Synthesis of polymer-functionalized nanoparticles and development of smart fluids for enhanced oil recovery

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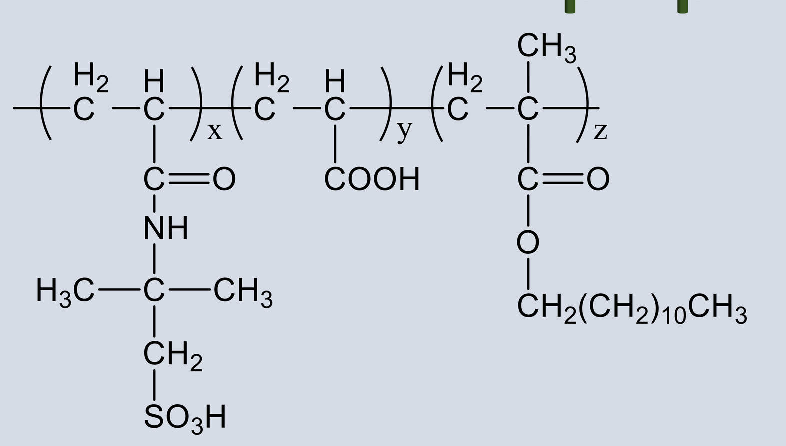
Introduction

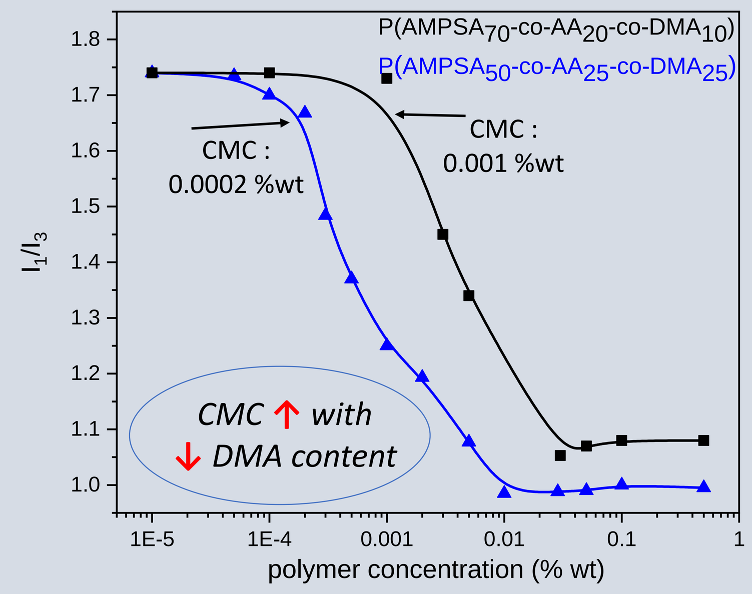
The use of polymer functionalized inorganic nanoparticles (PNPs) for enhanced oil recovery (EOR) from reservoir rocks seems well-promising [Hu, et al. *RSC Adv.*, **2018**, *8*, 30491]. The PNPs combine the advantages of small size, large surface area, high surface energy with the plentiful hydroxyl on the surface of the inorganic nanoparticles [Yoshio, et al. *Chem. Lett.*, **2011**, *40*, 348] and multifunctionality or responsiveness of the designed polymers. Herein, comb-type amphiphilic terpolymers consisting of the hydrophilic and anionic monomers 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) and acrylic acid (AA) that offer a hydrophilic character and the hydrophobic monomer dodecyl methacrylate (DMA), were synthesized through free radical polymerization (FRP). The self-organization in aqueous solutions of the terpolymers is investigated by means of fluorescence probing. Next, the synthesis of polymer-coated SiO_2 nanoparticles (PNPs) was approached by post-grafting on amine-functionalized silica nanoparticles (SiO_2-NH_2 NPs) or by surface-initiated FRP of AMPSA from surface of the SiO_2-NH_2 NPs, initiated by ammonium cerium (IV) nitrate (CAN). Dilute dispersions of the terpolymers or the PNPs were mixed with salts (NaCl, $CaCl_2$), and their dynamic surface tension and oil/water interfacial tensions were measured by the pendant drop method. Oil-in-water Pickering emulsions were prepared by mixing n-dodecane with aqueous polymer solutions with ultrasound probe, their rheological behavior was investigated, and their stability was evaluated macroscopically, with optical inspection of the transient changes of phase volumes inside a volumetric tube, and microscopically by measuring the oil drop-size distribution. Finally, visualization tests of the immiscible displacement of residual n-dodecane by aqueous terpolymers dispersions in a glass-etched pore network were used to assess the potential for application to EOR processes.

