Functional monomers

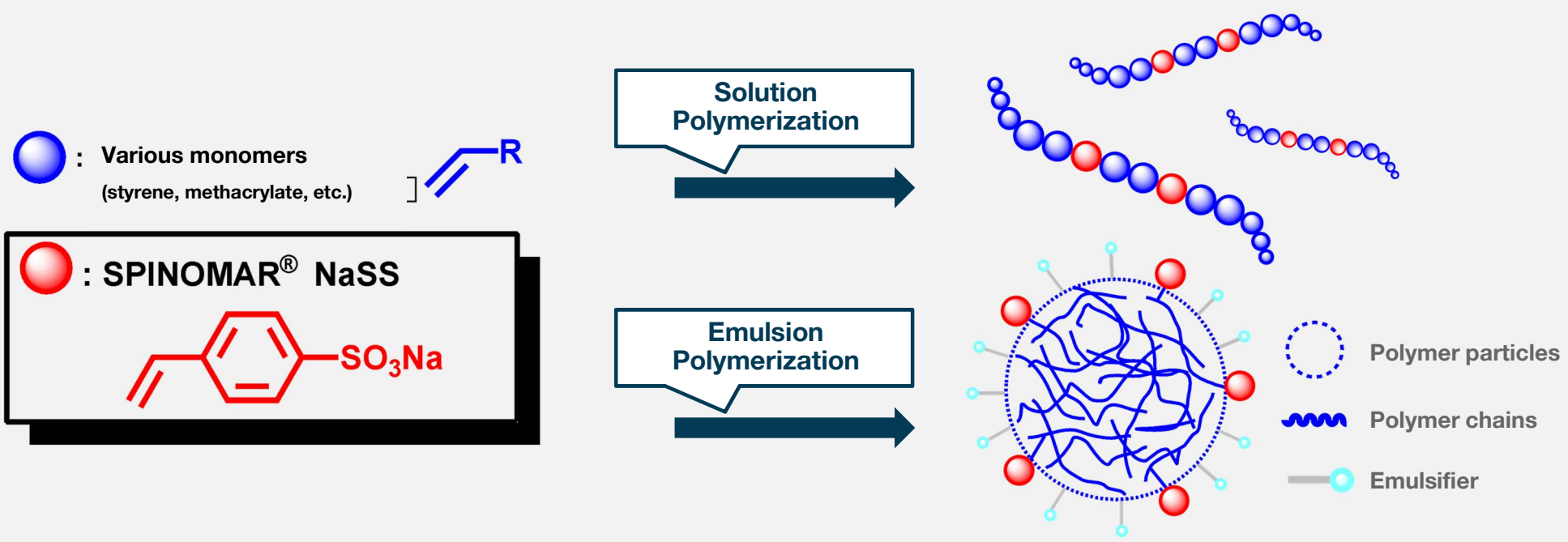
SPINOMAR® NaSS

TOSOH FINECHEM CORPORATION

INDEX

Polymer modification with SPINOMAR NaSS

SPINOMAR NaSS is a sulfonate vinyl monomer that combines excellent surface activity and polymerizability. Copolymerization with acrylic and styrene monomers can impart cationic dyeing properties, thermal and chemical stability, dispersibility, and antistatic properties to various polymers.



