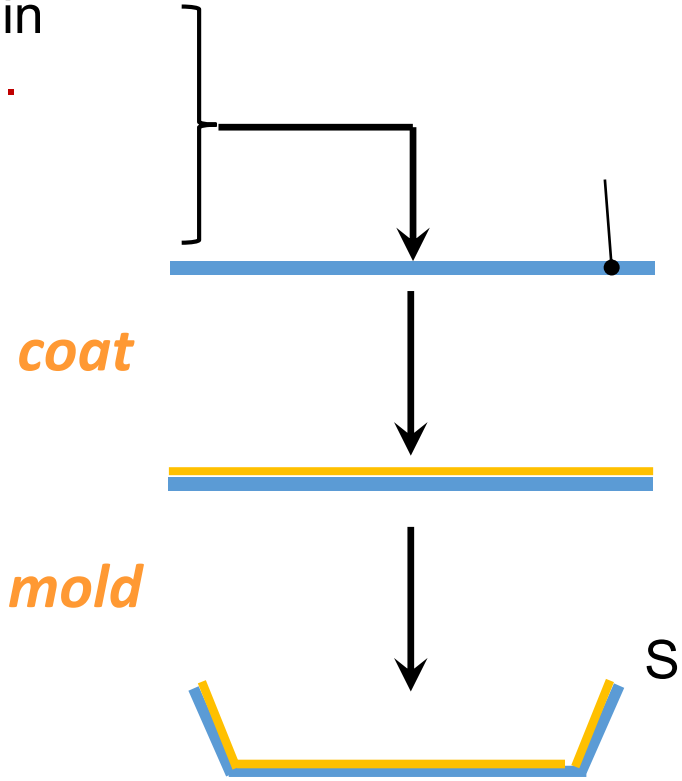
Fig.3 Dried film was immersed in water for 48h at RT

Anti-static Coating：plastic tray

Water-base binder resin
POLYNASS, NaSS aq.
Other additives



NaSS　　POLYNASS



Plastic sheet

Surface resistivity [Ω/□]
2E+06～4E+10

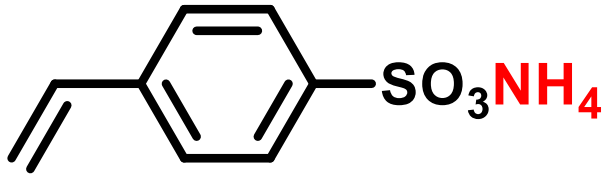
Tray for carrying semiconductor wafers

Agenda

4. Introduction of “AmSS”

What is AmSS ?

Features



1. Metal-Less
2. Organic solvent soluble
3. Good Surface Activity , High reactivity etc…

Basic Infomation

〔Regulatory information〕

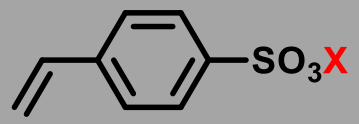
CAS No.	19922-72-6
MITI(JAPAN)	3-1948
TSCA(USA)	-
REACH(EU)	-

〔Composition〕

Item		Representative Value	Specification 【Provisional】
AmSS [1)]	wt%	97.5	≧95
Na^+	wt%	0.3	(≦0.5)
Br^-	wt%	≦0.1	(≦0.1)
Water	wt%	0.1	-

1) Vinyl activity by redox titration

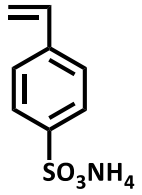
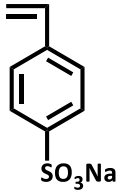
Features of SS monomers

	AmSS (X = NH_4)	NaSS (X = Na)
【Grade】	【Development】	【Commercial】
Solubility	**Good**	**Fair**
Stability *	**Good**	**Excellent**
Heat-resistant	**Good** (decomposition temp.ca.300℃)	**Excellent** (decomposition temp.ca.400℃)
Purity	**Excellent** (≧95%)	**Good** (≧84%)
Metal Content	**Low** (＜0.5wt%)	**High** (11~12wt%)

*Characteristics that make it difficult to spontaneously polymerize.

