

Self-assembly of charged molecular colloids with model polyelectrolytes

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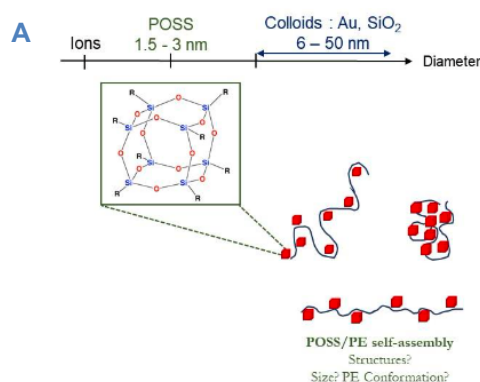
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Résumé :

Polyhedral oligomeric silsesquioxanes (POSS) are molecular colloids with a size range of 1–3 nm (figure A), occupying an intermediate space between ions and nanoparticles. Their properties in solution can be tuned via the nature and length of the pendant groups. This tunability makes POSS ideal for studying their interactions in aqueous environment to form self-assemblies of positively and negatively charged POSS with flexible and semi-flexible polyelectrolytes (PEs), such as polystyrene sulfonate (PSS), ionene, alginate, and chitosan. Previous research had mentioned complexes with nanoparticles⁹ (gold and silice), such as coacervates, or precipitates, with potential applications in phase separation processes, including extraction and depollution[1]. While the interactions of PEs with ions and colloids are well-documented[2–9], little research has focused on molecular colloids of this intermediate size^{5,6}. Preliminary small-angle X-ray scattering (SAXS) experiments have shown the formation of larger self-assembled objects by mixing positively charged POSS (R = -CH₂-CH₂-CH₂-NH₃⁺, chloride counterion) with PSS⁵, a negatively charged PE. The SAXS data show a significant increase in scattering intensity at low q, indicating the formation of large self-assembled structures, sample shows a precipitate (figure B). These findings suggest that POSS/PE interactions lead to complex architectures, opening the path for a systematic phase diagram exploration and the identification of key parameters governing self-assembly, such as ionic strength, charge ratio, pendant group chemistry, PE charge density, and polymer rigidity.



Fig(A) self-assembly POSS-NH₂ with PE

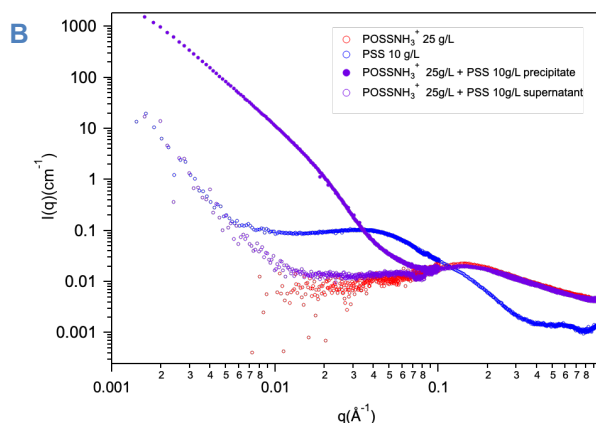


Fig (B) SAXS curves of aminopropyl-POSS, PSS and their mixture

Références :

- (1) Valley, B.; Jing, B.; Ferreira, M.; Zhu, Y. *ACS Appl. Mater. Interfaces* **2019**, *11*, 7472–7478. doi:10.1021/acsami.8b21674
- (2) Sakhawoth, Y.; Michot, L.; Levitz, P.; Rollet, A.-L.; Sirieix-Plenet, J.; Merino, D. H.; Malikova, N. *Langmuir* **2019**, *35*, 10937–10946. doi:10.1021/acs.langmuir.9b00939
- (3) Hotton, C.; Sakhawoth, Y.; Rollet, A.-L.; Sirieix-Plenet, J.; Tea, L.; Combet, S.; Sharp, M.; Hoffmann, I.; Nallet, F.; Malikova, N. Ion-Specific Effects in Polyelectrolyte Solutions: Chain-Chain Interactions, Chain Rigidity and Dynamics. February 6, 2024. doi:10.26434/chemrxiv-2024-drcrc
- (4) Malikova, N.; Rollet, A.-L.; Čebašek, S.; Tomšič, M.; Vlachy, V. *Phys. Chem. Chem. Phys.* **2015**, *17*, 5650–5658. doi:10.1039/C4CP05469E
- (5) Shi, L.; Carn, F.; Boué, F.; Buhler, E. *Phys. Rev. E* **2016**, *94*, 032504. doi:10.1103/PhysRevE.94.032504
- (6) Ferreira, M.; Jing, B.; Lorenzana, A.; Zhu, Y. *Soft Matter* **2020**, *16*, 10280–10289. doi:10.1039/D0SM01565B
- (7) Sheparovych, R.; Sahoo, Y.; Motornov, M.; Wang, S.; Luo, H.; Prasad, P. N.; Sokolov, I.; Minko, S. *Chem. Mater.* **2006**, *18*, 591–593. doi:10.1021/cm051274u
- (8) Sedláček, M. *J. Chem. Phys.* **1996**, *105*, 10123–10133. doi:10.1063/1.472841
- (9) Jouault, N.; Kumar, S. K.; Smalley, R. J.; Chi, C.; Moneta, R.; Wood, B.; Salerno, H.; Melnichenko, Y. B.; He, L.; Guise, W. E.; Hammouda, B.; Crawford, M. K. *Macromolecules* **2018**, *51*, 5278–5293. doi:10.1021/acs.macromol.8b00432