# Effect of microstructure in acrylic acid and styrenesulfonate based copolymer on calcium sulfate hemihydrate dispersion

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# **Abstract**

Superplasticizers are indispensable for enhancing the dispersion of cementitious particles while reducing water. These additives improve slurry workability and contribute to the production of dense, and high-strength materials. In this study, we highlight the synergistic effect of carboxylate (-COO-) and sulfonate (-SO<sub>3</sub>-) groups through precise microstructure control for high-performance superplasticization in gypsum. Using acrylic acid (AA) and sodium 4-styrenesulfonate (SS) as monomers, we synthesized homopolymers, random copolymers, and block copolymers via RAFT polymerization. The synthesized polymers were evaluated based on adsorption capacity, zeta potential, and adsorption layer thickness. Our results demonstrated that the tailored distribution of -COO- and -SO<sub>3</sub>- groups within the block microstructure of polymer significantly enhanced adsorption efficiency, electrostatic interactions, and steric repulsions resulting in superior fluidity in CSH slurries. The block copolymer exhibited an impressive water reduction ratio of 57.7%, outperforming the conventional superplasticizers (15–30%)[1]. Additionally, a higher proportion of SS in the block copolymer effectively offset the usual delayed hydration effects of PAA. This work underscores the importance of microstructure optimization in copolymer design for advanced gypsum superplasticizer performance.