Solubility in various solvents

Solubility in various solvents

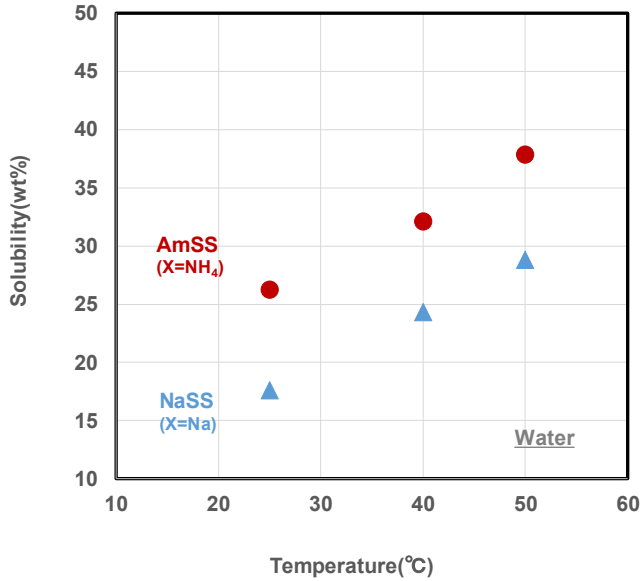
Solvent	 AmSS	 NaSS
H_2O	26.2	21.2
DMSO	43.9	27.3
DMAc	33.2	8.0
NMP	31.5	8.6
DMF	27.0	8.7
DMI	22.0	5.4
MeOH	13.2	4.4
EtOH	3.1	0.3
IPA	0.13	0.03
MeCN	0.04	No data
Acetone	0.03	No data

(wt%, 25℃)

Solubility in water (temperature dependence)

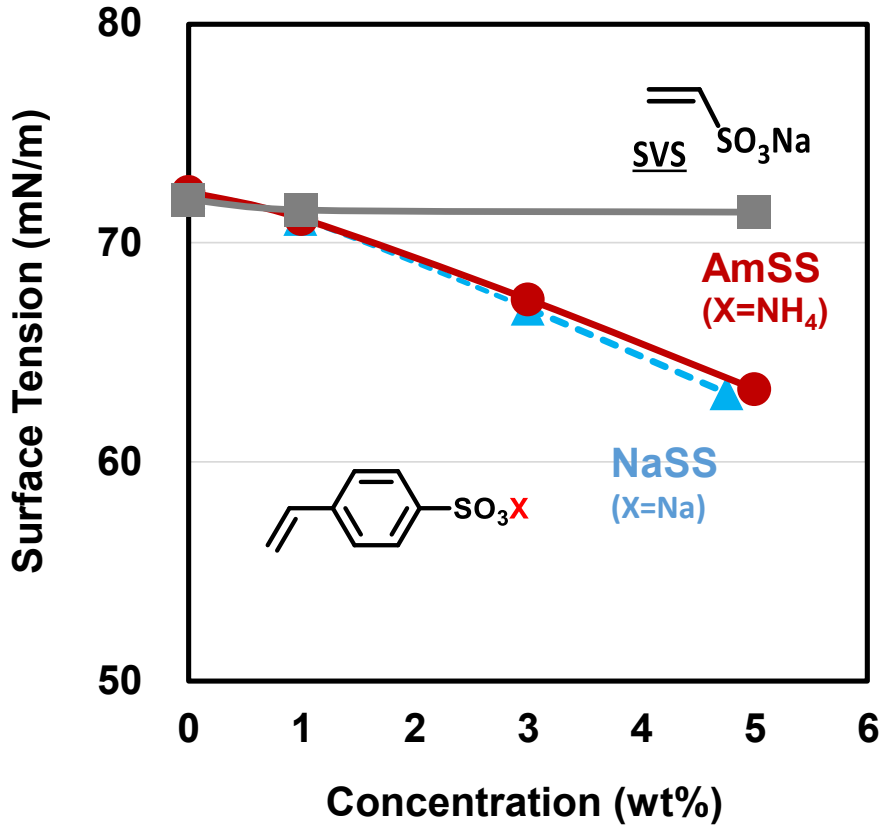
Temp. (℃)	AmSS	NaSS
25	26.2	17.6
40	32.1	24.3
50	37.8	28.8

(wt%)



