

Supporting information to

## Encapsulation of unmodified Gibbsite *via* conventional emulsion polymerization using charged co-oligomers

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### Synthesis of Gibbsite

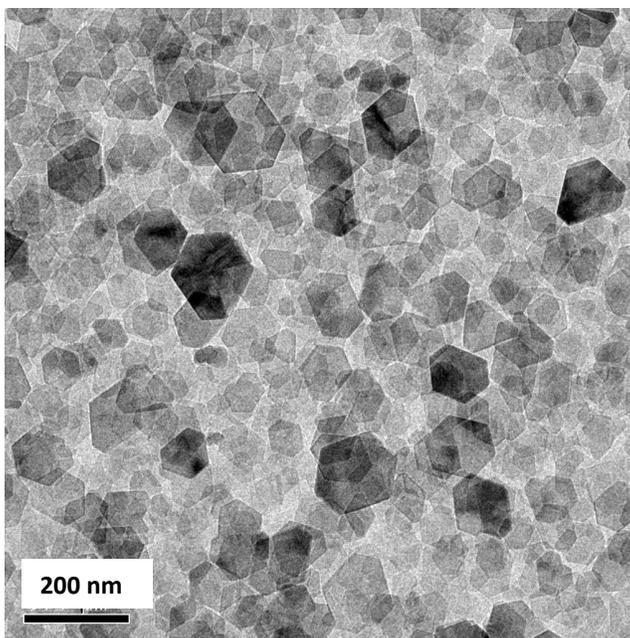


Figure S1. TEM image of the unmodified Gibbsite platelets.

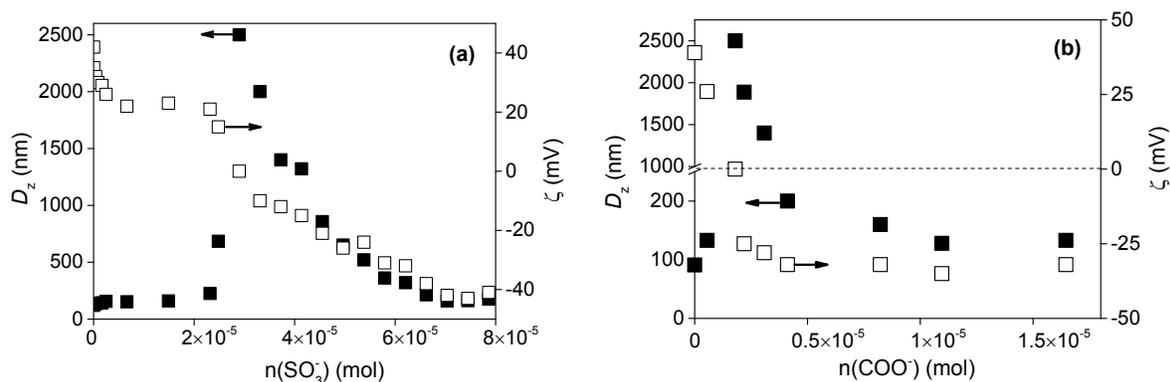
### Encapsulation experiments using SDBS as stabilizer

In order to encapsulate the unmodified Gibbsite platelets we tried to use a commercially available surfactant, sodium dodecylbenzene sulfonate (SDBS), as stabilizer in conventional starved-feed emulsion polymerisation. To estimate the required amount of SDBS for the initial Gibbsite platelet stabilization, we conducted adsorption studies. It was observed that much larger amounts of SDBS are required to stabilize the initial Gibbsite platelets as compared to anionic co-oligomer, e.g. BA<sub>4</sub>-co-AA<sub>8</sub>. For example, in case of anionic co-oligomer colloiddally stable platelets are obtained at around 100 mg/g of Gibbsite, whereas in SDBS case 3000 mg/g of Gibbsite is required to reach the same stability.