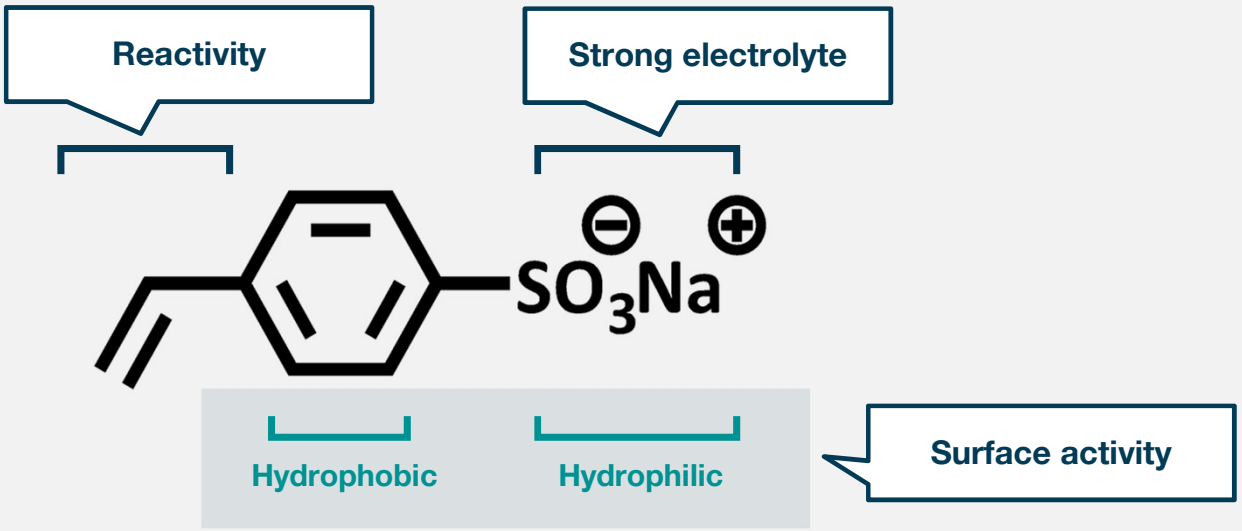
SPINOMAR NaSS Features

○Surface activity
Exhibits moderate surface activity and is suitable for emulsification and dispersion applications

○Strong electrolyte
Ionic compounds that exhibit water solubility due to sulfo groups

○Reactivity
High radical polymerizability; suitable for copolymerization with various monomers

○High heat resistance, excellent storage stability, low toxicity



Feature
1

Surface activity

SPINOMAR NaSS exhibits higher surface activity than other sulfonic acid monomers.
This property, which is attributed to the aromatic ring, makes it suitable for emulsion polymerization and various dispersion applications.

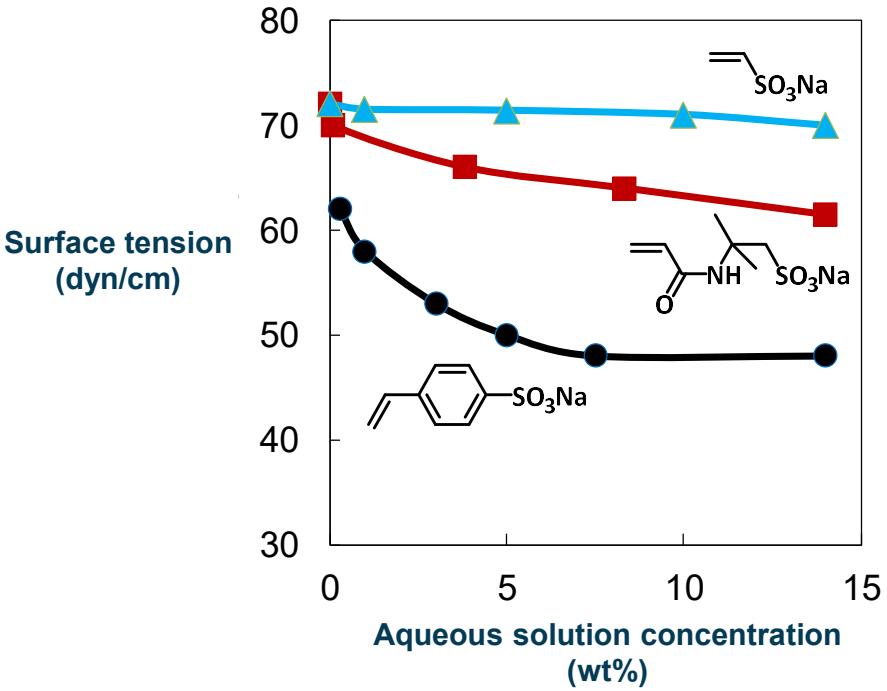


Fig. 1. Surface tension of aqueous sulfonic acid monomer solutions
Wilhelmy method (measured at 25°C , platinum plate)

