Supporting Information for "Macromolecule based platforms for developing tailor made formulations for scale inhibition"

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The supporting information (SI) includes three tables (S1-S3).

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Table S1. Common scales and their properties.

Crystal composition	Crystal name	Properties	Ref.
Calcium carbonate ($CaCO_3.xH_2O$)	Calcite (x = 0)	• The most stable form • Trigonal-rhombohedral • Favored at T < 30 ˚C • K_{sp} = 3.3×10^{-9} at 25 ˚C	[1–4]
	Aragonite (x = 0)	• Second most stable form • Orthorhombic • Favored at T > 70 ˚C • K_{sp} = 4.6×10^{-9} at 25 ˚C	[1,3–5]
	Vaterite (x = 0)	• Third most stable form • Hexagonal • K_{sp} = 1.2×10^{-8} at 25 ˚C	[1,3,4,6]
	Amorphous calcium carbonate (ACC)	• The transient and most unstable form seen prior to crystallization • Disordered	[7]

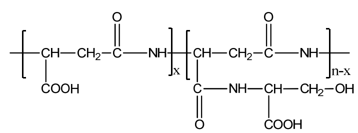
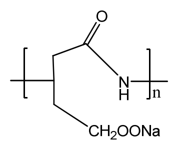
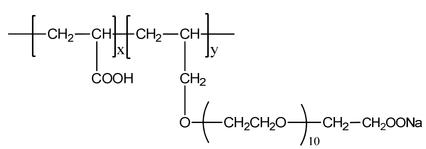
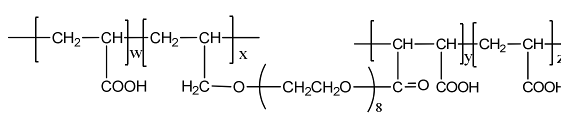
	Calcium carbonate monohydrate (x = 1)	• Metastable phase • Hexagonal	8
	Calcium carbonate hexahydrate (Ikaite, x = 6)	• Metastable • Hydrogen bond mediated growth (e.g., pyramidal shape) • Forms at low temperatures, such as cold saline sea water	9
Calcium sulphate ($CaSO_4.xH_2O$)	Gypsum (x = 2)	• The most abundant sulphate mineral • The stable phase below 42 ˚C and at relative humidity above the gypsum–anhydrite equilibrium curve • Monoclinic	10
	Bassanite (calcium sulphate hemihydrate, known as plaster of Paris, x = 0.5)	• The result of gypsum dehydration • Below 97 ˚C, the hemihydrate is metastable with regards to gypsum • Microscopic needles	
	Calcium sulphate anhydrite (x = 0)	• Stable at T > 42 ˚C • Orthorhombic, dipyramidal	
Aluminosilicates ($Al_2O_3.SiO_2$)	Andalusite	• Coarsest grain size • Orthorhombic	11,12
	Kyanite	• The most abundant polymorph • Triclinic	
	Sillimanite	• Orthorhombic	

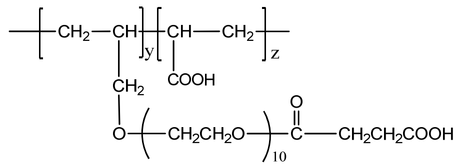
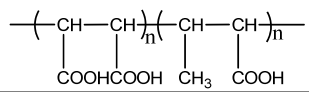
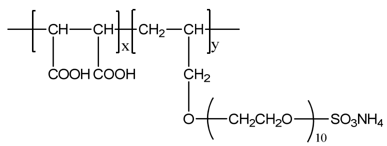
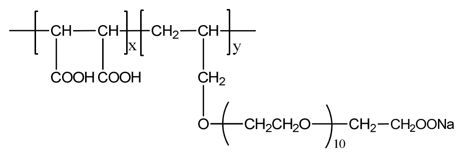
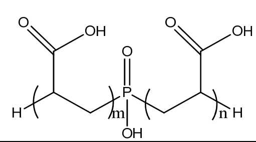
Table S2. Examples of crystal modifier macromolecules and the corresponding mechanisms.