Adsorption is governed by electrostatic interaction, where surface functional groups, charge density, molecular weight and hydrophobicity can strongly affect the adsorption process.<sup>1</sup> We

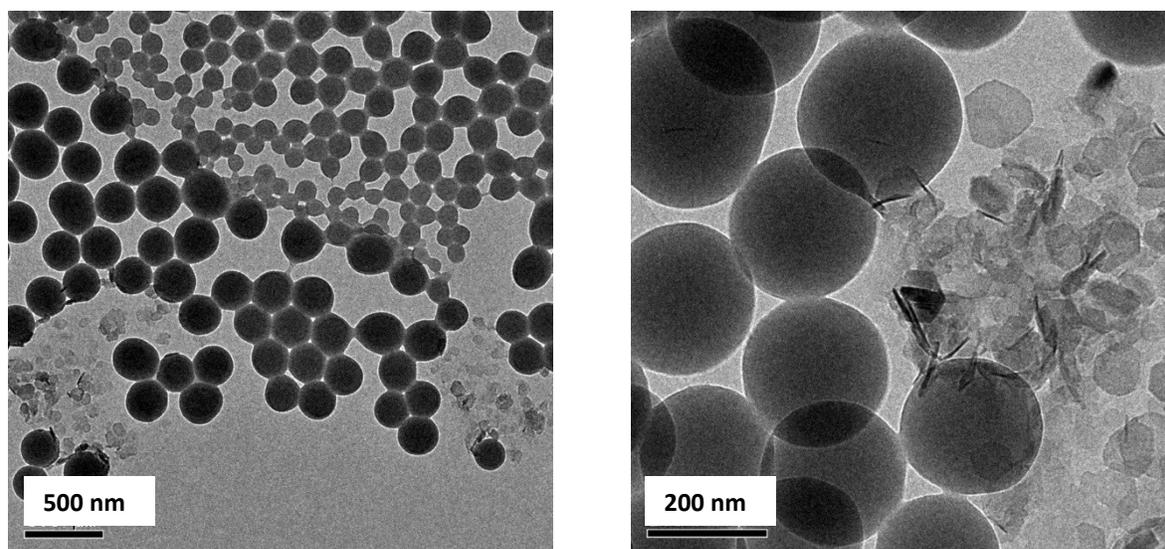
<sup>1</sup> T. T. Nguyen and B. I. Shklovskii, *Phys. A*, 2001, **293**, 324-338.

therefore compared the amount of negative charges necessary for stabilization in both cases (Fig. S2).



**Figure S2.** Effect of  $n(\text{SO}_3^-)$  of SDBS (a) and  $(\text{COO}^-)$  of  $\text{BA}_4\text{-co-AA}_8$  (b) on  $D_z$  and  $\zeta$  of the Gibbsite platelets at pH = 7. Note: in case of anionic co-oligomer overall amount of negative charges was used.

As can be seen from Fig. S2 much higher amounts of negative charges are required to stabilise the initial Gibbsite platelets when using SDBS. Consequently a high fraction of unadsorbed SDBS amount can be present in the reaction mixture, leading to possible self-assembly and formation of Gibbsite-free latex particles. TEM analysis was used to examine particle morphology of the resulted nanocomposites (Fig. S3).

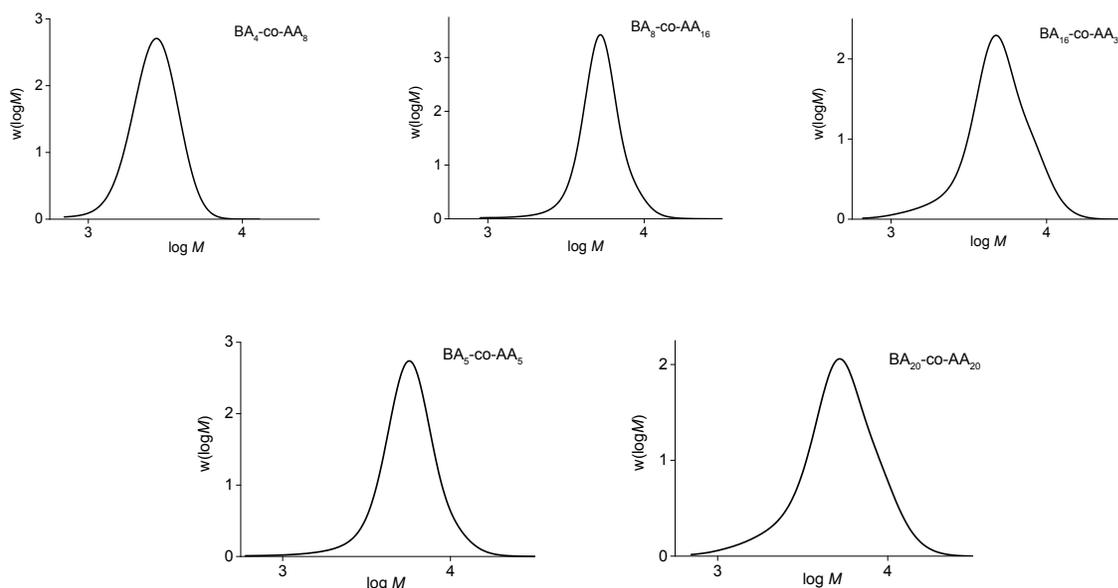


**Figure S3.** TEM images of the final polymer-Gibbsite nanocomposites using SDBS as stabiliser. Conditions:  $V = 25$  mL,  $T = 80^\circ\text{C}$ ,  $m_{\text{Gibbsite}} = 0.02$  g,  $\text{VA-086} = 2$  wt% based on monomer weight, 4.5 g of monomer mixture was fed at a rate  $9 \text{ mg min}^{-1}$ .