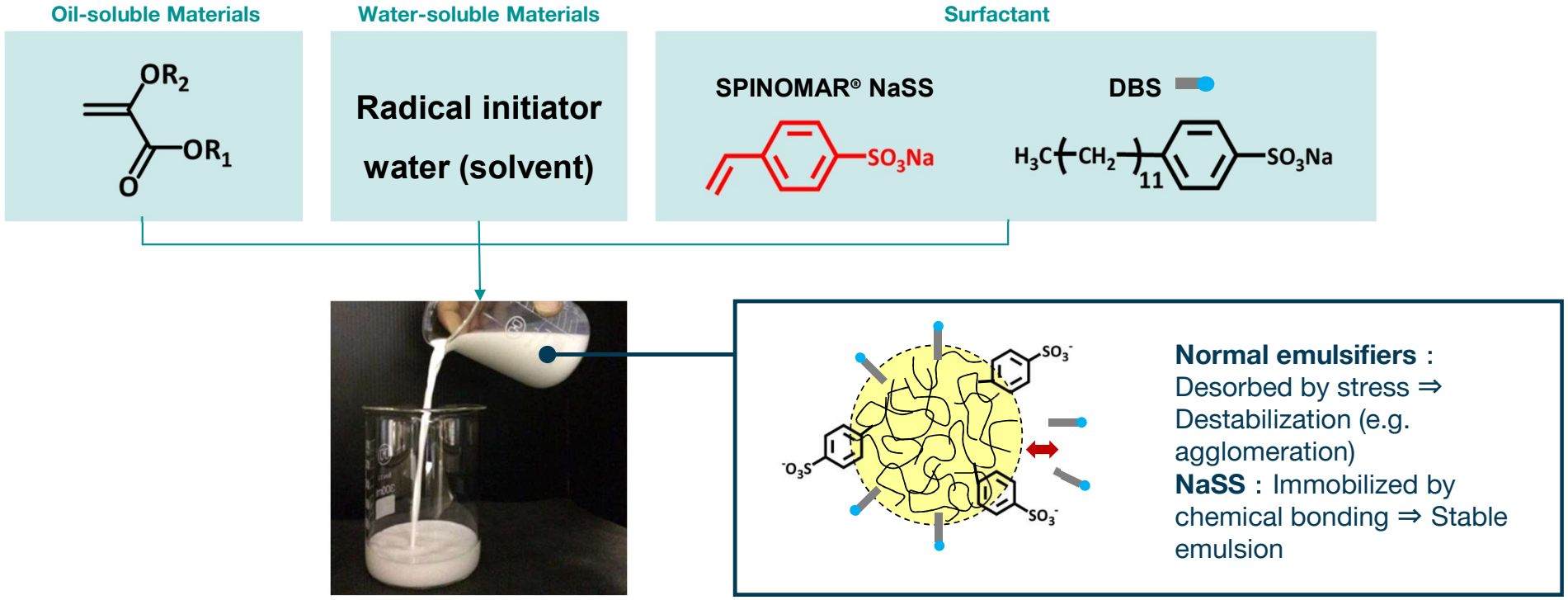
VSNa: Sodium vinyl sulfonate
AMPS: 2-Acrylamido-2-methylpropane sulfonic acid

Feature
1

Surface activity

Emulsion polymerization and effect of NaSS addition

SPINOMAR NaSS is covalently bonded to the surface of polymer particles during emulsion polymerization, and the repulsion between sulfo groups provides excellent colloidal stability.



Feature 2

Reactivity

SPINOMAR NaSS has high radical reactivity and good copolymerization with conjugated monomers such as styrene and methacrylate.
In the case of copolymerization with non-conjugated monomers such as N-vinylpyrrolidone and maleic acid, adjustments must be made to the monomer feed conditions.

Monomer	Q	e	Copolymerizability with NaSS
SPINOMAR NaSS	2.49	-0.59	-
2-Acrylamido-2-methylpropane sulfonic acid	0.39	0.22	-
Sodium vinyl sulfonate	0.06	0.41	-
Styrene	1.00	-0.80	**Good**
Methyl methacrylate	0.74	0.40	
Methacrylic acid	2.34	0.65	
Sodium methacrylate	1.36	-1.18	
Acrylonitrile	0.60	1.20	**Polymerization conditions must be adjusted**
Acrylamide	1.15	1.30	
Methacrylamide	1.46	1.24	
N-Vinylpyrrolidone	0.14	-1.14	
Maleic acid	0.75	1.50	

Q: Degree of resonance stabilization, e: Degree of polarity

Feature 2

Reactivity

Example (1-1) Solution polymerization

Copolymerization of NaSS / n-Butylmethacrylate and NaSS / n-Butyl acrylate

→ Copolymerization proceeds well even in batch preparation.