Amphiphilic terpolymers



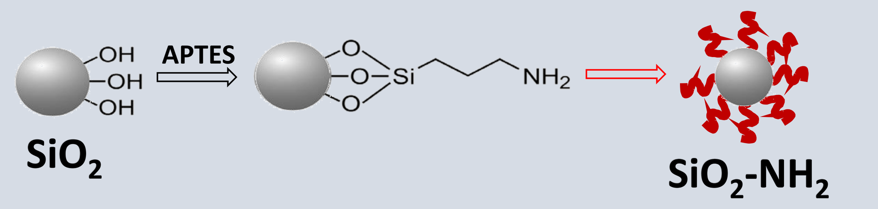
P(AMPSA$_x$-co-AA$_y$-co-DMA$_z$)

***Pyrene probing** for the determination of the Critical Micelle Concentration (CMC)*

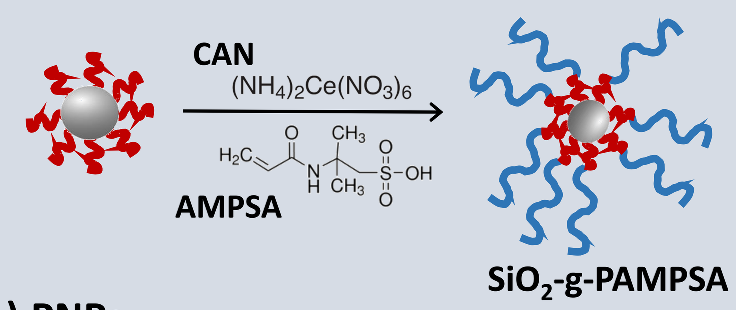


PNPs synthesis

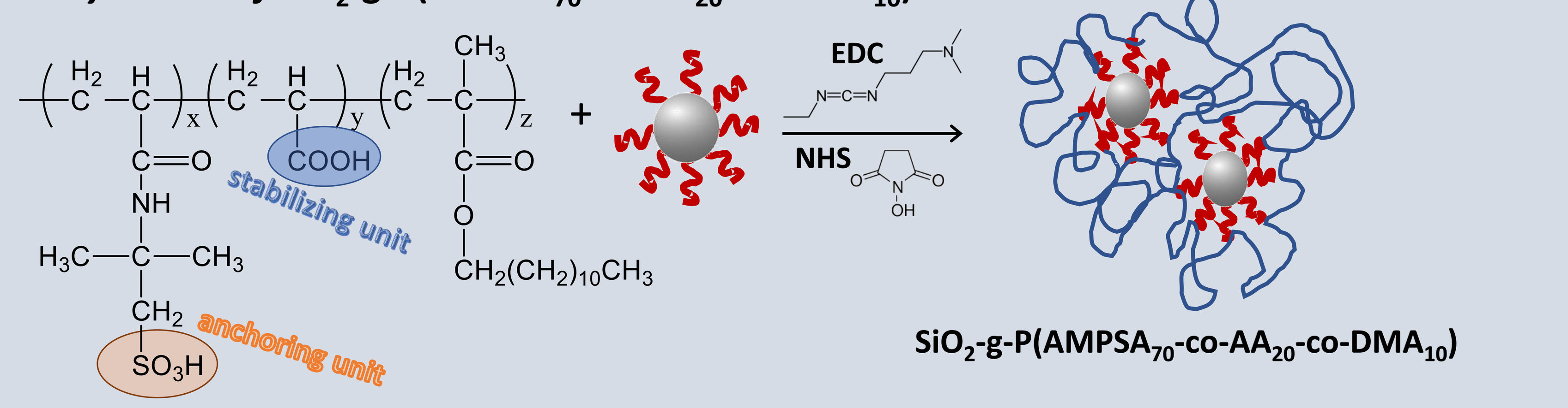
- *Modification of the bare SiO_2 NPs with APTES*



