Kinetically Controlled Block Polymer Micelles: Cavitation Induced Exchange and Templates for Nanomaterials

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Kinetically trapped micelles are emerging as a novel platform for a wide range of applications including drug delivery, nanoreactors, and templates for porous nanomaterials. Kinetic control affords decoupling of micelle size from subsequent applications. However, micelle homogenization and size tuning are inherently difficult due to the high barrier toward micelle chain exchange processes. These challenges can be resolved with the use of sonication, which enables switchable exchange where cavitation leads to chain exchange and cessation returns micelles to kinetic entrapment. Small-angle neutron scattering (SANS) measurements were used to quantify exchange during cavitation induced exchange (CIE). The extent of exchange was observed to linearly with CIE time and the rate of exchange was uniquely found to be directly proportional to the polymer concentration.  

The absence of chain exchange is particularly useful when micelles are used as templates, where such precision control is impossible under the constraints of equilibrium. Thus, this novel exchange technique creates opportunities to utilize kinetically trapped micelles for the fabrication of nanomaterials.

Kinetically trapped micelles were recently developed to enable independent control over pore and wall dimensions relying upon kinetic control of micelles for constant pore size. The approach was termed Persistent Micelle Templates (PMT). In these systems, chain exchange is suppressed with water in solution. Unfortunately, the addition of water-reactive precursors to increase wall-thickness subsequently lowers the barrier to exchange. A novel approach was developed to overcome this limitation using ex situ hydrolysis of TiO$_2$. This largely decouples micelle kinetic control from nanoparticle chemistry and allowed for significant expansion of precursor additions while maintaining PMT control. This synthetic strategy, along with parallel batching afforded remarkable precision tuning of 1.6 Å wall increments over 26 material loadings. Li$^+$ intercalation studies over the systematic nanomaterial series allowed for nanostructure-performance driven relationships to be identified. Turning towards enhancing application, the first PMT study of SnO$_2$ films has shown promise in systematic control over nanoarchitecture with potential in enhanced battery materials. This body of work supports the size tuning and homogenization of kinetic controlled micelles via CIE and development of subsequent processing chemistries to support robust deployment of these micelles as templates.


(2) Lantz, K.; Clamp, N. B.; van den Bergh, W.; Sarkar, A.; Stefik, M. *Small* **2019**, Accepted.