Fig. 2-1: Conversion rate transition of NaSS-BMA copolymerization*

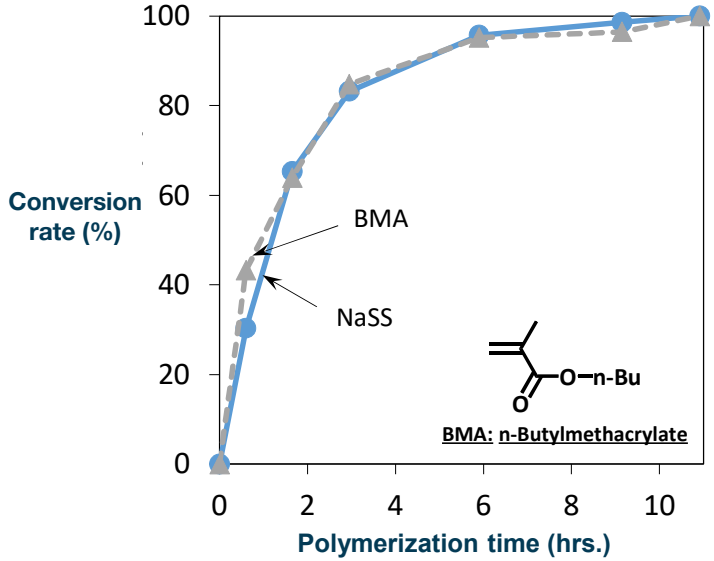
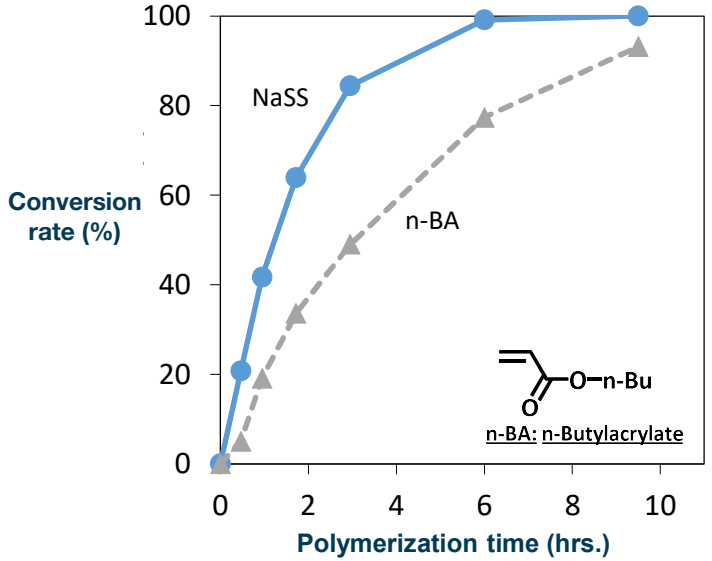


Fig. 2-2: Conversion rate transition of NaSS-n-BA copolymerization*



*NaSS, comonomer (equimolar amount with NaSS), and V-50 (initiator) are prepared in a batch in a water/ethanol mixture and heated to 60°C. Water-soluble initiators can be widely used.

Feature 2

Reactivity

Example (1-2) Solution polymerization

Copolymerization of NaSS / N-vinylpyrrolidone

→ Adjusting the polymerization formulation may enable the copolymerization of monomers with different reactivity.

Fig. 2-3: Conversion rate of NaSS-N-VPD copolymerization (batch)*

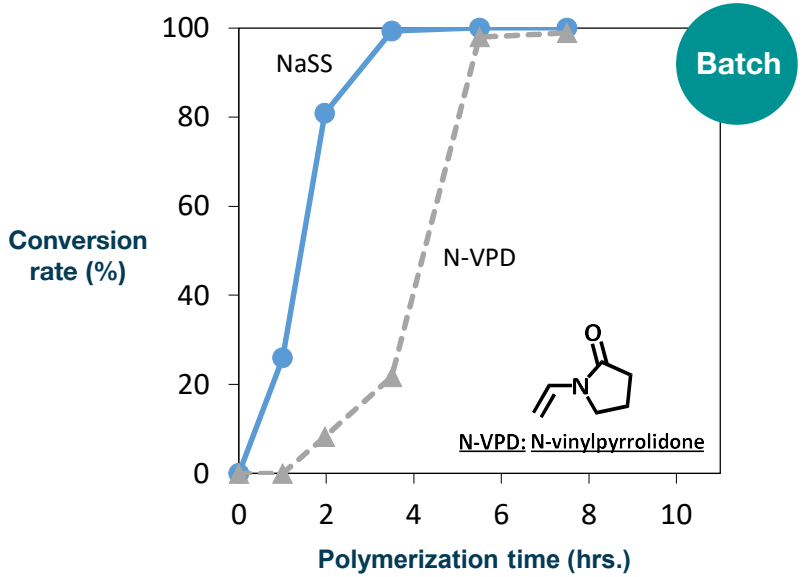
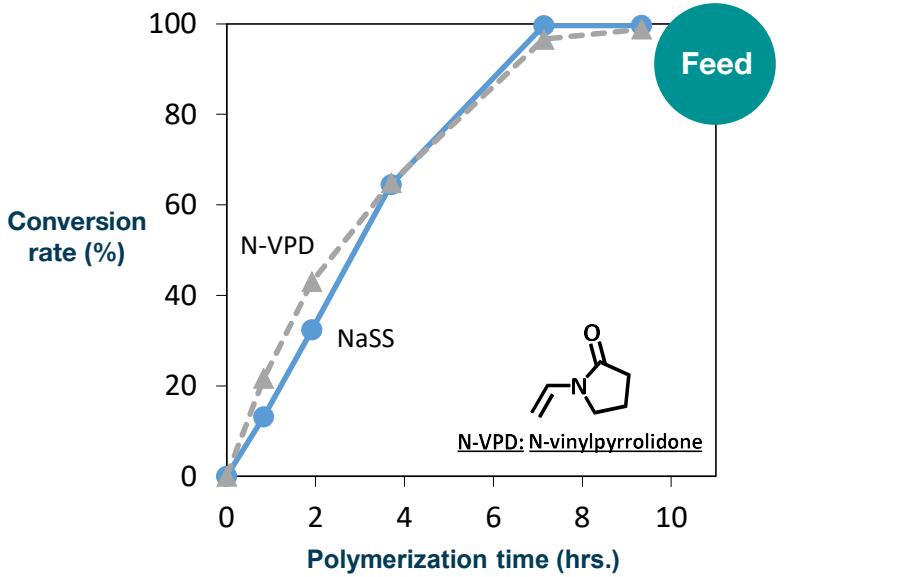