Surface Activity

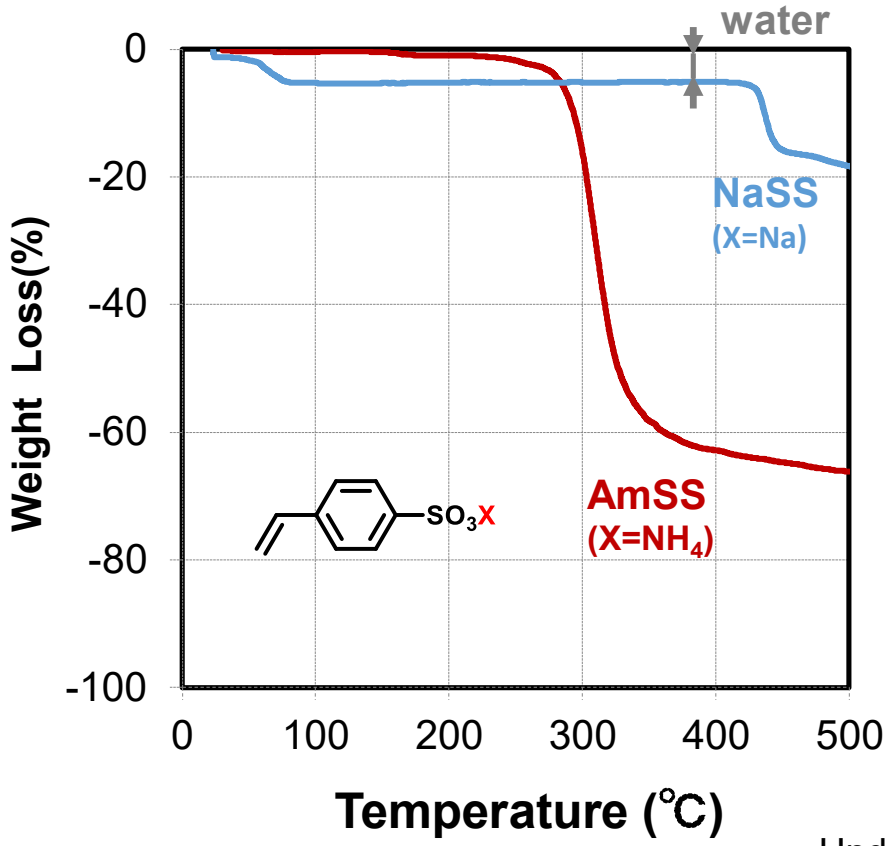
Similar to NaSS, Well suited for emulsion polymerization



Wilhelmy method
(Pt plate, 25℃, solution in water)

Heat-resistant

AmSS also has sufficient heat resistance



Under nitrogen atmosphere
Temp.: R.T. → 500℃, 10℃

Polymerizability

Excellent Radical Reactivity

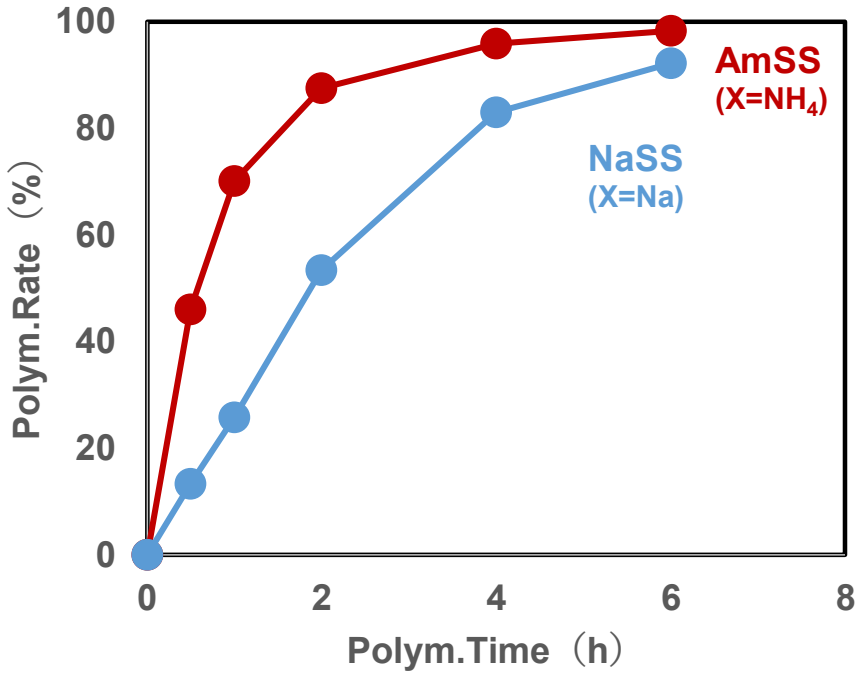
Comparison of homopolymerization in water

