

Computer Modeling of Complex Block Copolymer Micelles with Metal-Ligand Self-Assembly

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ABSTRACT

For many applications of nanostructured materials it is essential to understand the principles controlling self-assembly, which is often a challenging task due to the heterogeneity of building blocks, (different chemical nature, size, shape, deformability, etc.) and the presence of multiple interactions. Computer modeling can considerably facilitate this task and guide experimental and industrial research. The aim of the present research to gain understanding of the molecular mechanism(s) of self-assembly of nanostructures formed by diblock copolymer micelles interconnected by means of metal-ligand complexation. The interest to these systems is based their potential future applications in mechano-sensors, actuators and self-healing materials. Our results show that the number of crosslinks between micelles, which determines viscoelastic properties of these materials strongly depends on polymer concentration and the fraction of metal ions relative to ligands.

Keywords: polymer micelles, supramolecular complexes, self-assembly, smart materials

1 INTRODUCTION

The rapid development of nanoscience and nanotechnology has considerably expanded the range of building blocks for complex self-assembled nanostructure formation, which show great potential for numerous advanced applications.[1] Obviously, for most practical applications of nanostructured materials it is essential to achieve a robust and reproducible self-assembly. Thus understanding the dominant factors driving self-assembly, and often secondary factors, which can shift the equilibrium from one to another state is important. One of the challenges is the heterogeneity of building blocks, including elements of different nature, size, shape, deformability, etc. Another challenge is the presence of multiple interactions and multiple equilibria, which complicates characterization of these systems and understanding the fundamental principles of self-assembly of such complex nanostructures. Computer modeling can significantly contribute this task by uncovering the main driving forces of self-assembly and identifying self-assembling motifs and conditions resulting in one or another pattern of system behavior. The aim of the present

research to gain understanding of molecular mechanism of self-assembly of nanostructures formed by diblock copolymer micelles interconnected by means of metal-ligand complexation (Figure 1).

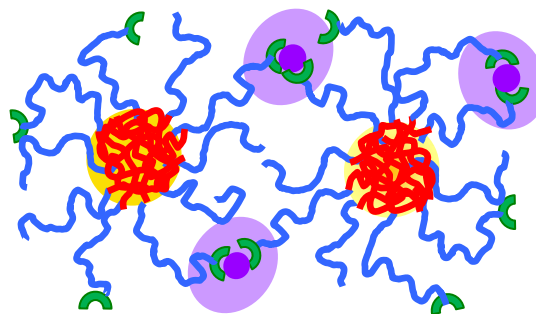


Figure 1: Schematic presentation of diblock copolymer micelles functionalized by ligands forming inter- and intramicellar complexes via metal-ligand association.

The interest to these systems is based on their excellent chemical and mechanical stimuli-responsive behavior, which can find future applications as mechano-sensors, actuators and general self-healing materials including passive damper or vibration insulators. These system possess two levels of self-assembly: 1) self-assembly of diblock copolymers into micelles and 2) reversible intermicelle bridging by coordination bonding between metal ions and ligands attached to the corona of nanoparticles. Having different interactions responsible for different levels of self-assembly results in more versatile properties of these materials, which can be controlled at different levels by changing external conditions, as recently reported experimentally.[2-4] While the macro-scale properties of these materials can be successfully characterized experimentally, it is much harder to achieve molecular-level details of self-assembly which are required to identify the inter-relation between different levels of self-assembly under different external conditions and could provide the basis for new material creation. These details can be obtained from computer modeling.

2 SIMULATION DETAILS

To study the system behavior we applied Monte Carlo simulations. In our simulations each diblock copolymer contained 20 monomers with an equal fraction of

hydrophobic and hydrophilic beads. We use a 3D cubic lattice and the single site bond fluctuation model [5], where the bond length between two adjacent monomers can fluctuate between 1 and $\sqrt{2}$. Void sites are considered to represent solvent. Contacts between neighboring hydrophobic and hydrophilic beads or solvent increase system energy by ϵ , while neighboring contact between a hydrophilic block and solvent decrease it by the same amount. Metal ions occupied one lattice site, while ligands were considered to be part of the end-monomer of the hydrophilic block. The first reversible bond between metal and ligand decreased the system energy by 14.8kT, the second by 11kT and the third by 8kT. The energies are chosen based on experimental data for lanthanide metal ions [6]. We were interested in salt-screened conditions, so electrostatic interactions were not considered. Equilibration of the system was performed via standard moving and bonding updates, as discussed in our previous publications [7], [8]. The number of diblock copolymers was fixed at 800 and box size was changed to obtain data for different polymer volume fractions. The system was equilibrated for 2.5×10^6 MC time steps with last half of the simulation run time used for data analysis.

3 RESULTS

Firstly we have analysed the appearance of the system and analyze the degree of association (e.g. micelle aggregation number) in the presence and absence of reversible association with metal ions. The general observation is that in many cases the aggregation number does not noticeably change in the presence of metal-ligand complexation. At the same time the spatial distribution of the micelles (and/or average distance between micelles) oftentimes change, as intermicelle metal-ligand complexation promotes local aggregation of micelles. Of course, not all metal-ligand complexes result in crosslinking of different micelles. Especially at low polymer concentration, the probability of metal ion interaction with ligands belonging to the same micelle is high, resulting in flower-like micelles. With an increase in the polymer content in solution the probability of bridging increases and the number of metal-ligand complexes crosslinking different micelles increases.

The metal-to-oligomer ratio is also one of the important structural design parameters for the system. As is seen in Figure 2, for lanthanide-like metal ions the number of complexes with two or three ligands belonging to different micelles, i.e. contributing to network formation, seems to be maximal (about 13 bridges per micelle) near the stoichiometric composition (i.e. one metal per 3 ligands), while metal ion complexes with two or more ligands belonging to the same micelle is the largest (about 16 complexes per micelle) at one metal per 2 ligands composition indicating the leading role of 2:1 ligand metal complexes in backbiting. Obviously intermolecular

complexes act as effective crosslinks and hence ensure the viscoelastic properties of the system. For an excess of metal ions 1:1 ligand metal complexes begin to dominate the population of complexes and thereby reducing bridging (or backbiting complexation) and therefore diminishing the desirable viscoelastic properties of the material.

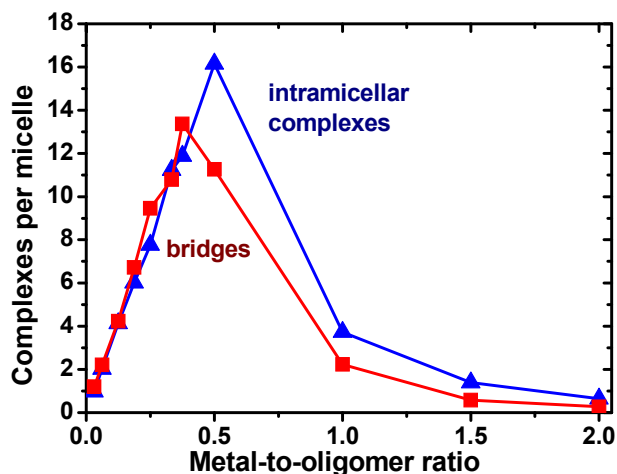


Figure 2: The number of lanthanide metal-ligand complexes crosslinking different micelles in solution (squares) and complexes with two or more ligands belonging to the same micelle (triangles) calculated per micelle.

The obtained results contribute to our understanding of self-assembly in complex systems, which can help in experimental research and industrial development of new materials.

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