- *Synthesis of the SiO_2-g-PAMPSA PNPs*



- *Synthesis of SiO_2-g-P(AMPSA$_{70}$-co-AA$_{20}$-co-DMA$_{10}$) PNPs*

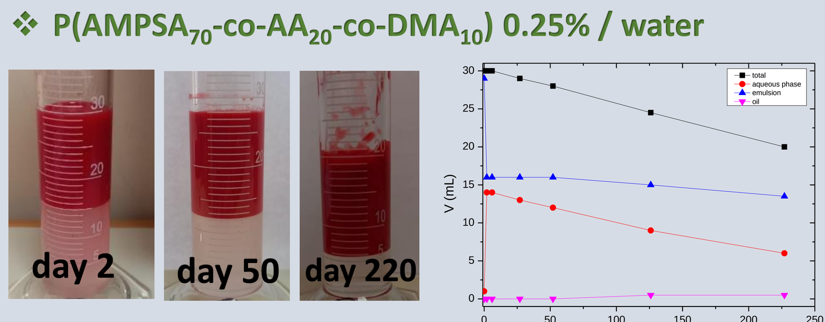


Stability of oil-in-water Pickering emulsions

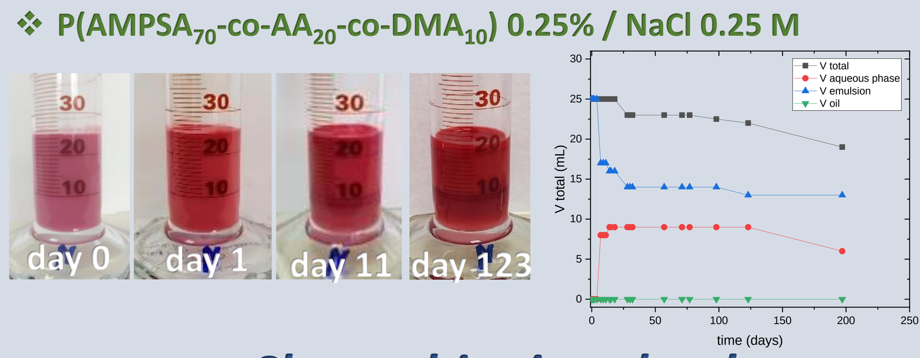
Visual appearance of P(AMPSA$_x$-co-AA$_y$-co-DMA$_z$) emulsions

- Aq. Phase (20mL): P(AMPSA$_x$-co-AA$_y$-co-DMA$_z$) in water or NaCl 0.25 M
- Oil phase (10mL): oil red / n-C12

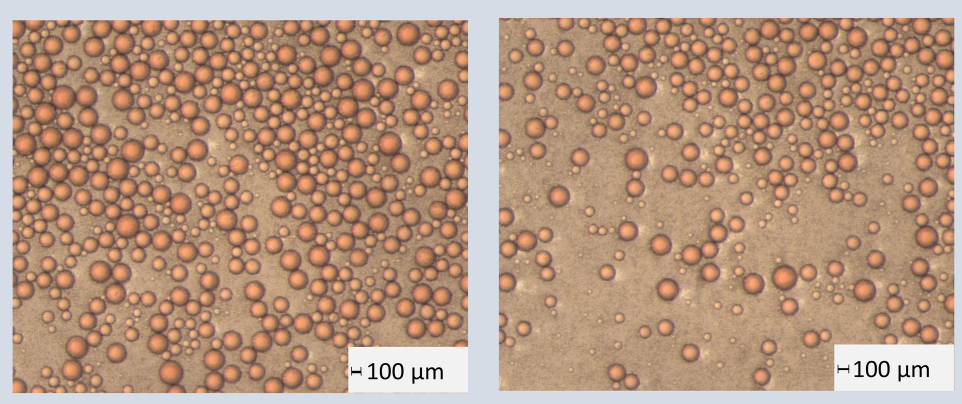
❖ P(AMPSA$_{70}$-co-AA$_{20}$-co-DMA$_{10}$) 0.25% / water