TEM images clearly showed a very low encapsulation efficiency, where most of the platelets were not encapsulated and only a small fraction of the resulting latex particles contained a Gibbsite platelet.

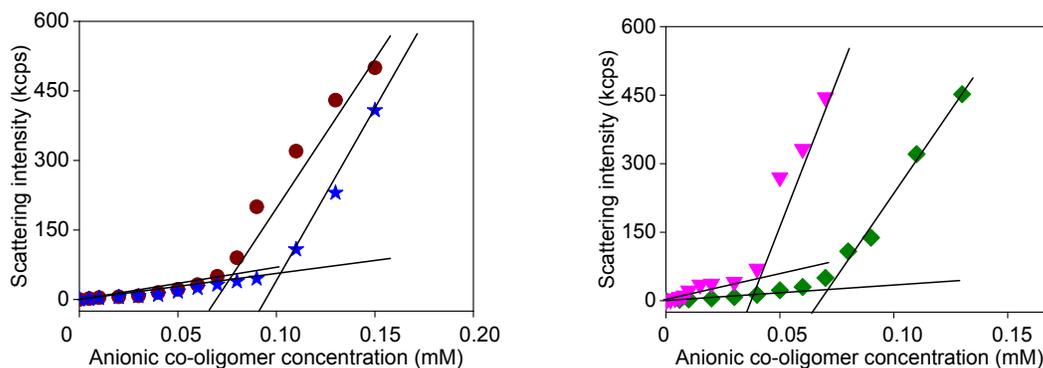
## Synthesis and characterization of anionic co-oligomers

Anionic co-oligomers were synthesized *via* atom transfer radical polymerization. The reactions were conducted at  $[M]:[I]:[CuBr]:[PMDTA] = 200:1:1:1$  in 10 vol% DMF. In order to achieve targeted co-oligomer chain length, the reactions were stopped at the necessary conversion. The molar mass distributions of the resulting copolymers are shown in Fig. S4.



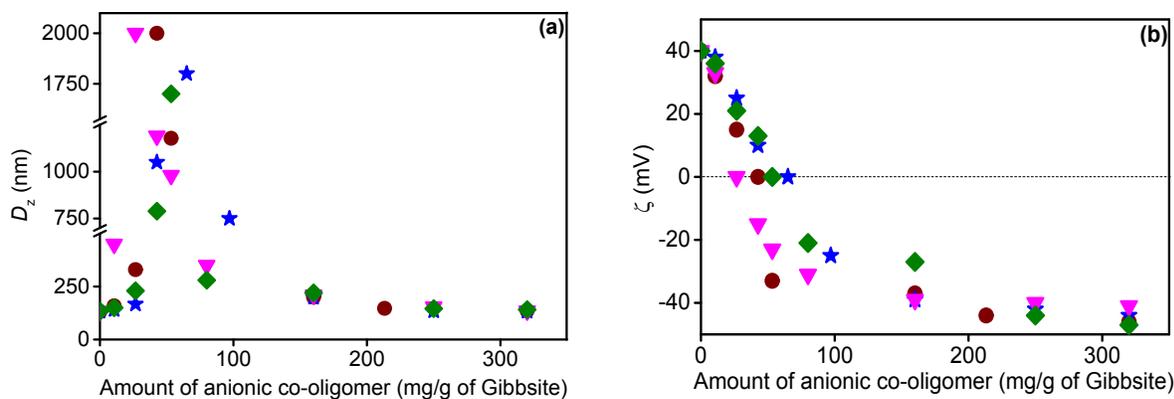
**Figure S4.** Molecular weight distribution of different anionic co-oligomers. SEC chromatograms were recorded against PS standards in THF.

The critical micelle concentrations of the co-oligomers were determined using light scattering intensity measurements and was estimated from the intersection of the two linear regression lines (Fig. S5).



