Macromolecular Assembly: From Irregular Aggregates to Regular Nanostructures

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Summary: Based on our long-term research on interpolymer complexation due to hydrogen bonding, we proposed several novel self-assembly approaches to polymeric micelles with regular structures. Differing from micelles of block and graft copolymers, our micelles don't have any chemical bonds between the core and shell. In addition, some of these approaches have been proved to be effective to fabricate hollow aggregates.

Keywords: hollow aggregates; hydrogen bonding; micelles; self-assembly

Introduction

As an efficient approach to nanoscale materials with well-defined structures, self-assembly has generated broad interest in chemistry and materials science. [1, 2] For instance, it is well known that block and graft copolymers can self-assemble into polymeric micelles with core-shell structure in nanometer dimensions; the micelles have great potentials for serving as carrier medium for catalysis and biology species. [3, 4]

Our previous studies showed that a polymer pair bound together by secondary binding forces, especially, hydrogen bonding, can lead to inter-polymer complexes. [5] However, because each proton-donating polymer chain can interact with many donor-accepting polymer chains and vice versa, the complexes formed in solution are often in the form of irregular aggregates. Therefore, although the complexes are products of spontaneous "molecular assembly" of the polymers, their application potential was seriously limited and consequently received much less attention than the well-organized polymeric molecular-assemblies such as micelles, vesicles and hollow aggregates.

Recently, we have devoted efforts to obtain regular assemblies, rather than irregular aggregates, mainly based on inter-polymer complexation. Four novel approaches have been suggested to produce a new type of micelles, in which no chemical bonds exsting between the core and shell.

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Assembly of Polymer Pairs in Solvent/Precipitant

The principle of solvent/precipitant method is as follows. When a solution of polymer A is added into a solution of polymer B which is a precipitant for A, chains of A aggregate but their precipitation can be prevented provided A and B could form interpolymer hydrogen bonding. Thus micelle-like particles with a compact A core surrounded by B shell are formed. Yuan et al reported that Poly(styrene-*co*-methacrylic acid) (SMAA) and poly(vinyl pyrrolidone) (PVPo) could self-assemble into spherical micelles with hydrodynamic radii around 100 nm in aqueous medium. In this system, SMAA with a small content of MAA units (3.55-13.1 mol %), which was insoluble in water, served as polymer A and water-soluble PVPo as polymer B. Using dynamic light scattering, it was found that the hydrodynamic radius of the micelles significantly increases with increasing initial concentrations of both SMAA and PVPo. The micelle size does not depend on the MAA content in SMAA monotonically, which can be rationalized by the coexistence of different stabilization mechanisms. As displayed in Figure 1, the core-shell structure of the micelles became visualized when adequate staining of the TEM specimens was employed. [6] It could be observed that separation between the core and corona occurred because of no "permanent connection", i.e., covalent bonds existing between them.

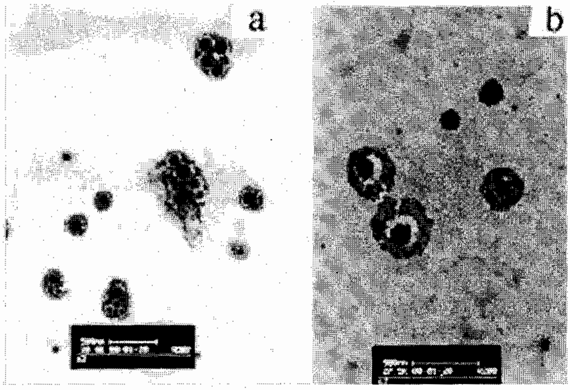

Figure 1. TEM micrographs of micelles of SMAA/PVPo and stained with RuO_4 for 60 min.