< recipe >

- Monomer : 10wt%

pH	AmSS	5.5
	NaSS	11.9

- Initiator V-50 : 0.15mol%
- Solvent : Water
- Temp. : 75℃



Usage Example：Soap-Less Emulsion Polymerization

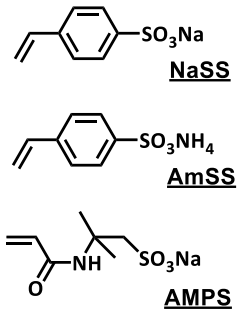
Component	
Styrene	33 wt%
Additive monomer	1 mol%
Emulsifier *	0.02 mol%
Ammonium persulfate	0.10 mol%
Water	~ 67 wt%

* Ammonium Dodecylbenzene Sulfonate

Additives

65°C × 5 hrs.

Additive monomer
AmSS, NaSS, AMPS



Emulsion

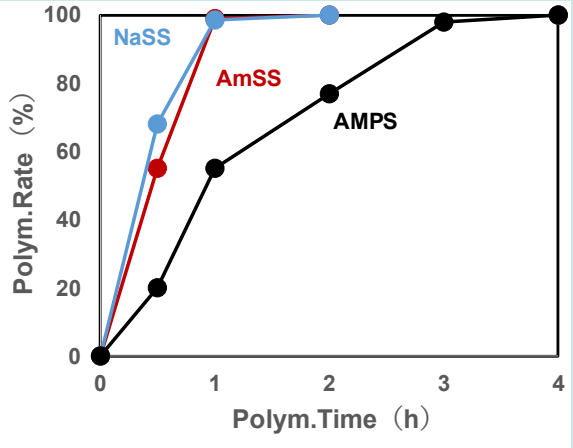


Fig. Time vs overall conversion by the solid content

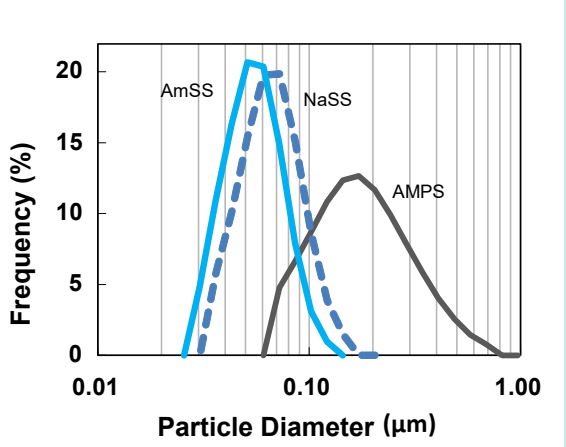
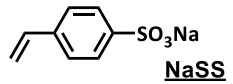


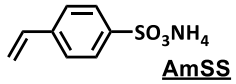
Fig. Particle size distribution measured by DSL

Properties of Emulsion：Benefits of Styrene Sulfonates

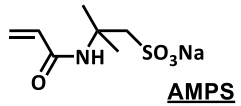
- Same benefits of AmSS and NaSS on emulsion properties



NaSS



AmSS



AMPS

- Low Aggregation
- High Stability to Organic solvent

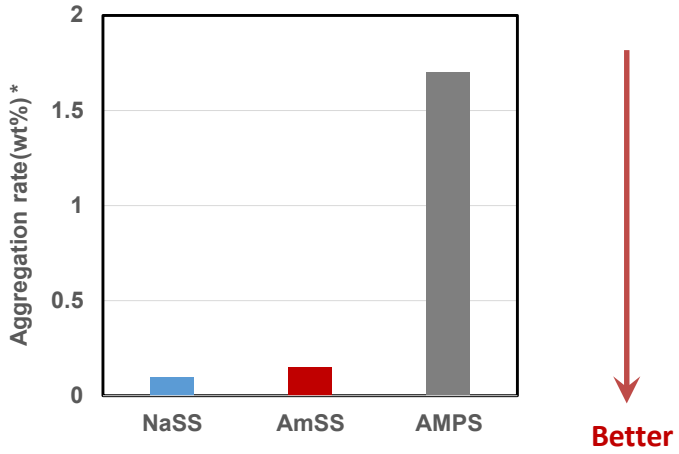


Fig. Aggregation rate after the polymerization (*aggregates/overall monomer × 100)