**Figure S5.** Scattering intensity from DLS measurement as a function of anionic co-oligomer concentration. Used anionic co-oligomers: (●)  $BA_8$ -co- $AA_{16}$ , (★)  $BA_{16}$ -co- $AA_{32}$ , (□)  $BA_5$ -co- $AA_5$  and (⊕)  $BA_{20}$ -co- $AA_{20}$ .

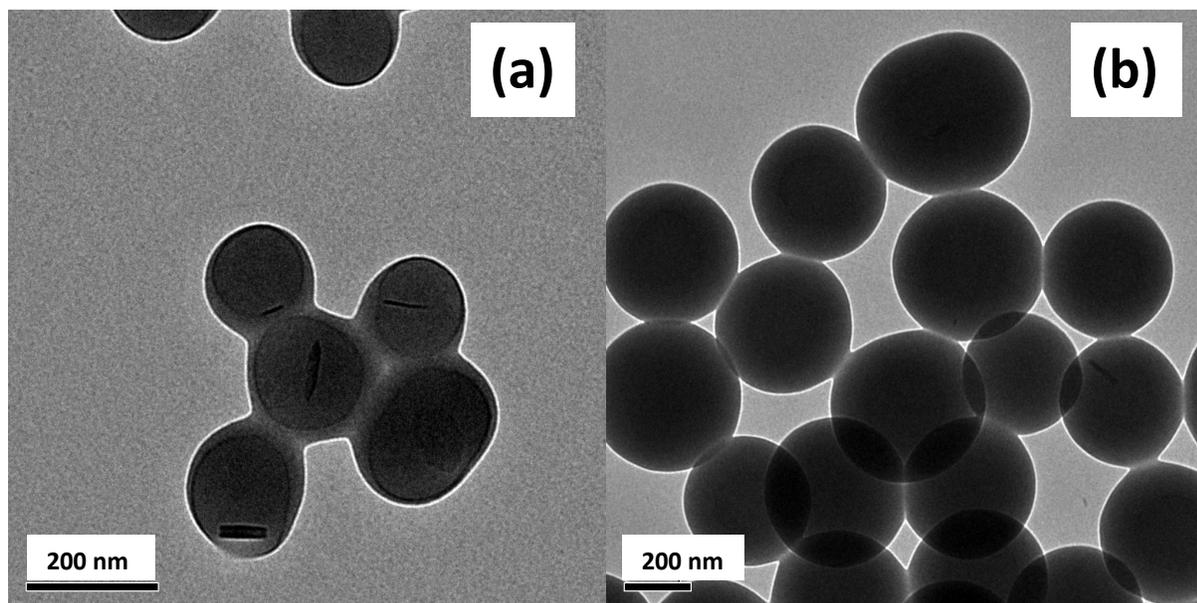
In order to establish the required amount of anionic co-oligomer for stabilization of the initial Gibbsite platelets, the dependence of the  $D_z$  and the  $\zeta$ -potential on the amount of co-oligomer was studied (Fig. S6).



**Figure S6.** Effect of anionic co-oligomer concentration on (a)  $D_z$  and (b)  $\zeta$  of the Gibbsite platelets at pH = 7. Used anionic co-oligomers: (●) BA<sub>8</sub>-co-AA<sub>16</sub>, (★) BA<sub>16</sub>-co-AA<sub>32</sub>, (□) BA<sub>5</sub>-co-AA<sub>5</sub> and (⊕) BA<sub>20</sub>-co-AA<sub>20</sub>.

### Encapsulation experiments at different co-oligomer concentration

Morphology of the resulted polymer-Gibbsite nanocomposites using different co-oligomer concentration was studied by using TEM (Fig. S7).



**Figure S7.** TEM images of the final polymer-Gibbsite nanocomposites at different [cooligomer]: (a) 0.05 mM and (b) 0.1 mM. Used anionic cooligomer: BA<sub>4</sub>-co-AA<sub>8</sub>. Conditions:  $V = 25$  mL,  $T = 80^\circ\text{C}$ ,  $m_{\text{Gibbsite}} = 0.02$  g, VA-086 = 2 wt% based on monomer weight, 4.5 g of monomer mixture was fed at a rate  $9 \text{ mg min}^{-1}$ .

Comparing results on Figure S7a with S7b it is clearly seen that increasing the co-oligomer concentration leads to the formation of Gibbsite-free particles due to secondary nucleation during the reaction. Whereas working below the CMC results in efficient encapsulation where every latex particle contains a Gibbsite platelet.