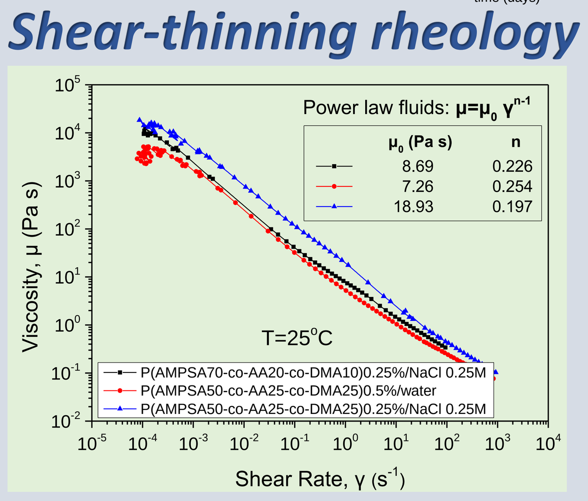
❖ P(AMPSA$_{70}$-co-AA$_{20}$-co-DMA$_{10}$) 0.25% / NaCl 0.25 M



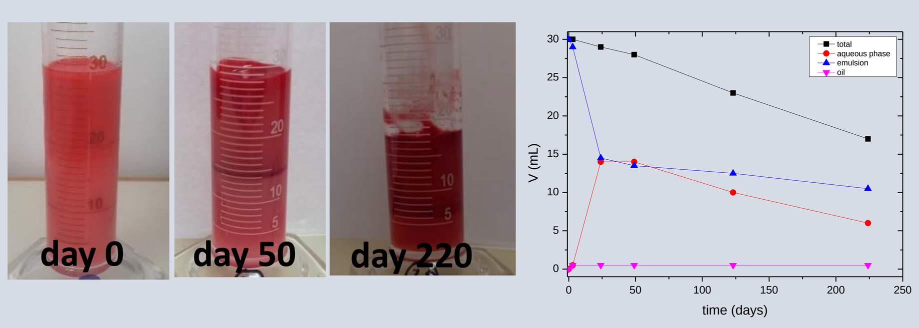
Microscope images



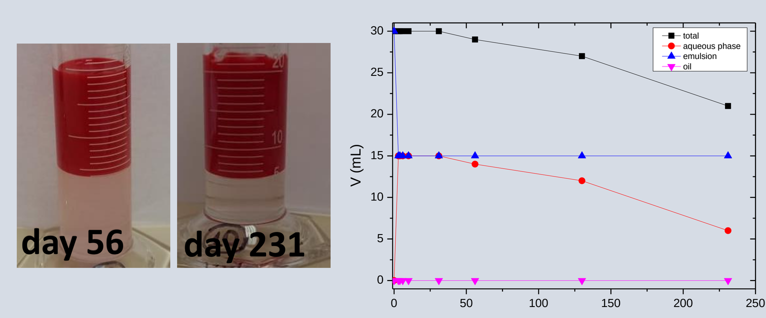
Shear-thinning rheology