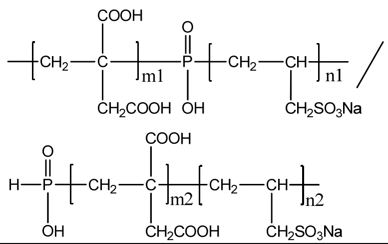
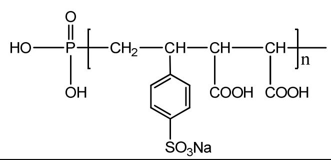
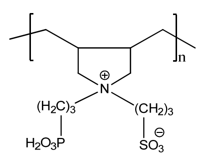
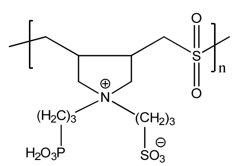
Crystallizing compound	Polymer additive	Mechanism/morphology	Ref.
Hydrocortisone acetate	• Hydroxypropyl methylcellulose (HPMC) • Methylcellulose (MC) • Polyvinyl pyrrolidone (PVP) • Polyethylene glycol (PEG, M_w = 400)	• Delayed nucleation time by polymer-crystal hydrogen bonding • Growth inhibition by polymer adsorption on crystal surface	[13]
Bicalutamide model drug	Polyvinylpyrrolidone (PVP)	• Crystal growth retardation • No effect on the nucleation rate	[14]
Various drugs with low solubility	Various polymeric precipitation inhibitors	• Bulk solution property modification, e.g., surface tension • Hydrodynamic layer alteration • Adsorption on crystal surface to inhibit growth by blocking solute molecules and distorting crystal structure, and flattening rough surfaces • Changing the crystal surface energy	[15]
Felodipine	Hydroxypropylmethyl cellulose (HPMC)	Nucleation inhibition (by a factor of 1000) and growth inhibition (by a factor of 2)	[16]
	Hydroxypropyl methylcellulose acetate succinate (HPMCAS)	Crystal growth inhibition when the polymer is stretched (pH = 6.8) as opposed to lower efficiency resulted from a coiled conformation (pH = 3)	[17]

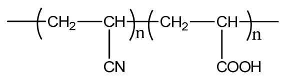
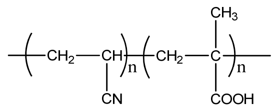
Hydrocortisone	Hydroxypropyl methylcellulose (HPMC)	Precipitation into a metastable crystal polymorph	18
$CaCO_3$	Polystyrene sulfonate (PSS)	• PSS-Ca globules help form metastable amorphous calcium carbonate (ACC). • PSS improves nucleation, resulting in mesoscale assembly: larger number of crystals with smaller size, rougher and more amorphous crystals	19,20
Inorganic crystals, such as $CaCO_3$	Double-hydrophilic block copolymers (comprising a nonionic block and an ionic block)	Various morphologies, such as disks, dumbbells, flowers, etc.	21,22
ZnO	Polyacrylamide	• Ringlike morphology due to the interaction between polymer amide groups with Zn^{2+} • Lowered surface energy • Directional growth inhibition	23

Table S3. Calcium scale inhibition efficiency of macromolecules.

Polymers	Structure	Conditions	Calcium salt	Inhibition efficiency	Ref.
PASP	(**1**)	M_w = 3-10 kDa, pH = 3.5-10.0	$CaCO_3$	In polymer concentration 0.001-0.01 M, calcite dissolution proceeded.	24
		80 ºC, 10 h,	$CaCO_3$ $Ca_3(PO_4)_2$	4 mg/L, 100% inhibition; 22mg/L, 100% inhibition.	25
		40 ºC, 25 h	$CaSO_4$	10 ppm, 100% inhibition	26
Polyether-based PAA		80 ºC, 6 h	$CaSO_4$	3 mg/L 82% inhibition	27
		M_w = 1.84 x 10^4 Da, 70 ºC	$CaSO_4$	3 mg/L, 98% inhibition	28

		60 ºC, 10 h	$CaCO_3$	8 mg/L, 98% inhibition	29
	(**2**)	80 ºC, 10 h	$CaCO_3$ $CaSO_4$	12 mg/L, 89% inhibition 3mg/L, 98.8% inhibition	30
PMA polymers		M_w = 10 kDa 90 ºC, 24 h, pH = 7-8.5	$CaCO_3$	20-25 ppm, 100% inhibition	31
Polyether-based PMA		80 ºC, pH = 9.0	$Ca_3(PO_4)_2$	6 mg/L, 90% inhibition	32
		80 ºC, pH = 9.0	$Ca_3(PO_4)_2$	6 mg/L, 99% inhibition	32
AA-APEM-H_3PO_4	(**3**)	60 ºC, 10 h	$CaCO_3$ $CaSO_4$	8 mg/L, 90.16% inhibition 4 mg/L, 96.94% inhibition	33
PPCA		80 ºC, pH = 6.7	$CaCO_3$	4-10 ppm, lattice parameter changed and the induction time increased.	34