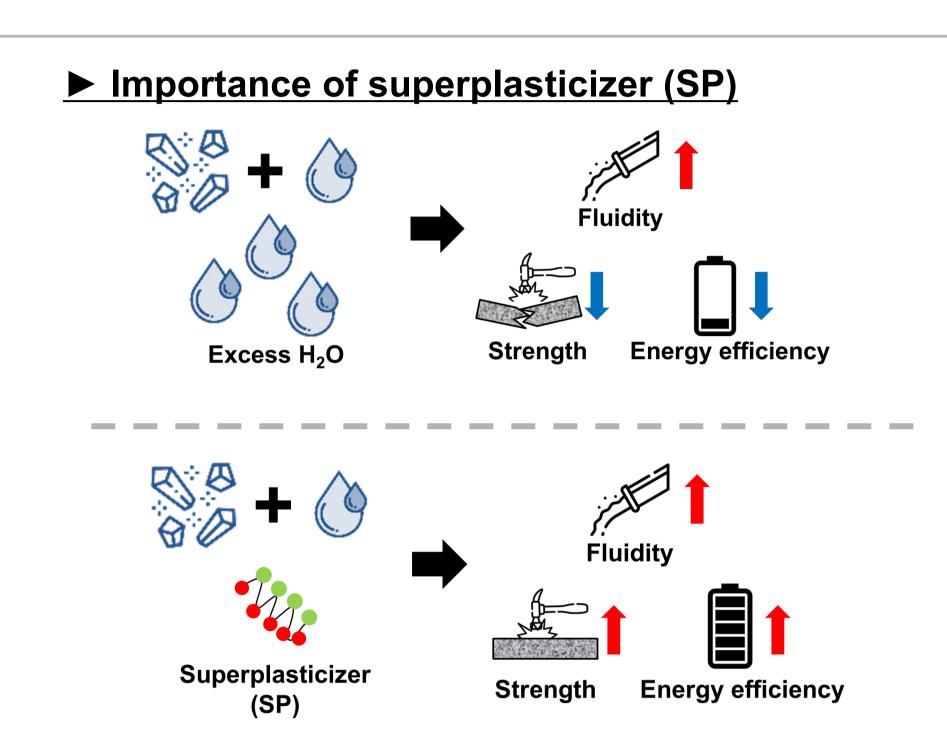
W/SP

# Introduction

**Gypsum board** 

# Superplasticizer (SP) Repulsion Adsorption **PNS PCE** Repulsion H<sub>2</sub>O H<sub>2</sub>O

W/O SP



# **Result & Discussion**

### Synthesis of polymers

**►** Adsorption amount

■ PSS120

▲ 40B120

♦ 40R120

40B240

0.2

**►** Fluidizing property

**■** PSS120

40B40

▲ 40B120

◆ 40R120

40B240

0.2

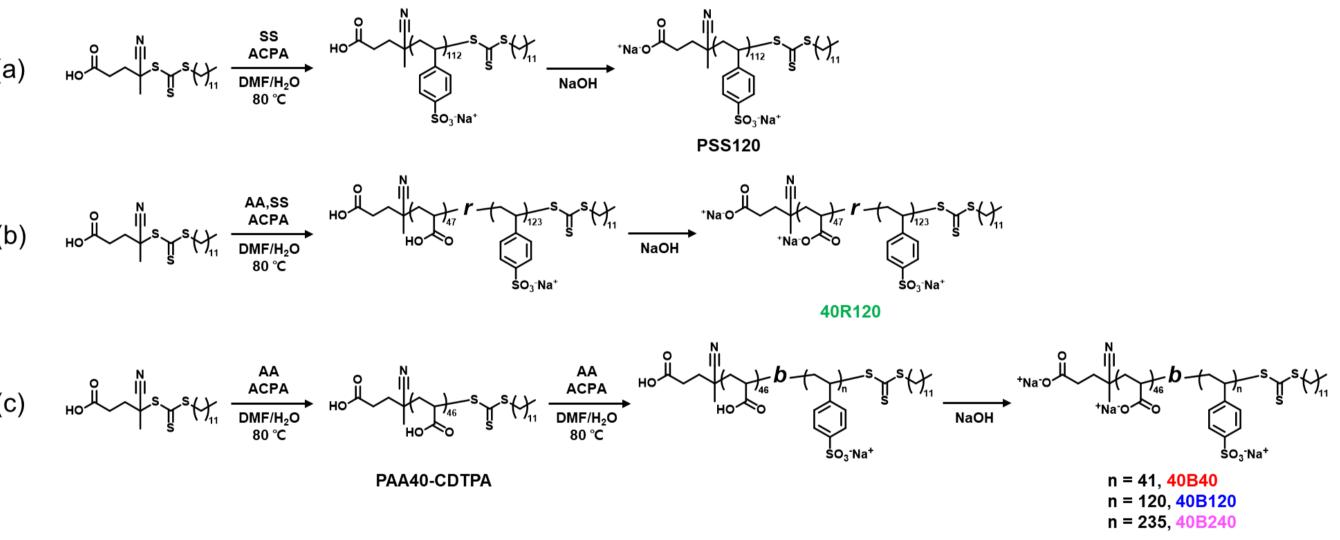
0.4

0.6

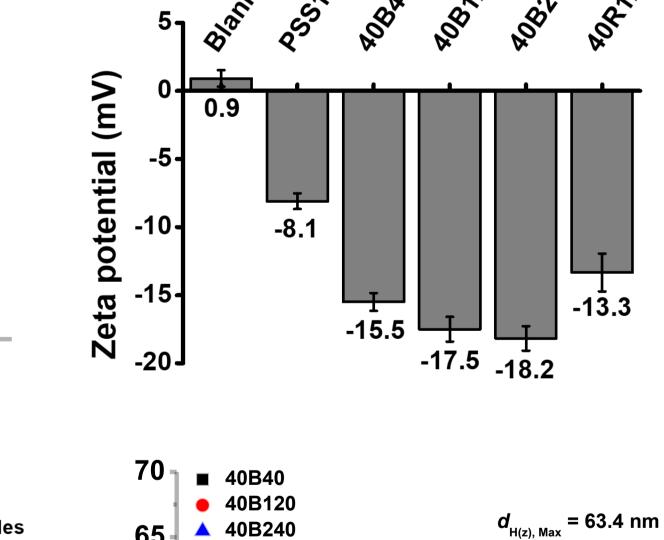
Polymer dosage (wt%)

amount (mg/g)

