COMPLEX MORPHOLOGIES FROM SELF-ASSEMBLY OF BLOCK-COPOLYMERS IN BINARY SOLVENTS

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Novel routes for the synthesis of hierarchical porous materials have recently highlighted the relevance of methacrylate-based copolymers, which in mixtures of selective and common solvents are able to spontaneously self-assemble into colloidal size aggregates such as vesicles or more complex mesophases including polymeric nanospheres with bicontinuous internal structure (BPNs) [1]. Nevertheless, the phase behaviour of this family of structure directing agents is only partially understood [1]. In this regard, computer simulations can be effective to provide a clear insight into the physical laws governing the associated kinetics and equilibrium. Motivated by their essential role in the preparation of complex self-assembled morphologies, we have developed transferable and computationally efficient coarse-grained (CG) models that reproduce the behaviour of a family of methacrylate-based copolymers in aqueous and organic solutions, melts and interfaces [2]. The CG potential derivation is based on a hybrid thermodynamic-structural approach which incorporates macroscopic and atomistic-level information. The target properties in the parameterisation are those that govern the self-association mechanism (i.e. interfacial tension, chain conformational entropy and excluded volume repulsive interactions [3]).

By direct molecular simulation, using our CG models, we obtain phase diagrams of methacrylate-based copolymers in mixtures of THF and water (Figure 1), which act as common and selective solvents, respectively. In particular, we focus on the morphological transformations of self-assembled aggregates as a function of the selective/common solvent ratio, polymer concentration and chain architecture. Our results demonstrate that in addition to chain related properties, solvent correlations play a fundamental role on determining and stabilising the polymer structures.

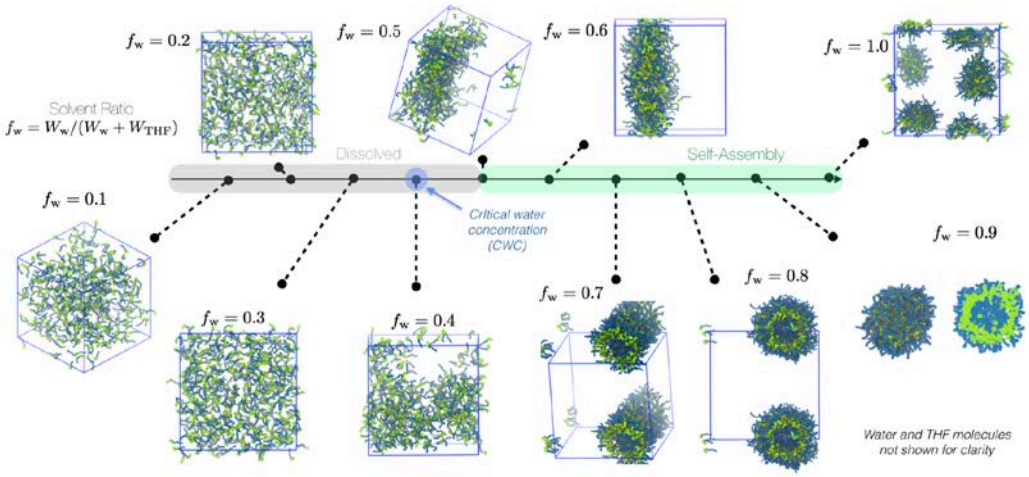

Figure 1. Morphological phase diagram of PEO6-b-PBMA4 at 10wt% in mixtures of water and THF for different solvent ratio (fw). In the simulation snapshots the PBMA and PEO blocks correspond to green and blue beads, respectively.

References

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