Fig. 2-4: Conversion rate of NaSS-N-VPD copolymerization (feed) transition**



*NaSS, N-VPD (equimolar amount with NaSS), and V-50 (initiator) are prepared in a batch in water and heated to 80°C.
**Heated to 80°C while feeding NaSS, V-50 (initiator) mixture solution into N-VPD aqueous solution (equimolar volume with NaSS).

Feature 2

Reactivity

Example (2) Emulsion polymerization

Example of synthesis of styrene/butyl acrylate emulsion

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

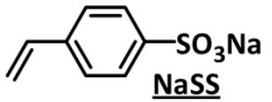
A additive

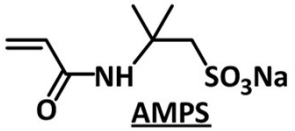
40°C × 3 hrs.

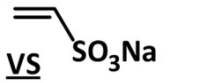
B, C, D Additives

40°C × 3 hrs.

Additive monomer
NaSS, AMPS,VS







Emulsion

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

Feature 2

Reactivity

Comparison of physical properties of emulsions*

High-quality emulsions can be synthesized by adding NaSS

＜Effect of NaSS addition＞
Reduction of general emulsifier additives; improvement of mechanical stability and water resistance; reduction of foaming, etc.

Fig. 3-1: Mechanical stability comparison
(Time to agglomeration at 5000rpm agitation)

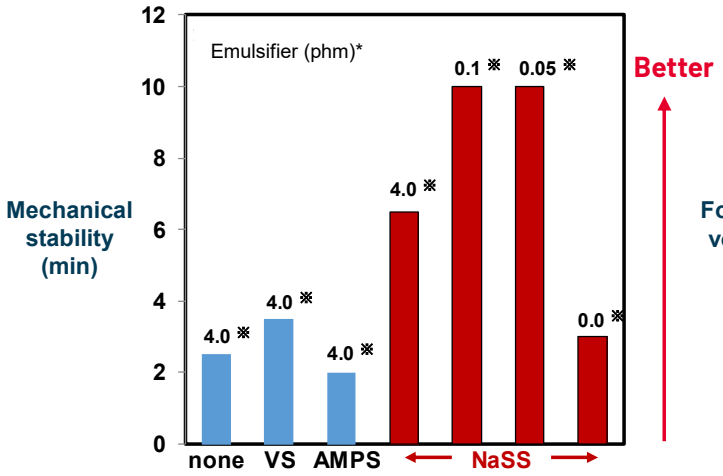


Fig. 3-2: Foaming properties comparison
(Amount of foaming when content with 3% solid emulsion is stirred in a vial)