Adsorption



# Zeta potential



▲ 40B240

**60** 

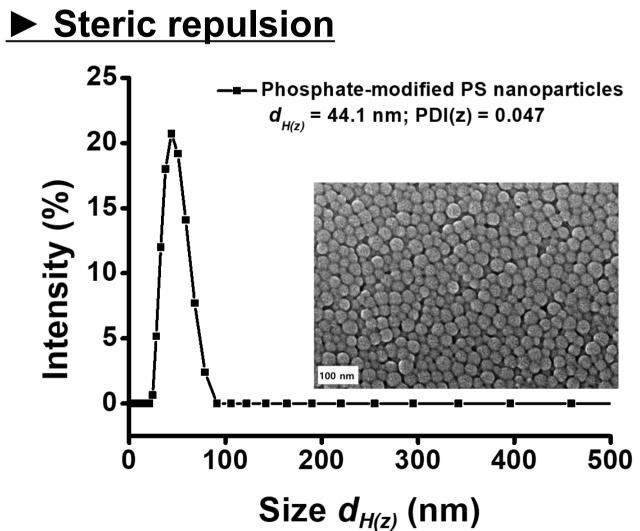
**55** 

**50** 

**45** 

(nm)

 $\boldsymbol{d}_{\mathsf{H}(z)}$ 



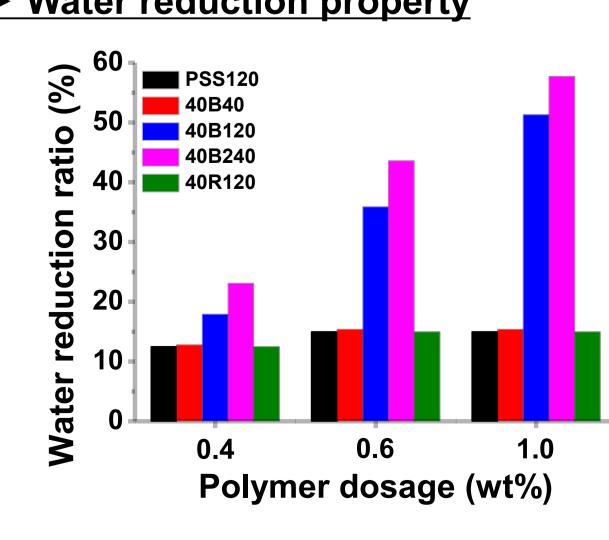
0.6

Polymer dosage (wt%)