❖ P(AMPSA$_{50}$-co-AA$_{25}$-co-DMA$_{25}$) 0.5% / water



❖ P(AMPSA$_{50}$-co-AA$_{25}$-co-DMA$_{25}$) 0.25% / NaCl 0.25 M

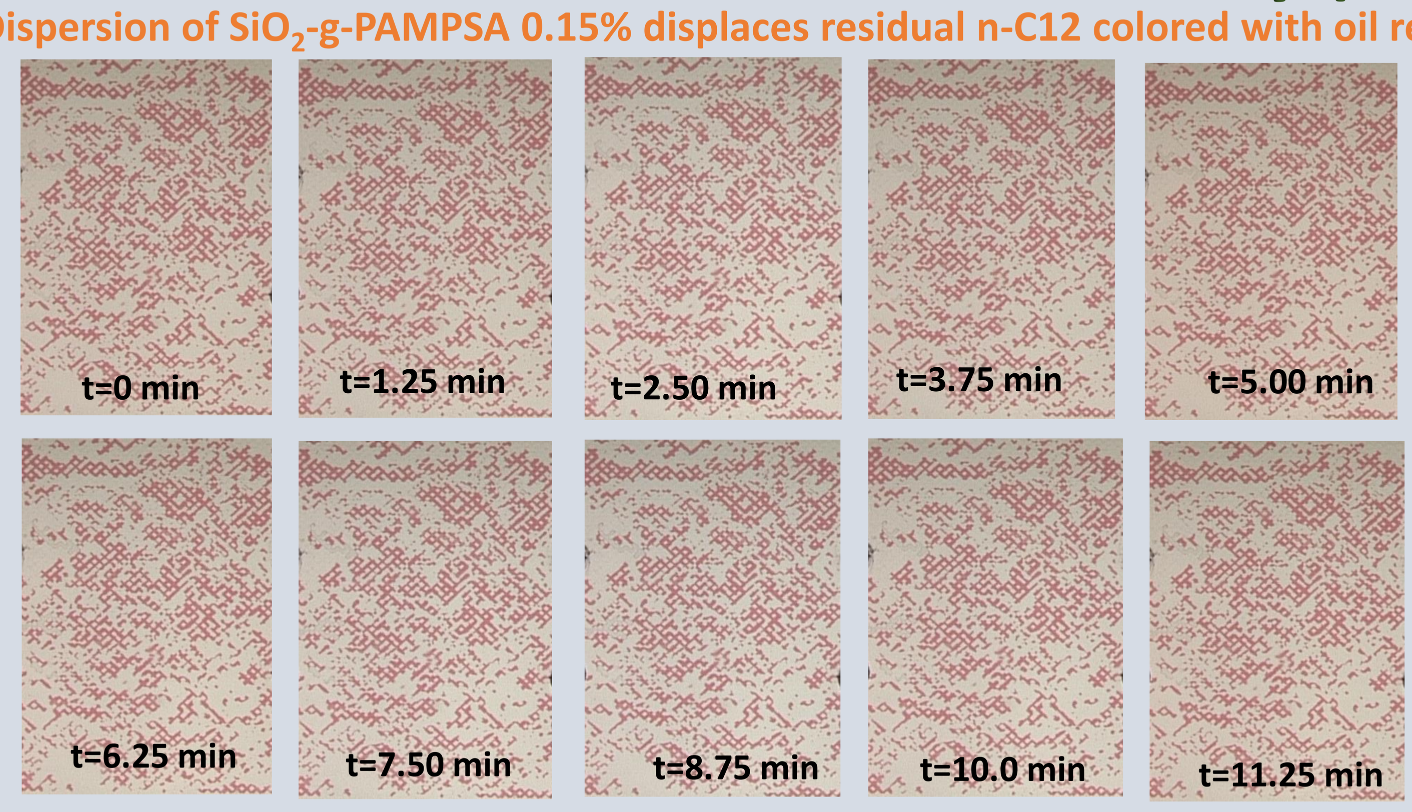


Visualization tests of enhanced oil recovery (EOR)