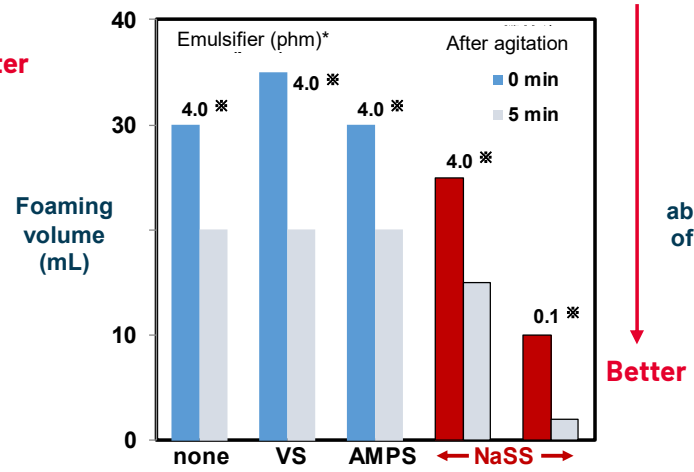
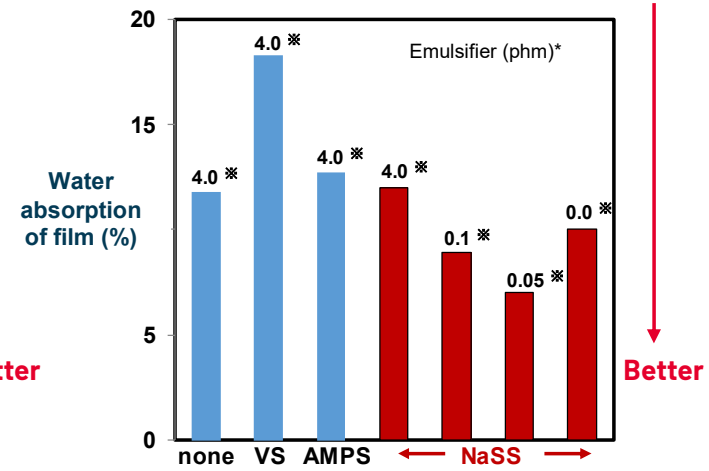
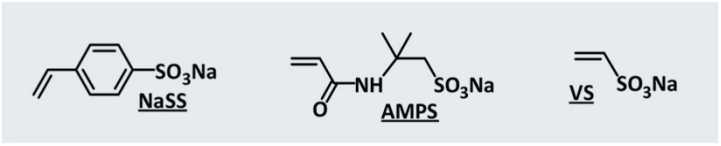


Fig. 3-3: Water resistance comparison
(Dry film immersed in water at room temperature for 48 hours)





*Comparison of physical properties of styrene/butyl acrylate emulsion synthesized in polymerization example (2)

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Feature
3

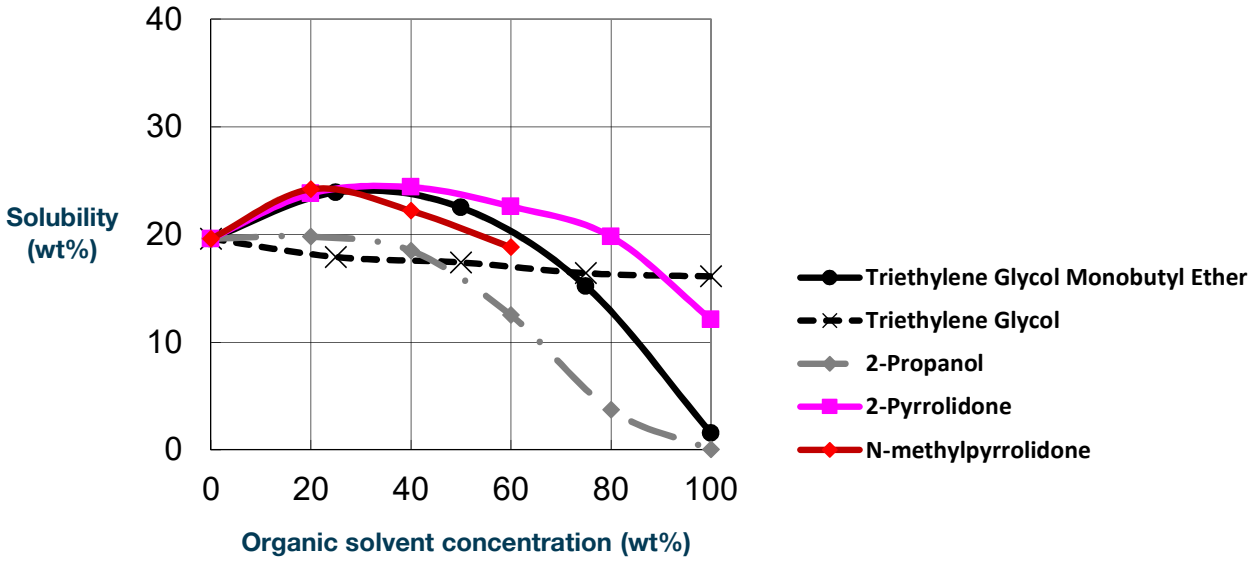
Strong electrolyte

SPINOMAR NaSS is a strong electrolyte compound with sulfo groups and dissolves well in water and water-soluble organic solvents.
Polymerization is possible with various solvents.