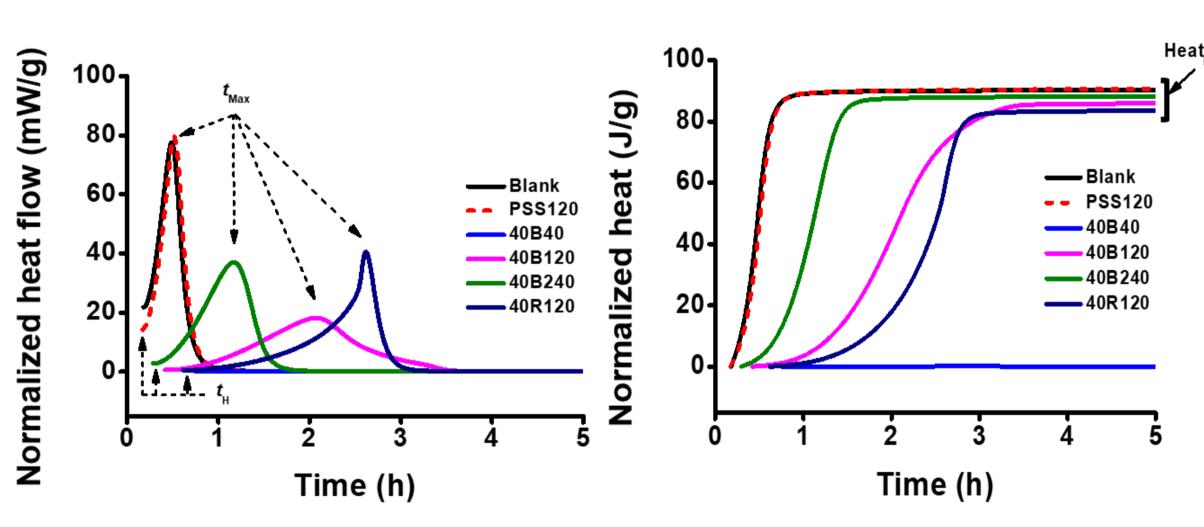
8.0

1.0

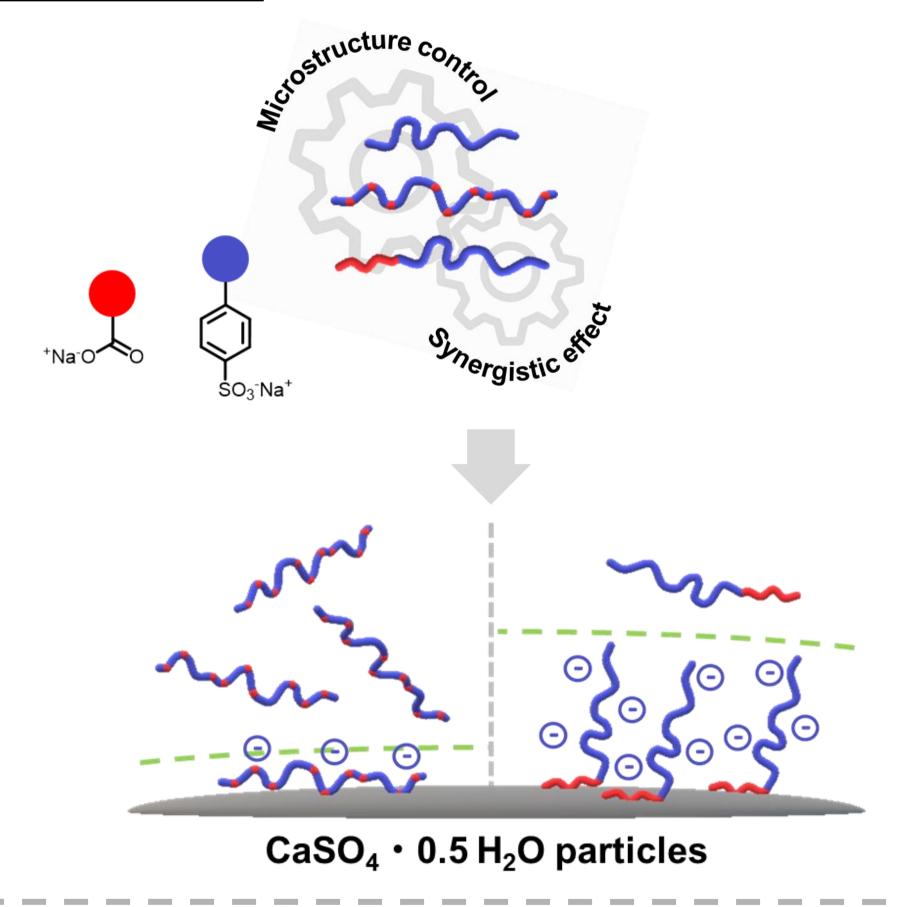
Water reduction property



# **►** Hydration kinetics



# **►** Expected mechanism



# Conclusion

- Copolymers with different microstructures were synthesized via RAFT polymerization and applied as superplasticizers for CSH.
- Block copolymers showed higher adsorption capacity on CSH surfaces than homo- and random copolymers, along with stronger negative charge.
- Increased PSS block length in block copolymers enhanced steric repulsion.
- Strong electrostatic and steric repulsions in block copolymers led to superior dispersion performance.
- Hydration kinetics of CSH could be effectively regulated by adjusting the AA ratio in the block copolymer structure.

# Reference

Fluidity (cm)

10

[1] M.L. Vo, J. Plank, Dispersing effectiveness of a phosphated polycarboxylate in α- and β-calcium sulfate hemihydrate systems, Construction and Building Materials 237 (2020).

 $d_{H(z), Max} = 57.0 \text{ nm}$ 

 $d_{H(z), Max} = 49.3 \text{ nm}$ 

400 600 800 1000 1200

Concentration (mg/L)

[2] Kim, Hanyoung, et. al. "Microstructure control of acrylic acid-styrenesulfonate copolymers for high-performance gypsum superplasticizers." Materials Today Communications 45 (2025): 112268.