Taking advantage of no chemical bonds existing between the core and shell of the micelles formed in this process, Wang et al found that the resultant micelles could be converted to hollow nanospheres., Micelles with poly(4-vinyl pyridine) (PVPy) as the shell and hydroxyl-containing polystyrene, i.e., PS(OH), as the core were formed in a selective solvent mixture for PVPy. The results showed that the structure of the micelles varied from perfect spheres to rod-like and then network-like aggregates with increasing the hydroxyl content in PS(OH). Furthermore, shell-crosslinked micelles were prepared by the reaction of PVPy with the crosslinker of 1,4-dibromobutane under mild conditions. It is more interesting that further cavitation of the shell-crosslinked micelles was realized just by changing the medium from the selective solvent to common one to dissolve PS(OH) chains in the interior of the micelles. The resultant spheres were proved to be hollow by TEM and both Static and Dynamic Light Scattering. In addition, DLS, TEM, SEM and AFM studies manifested that the integrity of the assembled spheres maintained in the process of the crosslinking and cavitation.[7]

Assembly of Hydrogen Bonding 'Graft' Copolymer

The key point of this soluble 'graft' copolymer approach is restricting one kind of the interaction sites in desired positions along a polymer chain. For example, by mixing carboxyl-ended polystyrene (CPS) and poly(4-vinyl pyridine) (PVPy) in a suitable common solvent, hydrogen-bonded "graft" copolymer with PVPy backbone and CPS grafts was produced. Upon switching the common solvent to a selective one, say for CPS, micelles with PVPy core and CPS shell were formed. [8, 9]

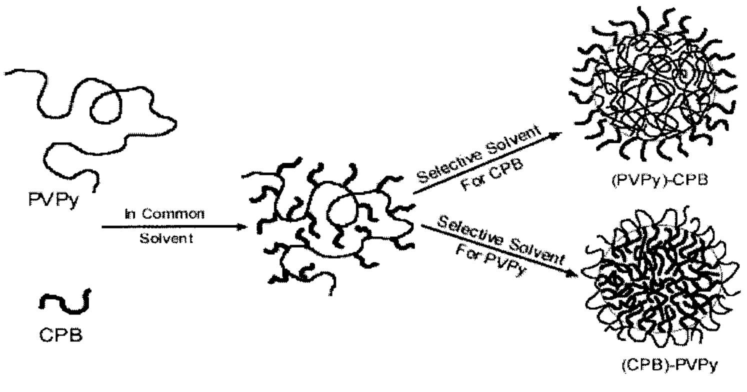

Figure 2. A schematic illustration of the formation of micelles of (PVPy)-CPB and (CPB)-PVPy.

Recently, we also reported "grafting" of carboxyl-ended polybutadiene (CPB) into PVPy in a common solvent and their micellization in two solvent mixtures, selective for CPB and PVPy, respectively. Thus, the stable micelles with PVPy being the core and CPB being the shell, denoted as (PVPy)-CPB, and the ones with CPB core and PVPy shell, denoted as (CPB)-PVPy, were formed in the corresponding selective solvent pairs. Dynamic light scattering study demonstrated that the average hydrodynamic radius $<R_h>$ of the micelles was mostly in the range from 50 to 150 nm depending on the solvent composition, polymer concentration, and the chain number ratio of CPB to PVPy, etc. (PVPy)-CPB was found more stable against dilution than (CPB)-PVPy. The two kinds of micelles differ in their diameter-composition dependence; namely, with increasing the ratio of CPB/PVPy, $<R_h>$ of (PVPy)-CPB decreases monotonically while that of (CPB)-PVPy increases at the low ratio range but decreases at the high ratio range. Besides, the core-shell structure of both micelles was clearly visualized by transmission electronic microscopy using staining techniques. Figure 2 is the schematic illustration of the formation of micelles of (PVPy)-CPB and (CPB)-PVPy. [10]