Table 1. Solubility of SPINOMAR NaSS (25°C)

Solvent	Solubility (wt%)
H_2O	19.6
	24.0 (40°C)
	28.7 (50°C)
DMF	8.7
DMSO	19.2
NMP	6.5
Ethanol	0.3
2-propanol	0.03
Toluene	Insoluble

Fig. 4: Solubility of NaSS (mixed solvents of water and aqueous solvents)



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Feature
4

High heat resistance and storage stability

SPINOMAR NaSS has excellent heat resistance and does not decompose at temperatures below 300°C (Fig. 5).
It is also extremely stable below 40°C in powder form, providing excellent storage stability (polymerization stability) (Fig. 6).

Fig. 5. SPINOMAR NaSS TG-DTA
(Room temperature → 500°C; heating rate: 10°C/min.)

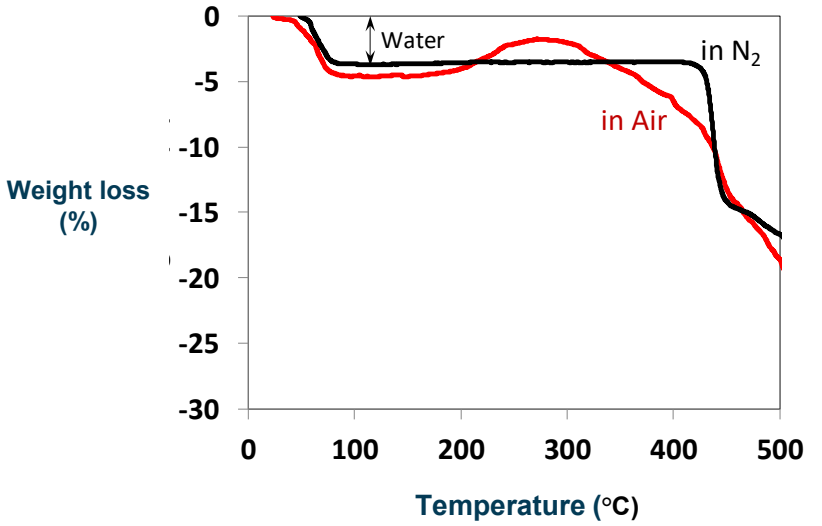
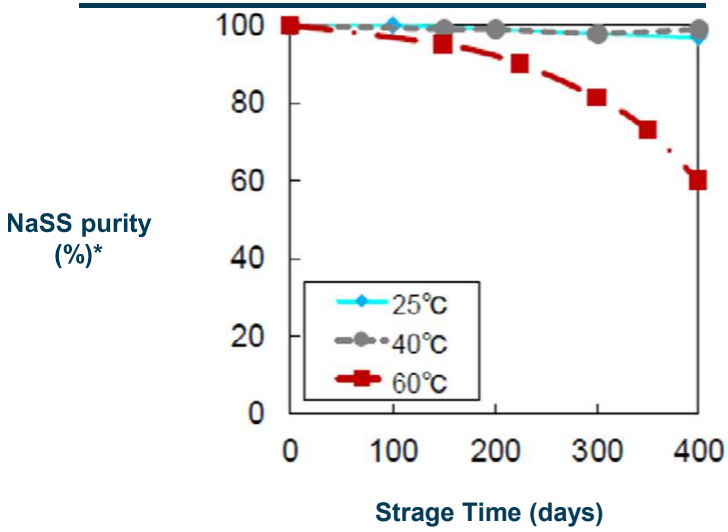


Fig. 6: Storage stability of SPINOMAR NaSS



* HPLC determination

Applications

SPINOMAR NaSS has been used in various fields as below.

Polymer emulsion

- ✓Water-based acrylic paint
- ✓Acrylic fiber
- ✓Water-based adhesives (tire cords, food packaging)
- ✓Paper chemicals (sizing agent)

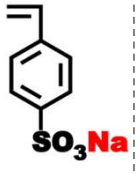
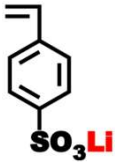
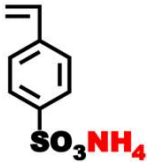
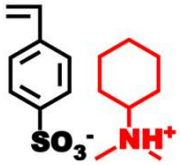
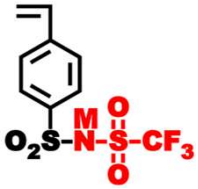
***Numerous other applications are possible.**

Aqueous polymer solution

- ✓Anti-scaling agent
- ✓Thickener
- ✓Allergen scavenger
- ✓Mold release agent
- ✓Chlorinated polyvinyl chloride
- ✓Pigment dispersion
- ✓Nanofiltration membrane
- ✓Cleaning agent (HD production)
- ✓Functional spreading agent
- ✓Oil drilling (gel breaker)

NaSS Analogs

We have been developing various NaSS analogs by focusing on the better solubility, metal-free or cross-linkability.