Dispersion of SiO_2-g-PAMPSA 0.15% displaces residual n-C12 colored with oil red

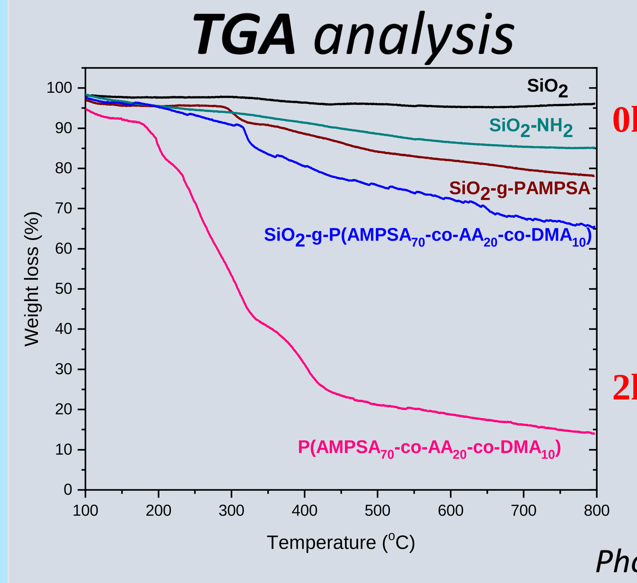
Flow direction

Q=0.72 mL/min

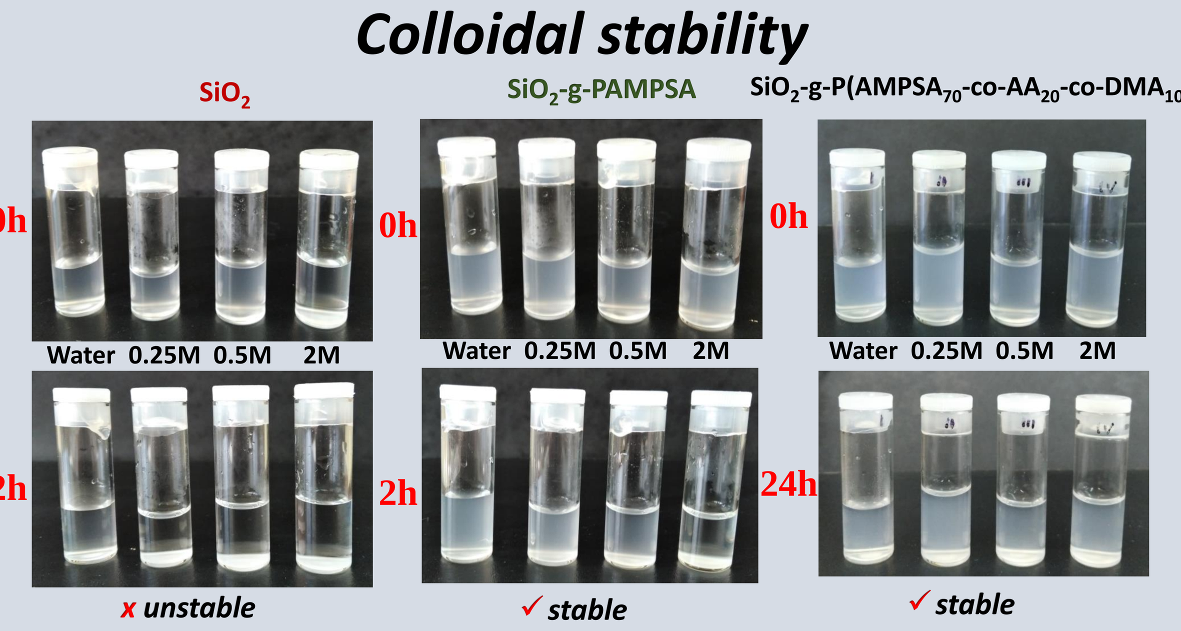


PNPs characterization

TGA analysis



Colloidal stability

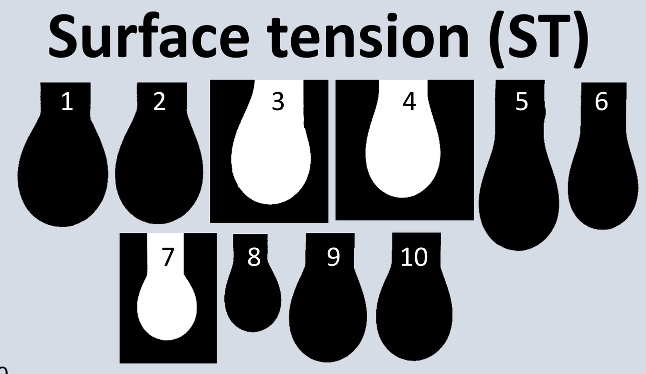


Photos of the 0.1 %wt SiO_2, SiO_2-g-PAMPSA and SiO_2-g-P(AMPSA$_{70}$-co-AA$_{20}$-co-DMA$_{10}$) PNPs dispersions in water or in NaCl (0.25 M, 0.5 M, 2 M)

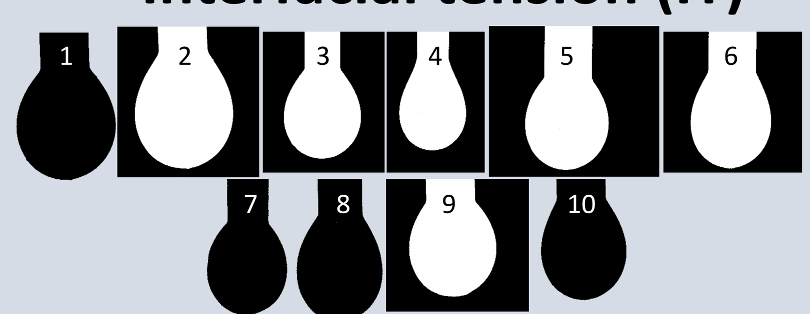
Interfacial properties of polymer or PNPs aqueous dispersions