IA/SAS/SHP		40 ºC, pH = 7.3	$CaCO_3$	0.5 mg/L, 100% inhibition	35
MA-SS		80 ºC, 10 h	$CaCO_3$	16 ppm, 98.2%	36,37
			$CaSO_4$	94% inhibition	38
PAA-PAMPS	**(4)**	M_w = 10 kDa, 90 min	$CaCO_3$	4.5 mM, 100% inhibition	39
Polyzwitterion acid (PZA)		M_w = 40 kDa , 40 ºC	$CaSO_4$	20 ppm, 100% inhibition	40
		40 ºC, 800 min	$CaSO_4$	20 ppm, 98% inhibition	41

Acrylonitrile copolymers	 (AN-AA) /  (AN-MAA)	60 ºC, pH = 7.0-8.5 80 ºC, pH = 8.0	$CaSO_4$, $CaCO_3$	5 ppm, 100% inhibition 10 ppm , 99% inhibition	42
Pectin-based copolymers	(**5**)	55 ºC, pH = 9.0	$CaSO_4$	97% inhibition, and 25 days induction time.	43
Polyglycerol	(**6**)		$CaCO_3$	Crystal structural transition was observed.	44
PAMAM dendrimers	(**7**)	80 ºC, 10 h,	$CaCO_3$	14 mg/L, 100% inhibition	45

References

1 T. Ogino, T. Suzuki and K. Sawada, *Geochim. Cosmochim. Acta*, 1987, **51**, 2757–2767.

2 J. R. Smyth and T. J. Ahrens, *Geophys. Res. Lett.*, 1997, **24**, 1595.

3 G. Wolf, E. Königsberger, H. G. Schmidt, L. Königsberger and H. Gamsjäger, *J. Therm. Anal.*, 2000, **60**, 463–472.

4 A. A. Al-Hamzah, C. P. East, W. O. S. Doherty and C. M. Fellows, *Desalination*, 2014, **338**, 93–105.

5 P. Character, N. Jan and W. L. Bragg, *Proc. R. Soc. London . Ser. A*, 1924, **105**, 16–39.

6 S. R. Kamhi, *Acta Crystallogr.*, 1963, **16**, 770–772.

7 L. Addadi, S. Raz and S. Weiner, *Adv. Mater.*, 2003, **15**, 959–970.

8 D. Kralj and L. Brečević, *Colloids Surfaces A Physicochem. Eng. Asp.*, 1995, **96**, 287–293.

9 A. R. Lennie, C. C. Tang and S. P. Thompson, *Mineral. Mag.*, 2004, **68**, 135–146.

10 A. E. Charola, J. Pühringer and M. Steiger, *Environ. Geol.*, 2007, **52**, 207–220.

11 D. L. Whitney, *Am. Mineral.*, 2002, **87**, 405–416.

12 B. Douglas and S.-M. Ho, *Structure and Chemistry of Crystalline Solids*, Springer-Verlag New York, 2006.

13 S. L. Raghavan, a. Trividic, a. F. Davis and J. Hadgraft, *Int. J. Pharm.*, 2001, **212**, 213–221.

14 L. Lindfors, S. Forssén, J. Westergren and U. Olsson, *J. Colloid Interface Sci.*, 2008, **325**, 404–413.

15 D. B. Warren, H. Benameur, C. J. H. Porter and C. W. Pouton, *J. Drug Target.*, 2010, **18**, 704–731.

16 D. E. Alonzo, S. Raina, D. Zhou, Y. Gao, G. G. Z. Zhang and L. S. Taylor, *Cryst. Growth Des.*, 2012, **12**, 1538–1547.

17 C. J. Schram, S. P. Beaudoin and L. S. Taylor, *Langmuir*, 2015, **31**, 171–179.

18 X. Yang, B. Shen and Y. Huang, *Cryst. Growth Des.*, 2015, **15**, 546–551.

19 T. Wang, H. Co and M. Antonietti, 2005, 3246–3247.

20 P. J. M. Smeets, K. R. Cho, R. G. E. Kempen, N. a. J. M. Sommerdijk and J. J. De Yoreo, *Nat. Mater.*, 2015, **14**, 394–399.