Monomer		Commercial grade		Developing grade				
								
		NaSS	LiSS	ETSS	AmSS	CHASS	DVBS	TfNS （Na）
Appearance		**Powder**	**Powder**	**Liquid**	**Powder**	**Powder**	**Powder**	**Powder**
Purity (%)		≧84	≧81	≧85	≧90	≧95	≧80	≧95
Solubility (wt%)	H_2O	20	42	**Insoluble**	25	>30	9	21
	DMF	9	32	**miscible**	27	>30	20	>50
	NMP	7	23	**miscible**	20	>30	20	>50
	Ethanol	0.3	17	**miscible**	4	>30	<0.1	7
	Toluene	**Insoluble**	**Insoluble**	**miscible**	**Insoluble**	1	**Insoluble**	**Insoluble**

PolyNaSS®

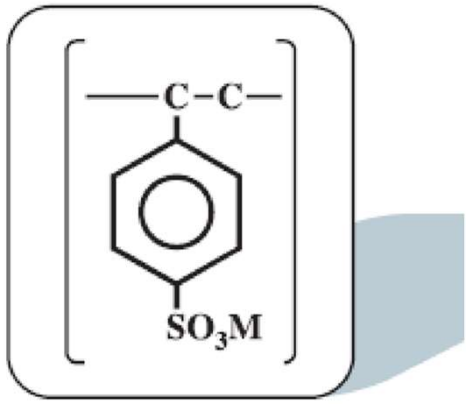
PolyNaSS is an aqueous homopolymer solution of SPINOMAR NaSS.

Three features

- ✓High thermal and chemical stability
- ✓Unique adsorption properties due to aromatic rings
- ✓High water solubility due being a strong electrolyte

Application

Anti-scaling agent
Dispersing agent, emulsion polymerization stabilizer
Rheology modifiers etc.



PolyNaSS grade

Various derivatives with different solubility, cationic species, and chemical structures are available.

	Sodium styrenesulfonate homopolymer					Copolymer
	PS-1	PS-5	PS-50	PS-100	PS-35	MA-2005L
Comonomer	-					MAA・Na
Appearance	**Red clear liquid**	**Light yellow clear liquid**			**Colorless clear liquid**	
Hue (APHA)	-	-	-	-	<60	<100
Resin content (wt%)	20~22					
Viscosity (mPa-s/25°C)	5~10	20~50	200~500	800~1600	200~500	<10
pH	7~9			8~11	11~13	8~10
GPC Mw ($\times 10^4$)	1~3	5~10	30~40	50~70	30~40	<1

Safety, laws, and regulations

Toxicity data

Test case	SPINOMAR NaSS	PolyNaSS
LD_{50}	≧16000mg/kg (mouse, oral)	≥8000mg/kg (rat, oral)
Ames test	Negative	Negative
Skin irritation	None (rabbit, 4 hrs.)	-

Applicable laws and regulations for products (excerpt)

	SPINOMAR NaSS	PolyNaSS
MITI (Japan)	(3) - 1903	(6) - 1040
TSCA (US)	Registered	Registered
REACH (Europe)	Registered	-
ECL (South Korea)	Registered	-

Packaging

Product name	SPINOMAR NaSS	PolyNaSS
	25kg paper bag (PE inner bag) 500kg PVC container	20kg PE can 200kg drum

Storage and handling precautions

Please read the Material Safety Data Sheet (MSDS) carefully before use.

1. Use appropriate protective equipment when handling.
2. If it comes in contact with skin, rinse with plenty of water.
3. Store in a cool, dark place, tightly closed to prevent drying, oxidation, and polymerization.
4. When storing in an aqueous solution, avoid acidic conditions as spontaneous polymerization is likely to occur.

Tosoh Finechem Corporation

Location

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Business

Organometallic compounds: Aluminum alkyls, aluminoxanes, organometallics
Bromine compounds: NaSS, styrene derivatives, alkyl bromides
Fluorine compounds: TFEA, CF_3I, fluorine compounds