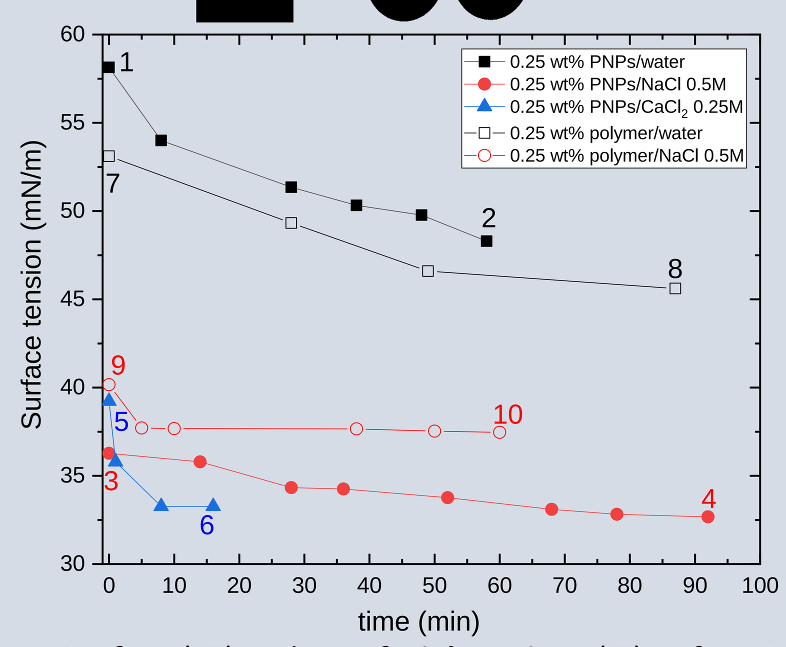
*Measurement of the **dynamic surface and interfacial tension** for aqueous phase/air and aqueous phase/n-dodecane (n-C12) systems with the **pendant drop method** and use of **OpenDrop** software [Berry et al., J. Coll. Inter. Sci., **2015**, 454, 226–237; http://opencolloids.com]*

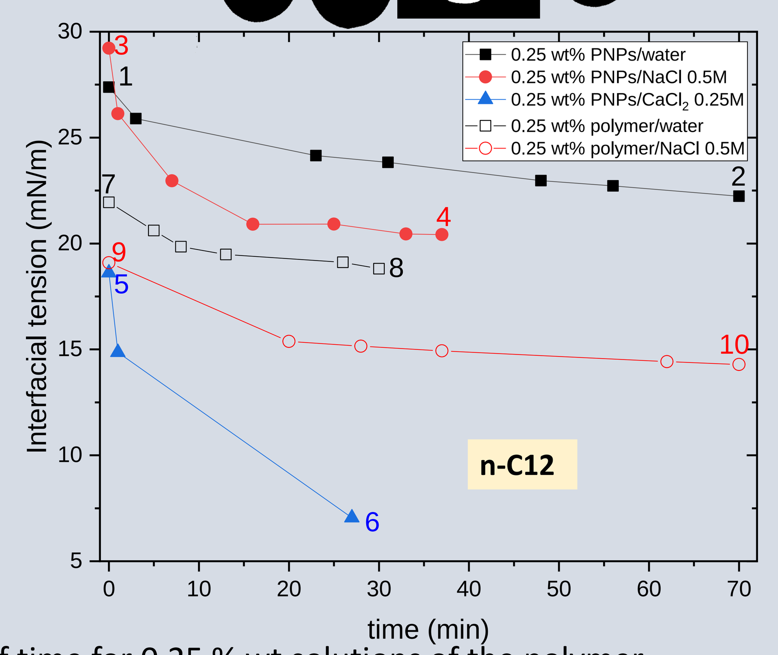
Surface tension (ST)



Interfacial tension (IT)







Surface (ST) and **Interfacial tensions** (IT) as functions of time for 0.25 % wt solutions of the polymer P(AMPSA$_{70}$-co-AA$_{20}$-co-DMA$_{10}$) or the SiO_2-g-P(AMPSA$_{70}$-co-AA$_{20}$-co-DMA$_{10}$) PNPs in water or in NaCl and $CaCl_2$. The images at the top show the drop shape at the initial and final stage.

✓ *Significant reduction of ST and IT is indicative of the stability of Pickering foams and emulsions*

Conclusions

- ✓ Successful synthesis of amphiphilic P(AMPSA-co-AA-co-DMA) terpolymers
- ✓ The terpolymers self-associate at polymer concentrations above the CMC
- ✓ The stability of the polymer-stabilized Pickering emulsions depend on the presence of NaCl
- ✓ Successful synthesis of polymer-functionalized SiO_2 nanoparticles (PNPs)
- ✓ The PNPs create stable dispersions in aqueous phase with and without the presence of salts
- ✓ Promising preliminary EOR tests

Acknowledgements

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