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Kinetics Pathways of Block Copolymer Self-assembly in Solution: transitions, logarithmical relaxations, molecular exchange and effect of crystallinity

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Self-assembled systems are generally highly dynamic structures characterized by molecular exchange, fluctuations and fusion/fission and morphological transitions. Examples include micelles formed by synthetic surfactants and block copolymers as well as lipid membranes. Despite their importance in technological and biomedical applications, the kinetic pathways associated with the formation and molecular transport of such self-assembled nanostructures are generally poorly understood. Time-resolved small-angle X-ray/neutron scattering (TR-SAXS/SANS) is powerful technique [1] that allow non-equilibrium kinetic processes such as nucleation processes [2,4] and morphological transitions [3,5] to be followed with structural resolution over time scales starting from a few milliseconds. Neutrons have the additional advantage of facile contrast variation through H/D substitution schemes, which also allow equilibrium processes such as molecular exchange and diffusion to be studied without perturbation [1,6-8].
In this presentation we will address the basic kinetic pathways found in block copolymer micelles formed by amphiphilic self-assembly. We will address both equilibrium and non-equilibrium kinetics and argue that the understanding of kinetic pathways can be utilized to manipulate and design the physical properties of self-assembled systems. The mechanism of molecular exchange in block copolymer micelles that was tediously studied at D11 in the early 2000s and the rather dramatic effect of polydispersity will be discussed in detail . Furthermore, we shall discuss the role of confinement and crystallinity on the stability and molecular transport processes in semi-crystalline micelles [8,10] and telechelic polymer micelles [11,12] and discuss the relevance to biological systems and biomedical applications.

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