Mechanism for Molecular Exchange Kinetics in Block Copolymer Micelles with Amorphous and Crystalline Cores

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Self-assembled systems, such as micelles, rely on various dynamic processes to achieve thermodynamic equilibrium. A primary mechanism for this equilibration process is molecular exchange, characterized by the continuous expulsion and insertion of unimers. However, this activated diffusion process is often slow or even arrested due to significant kinetic barriers, resulting in poorly defined, non-equilibrium structures in block copolymer systems. While the kinetics of micelle equilibration have been extensively studied, the focus has predominantly been on micelles with amorphous or liquid-like cores. When it comes to micelles with crystalline cores, additional challenges arise, including cooperative interactions, limited chain mobility, and confinement effects.

In this study, we employ two model systems: amorphous poly(ethylene-alt-propylene)-(polyethylene oxide) (PEP-PEO) and partly crystalline n-alkyl-PEO (Cn-PEO), both nearly monodisperse polymers in aqueous solutions. Early studies show that even low chain polydispersity gives rise to pseudo-logarithmic, extremely broad relaxation patterns, which can be related to the hypersensitivity of the chain length during the rate-determining expulsion step [1,2]. Utilizing small-angle X-ray scattering (SAXS/SANS), NMR, densitometry, and differential scanning calorimetry (DSC), we uncover a first-order phase transition in the micellar cores of Cn-PEO, analogous to the melting of a rotator-phase rather than a well-defined crystalline phase [4]. Fascinatingly, confinement induces a reduction in melting points that can be perfectly described by the Gibbs-Thomson equation [5].

Exploring molecular exchange kinetics through time-resolved small-angle neutron scattering (TR-SANS) [1,2,6], we elucidate the cooperative nature of the melting transition within confined micellar cores, contrasting with a decoupled, unimeric exchange process [7]. Crossing the melting point triggers a discrete change in activation energy. Furthermore, by co-assembling Cn-PEO with varying n-alkyl lengths, we demonstrate the tunability of melting points and, consequently, cooperativity, while the expulsion process remains non-cooperative.

Finally, we investigate "telechelic polymers" based on Cn-PEO-Cn, which form clustered micelles. [8] The results show that, unlike regular micelles, the kinetics occur in a multistep process involving a novel collision-induced single-molecule exchange mechanism. In this presentation, we will provide an overview of the major results from the last two decades, discuss these mechanisms in light of theoretical predictions, and outline future challenges.

References

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