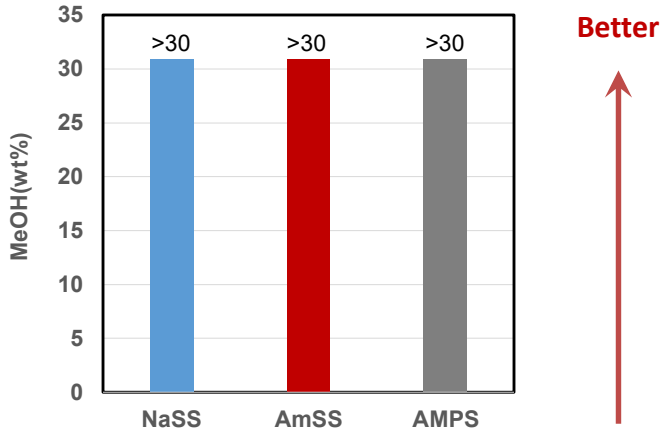
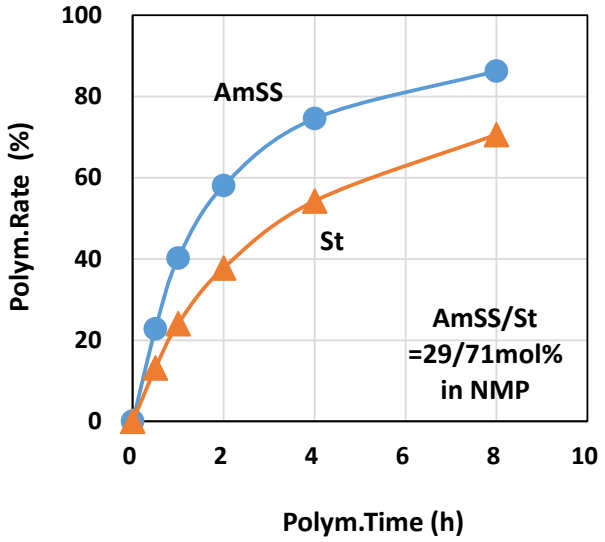
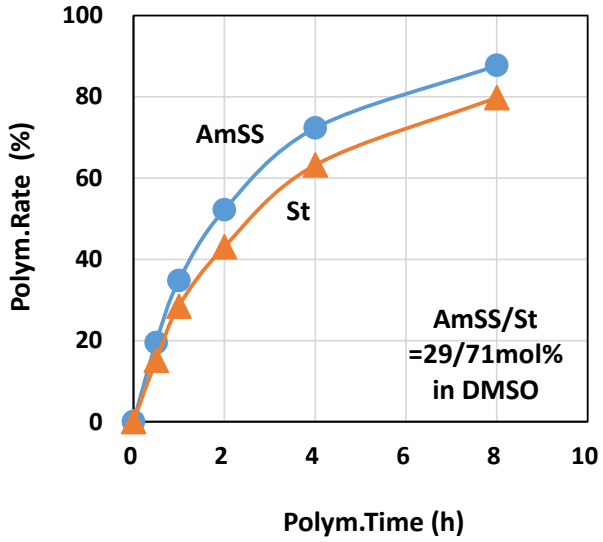


Fig. Stability to Methanol - Methanol conc. to aggregate -

Advantages of AmSS: Solubility

Good solubility and copolymerizability in organic solvents





recipe :