Assembly of Rod-Coil Polymer Pairs

As demonstrated in the literatures, the rod-coil block copolymers displayed different self-assembly behavior compared with coil-coil ones. [11, 12] Our work on the 'graft' copolymer approach was extended to a combination of rod-like and coil polymers. By simply mixing two polymers, that is, rod-like low molecular weight polyimide (PI) with two carboxyl end groups and coil-like PVPy in chloroform, which was their common solvent and not a selective solvent, spherical aggregates with a size in hundreds of nanometers were produced. The data of static and dynamic light scattering as follows indicated that the aggregate contained a hollow cavity. (1) The average density of the aggregates is only $1.3\text{-}1.8 \times 10^{-3}$ g/cm^3, which is about 2 orders of magnitude smaller than that of ordinary polymer micelles and surfactant free dispersed polymer particles. (2) For the spheres with low polydispersity, the $<R_g>/<R_h>$ values (0.92 and 1.15) are far different from the expected values by theory for a uniform sphere (0.774) and a polymer coil (1.50) but close to that for nondraining thin-layer hollow spheres (1.0). Furthermore, the presence of cavity was confirmed by observations of AFM (Figure 3).

As mentioned above, we previously found that PS oligomer with one carboxyl end group and PVPy formed micelles in selective solvent. However, in this case of coil-coil combination, no micelle formation occurred in common solvents. It is reasonable to think that grafts with enough stiffness are necessary for the formation of hollow spheres in nonselective solvents. Considering that each pyridine unit serves as a proton acceptor, one PVPy chain may carry many, up to 10^2 to 10^3, PI rods, the local concentration of PI rods surrounding one PVPy chain is much higher than the average, and consequently the requirement of effective packing of such crowded rods provides the driving force for forming large hollow spheres. This is analogous to the case of lyotropic liquid crystal in solution. [13]

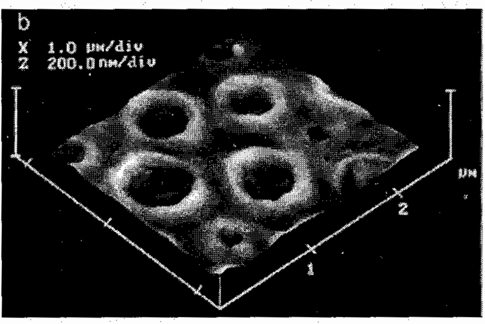

Figure 3. Morphologies of discrete hollow aggregates observed by AFM.

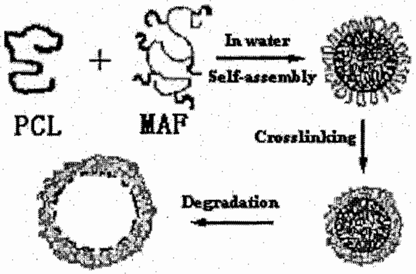

Figure 4. A schematic illustration of the self-assembly approach to hollow aggregates.

Self-Assembly of Random Copolymer with Short Grafts and Homopolymer

More recently, it was found that the polymer pair of poly(ε-caprolactone) (PCL) and graft-like copolymer MAF having a hydrophilic backbone and short PCL branches could self-assemble into micelles when the blend solutions in DMF are added into water. Stabilized by the hydrophilic main chains of MAF with PCL branches anchoring into the aggregates, the PCL didn't form macroscopic precipitation and micellar nanoparticles with PCL core and MAF shell were produced. Differing from the aggregates obtained in the approaches mentioned above, this new kind of micelles didn't have hydrogen bonding between the core and shell. The affinity between the PCL homopolymer and the short PCL branches is believed to be beneficial to the formation of the micelles. Moreover, the micellar shell could be chemically cross-linked to form "shell cross-linked knedel-like nanoparticles (SCKs)". Further degradation of the core by enzyme could lead to the final formation of the hollow aggregates.

Figure 4 is a schematic illustration of this self-assembly approach to hollow aggregates.[14]

Conclusion

We presented four entirely new approaches to polymeric micelles with well-defined structures. The common characteristic of the micelles is that there is no chemical bond between the core and shell, so they can be defined as non-covalently connected micelles (NCCMs). Moreover, three of these methods have been proved to be effective to produce hollow aggregates. As these routes are all based on commonly non-expensive polymer products and simple processes, they are promising in further applications to fabricate supramolecuar materials for various areas such as medicine, catalysis and photoelectronics etc.

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