21 H. Colfen, *Macromol. Rapid Commun.*, 2001, **22**, 219–252.

22 A. N. Kulak, P. Iddon, Y. Li, S. P. Armes, H. Cölfen, O. Paris, R. M. Wilson and F. C. Meldrum, *J. Am. Chem. Soc.*, 2007, **129**, 3729–3736.

23 Y. Peng, A. W. Xu, B. Deng, M. Antonietti and H. Cölfen, *J. Phys. Chem. B*, 2006, **110**, 2988–2993.

24 K. Burns, Y. T. Wu and C. S. Grant, *Langmuir*, 2003, **19**, 5669–5679.

25 J. Chen, L. Xu, J. Han, M. Su and Q. Wu, *Desalination*, 2015, **358**, 42–48.

26 S. A. Ali, I. W. Kazi and F. Rahman, *Desalination*, 2015, **357**, 36–44.

27 C. Fu, Y. Zhou, G. Liu, J. Huang, W. Sun and W. Wu, *Ind. Eng. Chem. Res.*, 2011, **50**, 10393–10399.

28 K. Cao, Y. Zhou, G. Liu, H. Wang and W. Sun, *J. Appl. Polym. Sci.*, 2014, **131**, 40193(1)–40193(9).

29 G. Liu, M. Xue, J. Huang, H. Wang, Y. Zhou, Q. Yao, L. Ling, K. Cao, Y. Liu, Y. Bu, Y. Chen, W. Wu and W. Sun, *Front. Environ. Sci. Eng.*, 2014, **9**, 545–553.

30 Y. Liu, Y. Zhou, Q. Yao, J. Huang, G. Liu, H. Wang, K. Cao, Y. Chen, Y. Bu, W. Wu and W. Sun, *J. Appl. Polym. Sci.*, 2014, **131**, 39792(1)–39792(12).

31 B. Senthilmurugan, B. Ghosh, S. Kundu and B. Kameshwari, *Pet. Sci. Technol.*, 2011, **29**, 2077–2085.

32 C. Fu, Y. Zhou, H. Xie, W. Sun and W. Wu, *Ind. Eng. Chem. Res.*, 2010, **49**, 8920–8926.

33 Y. Chen, Y. Zhou, Q. Yao, Y. Bu, H. Wang, W. Wu and W. Sun, *Desalin. Water Treat.*, 2014, 1–11.

34 T. Chen, A. Neville, K. Sorbie and Z. Zhong, *Chem. Eng. Sci.*, 2009, **64**, 912–918.

35 Z. Liu, S. Wang, L. Zhang and Z. Liu, *Desalination*, 2015, **362**, 26–33.

36 C. Wang, S. P. Li and T. D. Li, *Desalination*, 2009, **249**, 1–4.

37 Wang, *Polym. Polym. Compos.*, 2013, **21**, 449–456.

38 C. Wang, T. Shen, S. Li and X. Wang, *Desalination*, 2014, **348**, 89–93.

39 M. Dietzsch, M. Barz, T. Schüler, S. Klassen, M. Schreiber, M. Susewind, N. Loges, M. Lang, N. Hellmann, M. Fritz, K. Fischer, P. Theato, A. Kühnle, M. Schmidt, R. Zentel and W. Tremel, *Langmuir*, 2013, **29**, 3080–3088.

40 S. A. Haladu and S. A. Ali, *J. Polym. Sci. Part A Polym. Chem.*, 2013, **51**, 5130–5142.

41 S. A. Ali and S. A. Haladu, *Polym. Int.*, 2014, **63**, 1682–1690.

42 P. Shakkthivel, R. Sathiyamoorthi and T. Vasudevan, *Desalination*, 2004, **164**, 111–123.

43 K. Chauhan, R. Kumar, M. Kumar, P. Sharma and G. S. Chauhan, *Desalination*, 2012, **305**, 31–37.

44 G. Wang, L. Li, J. Lan, L. Chen and J. You, *J. Mater. Chem.*, 2008, **18**, 2789.

45 US Patent 2014/0319067 A1, 2014.