- AmSS/St=29/71mol.r
- Overall Monomer : 31wt%

- Initiator AIBN : 1mol%
- Solvent : NMP or DMSO
- Temp. : 70℃

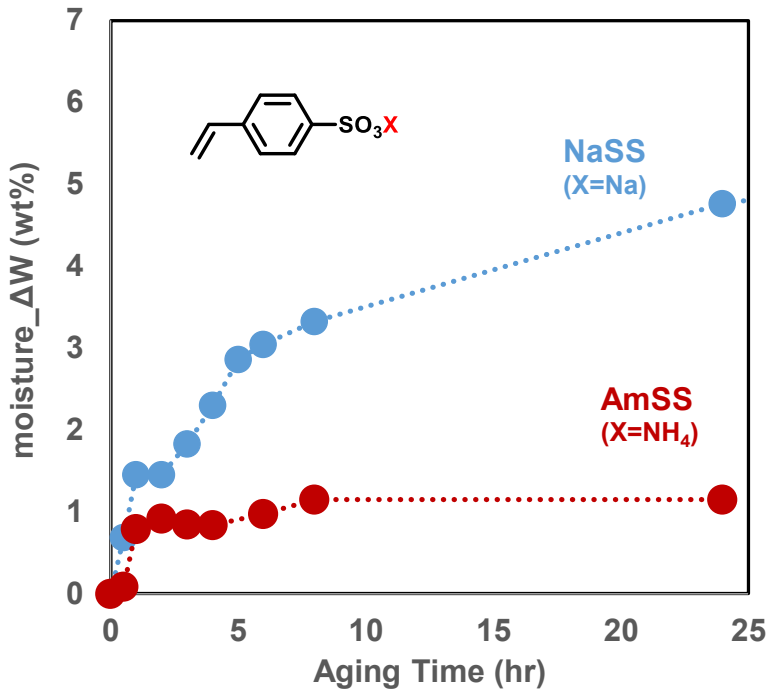
Advantages of AmSS: Metal-less

- Improved moisture and water resistance
- Expanding to metal-free or less applications

  - Special coatings
  - Electronic materials

etc…

<Moisture absorption test>



*After dehydrating the sample by vacuum drying, track the weight change over time under the following atmosphere

- Shelf dryer／Petri dish／powder sample
- 30℃/75%RH

Water resistance: Effect of metal-less

- AmSS-coatings show good water resistance
  - Low swelling, keep strength
  - Prevents clouding of the coating

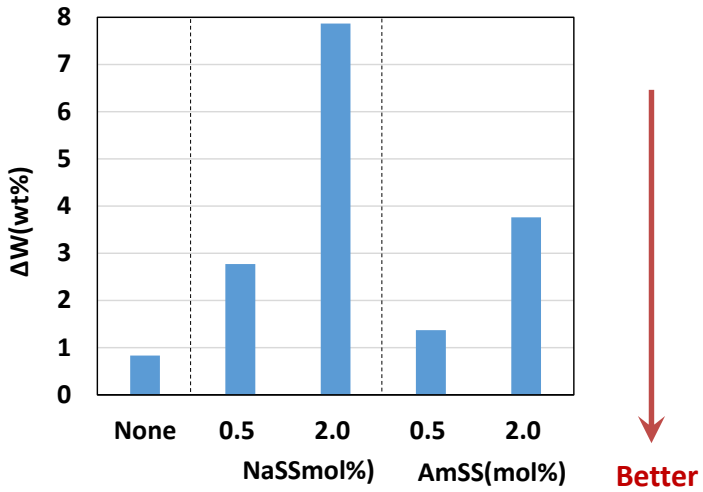


Fig1. Weight gain after immersion

<Polymerization Recipe>
- Monomer
  - St/BA : 50/50wt.r
  - AmSS(NaSS) : 2mol%
  - Overall : 48wt%
- Initiator V-40 : 1mol%
- Solvent : DMAc
- 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℃×25h

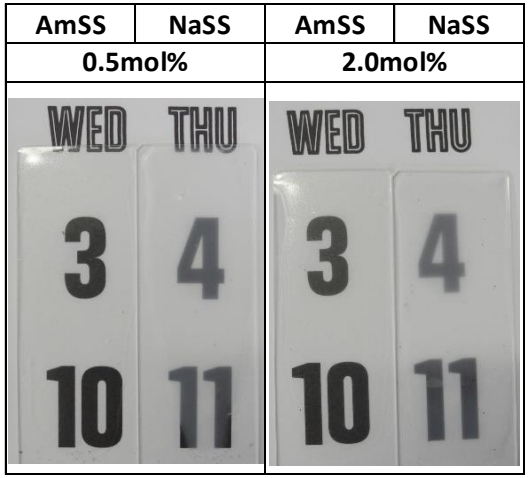


Photo1. Appearance of the film after immersion

Contact

BOOTH NO. 26
TOSOH USA

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