Laboratory of Macromolecular Assemblies

Professor: Takahiro Sato

Assistant Professor: Akihito Hashidzume

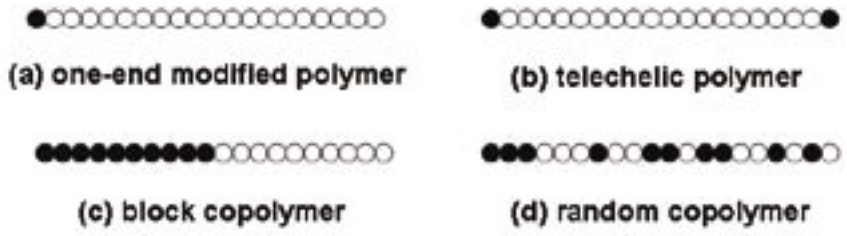
URL: http://www.chem.sci.osaka-u.ac.jp/lab/morisima/index.html

E-mail: tsato@chem.sci.osaka-u.ac.jp

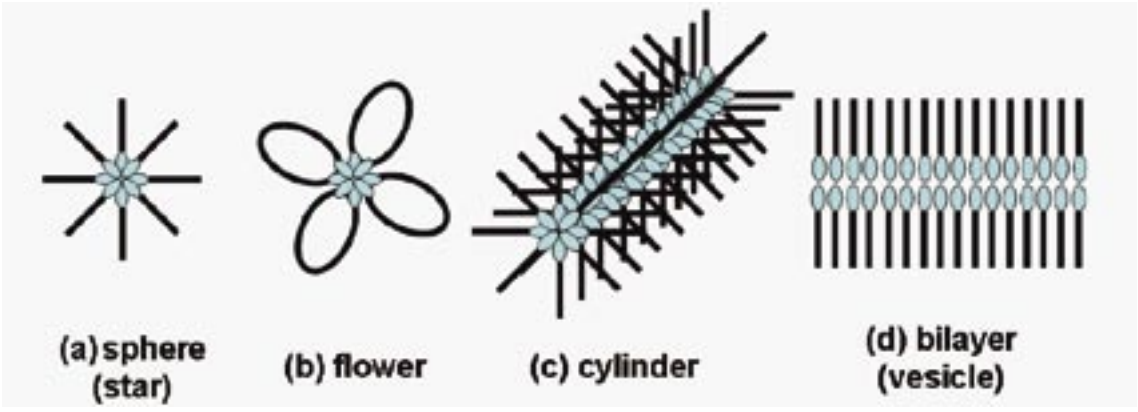
Structural Analysis of Macromolecular Assemblies

Biological systems maintain their living activities through recognition, selection, and regulation at the molecular level. In these molecular processes, biomacromolecular assemblies of proteins and nucleic acids play important roles, and thus structural analyses of macromolecular assemblies are basic and important tasks, essential to understanding living processes. Considerable interest in macromolecular assemblies has also arisen in the field of synthetic polymers in recent years. These assemblies are often stimulus-responsive and are potentially useful in a variety of commercial applications.

We have studied the structure of both biological and synthetic macromolecular assemblies. The following scheme illustrates some synthetic amphiphilic macromolecules with various architectures that



we have investigated. Here, the solid and open circles represent hydrophobic and hydrophilic monomer units, respectively. When those amphiphilic macromolecules are dissolved in water, hydrophobic monomer units (filled circles) tend to gather around each other to form hydrophobic cores, and the macromolecules self-associate to construct various types of micelles, as shown in the following



[diagrams][scheme].

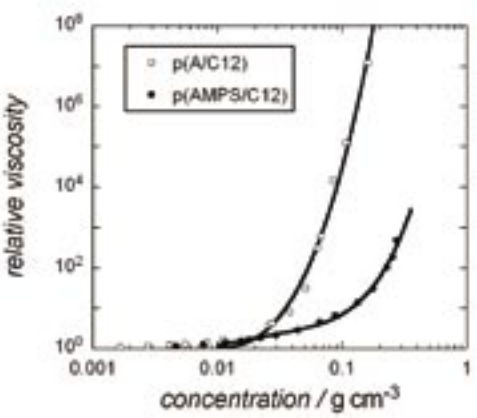
Structural analyses of micelles such as these were made using static and dynamic light scattering, ultracentrifugation, fluorescence, viscometry, and size-exclusion chromatography on-line multi-angle light scattering (SEC-MALS). These methods enable *in-situ* measurements to be carried out on the micelles in solution, which is especially necessary when investigating weakly associating micellar

systems, and these techniques are therefore superior to various types of microscopy (electron microscopy, atomic force microscopy, etc). For example, we studied the association behavior of polymer living anions in a non-polar solvent using light scattering to determine the association number and association constant, which are important parameters when analyzing the reaction kinetics of living anionic polymerization. Having determined these parameters, we then estimated, for the first time, the *true* propagation reaction rate constant for the anionic polymerization of butadiene in cyclohexane.

Biomacromolecular assemblies often possess [even] more complex structures. To date, we have studied renatured structures of thermally denatured double-helical polysaccharide and globular proteins as well as complexation between a globular protein and ionic polysaccharide. SEC-MALS is a powerful technique with which to characterize these sorts of assembly structures.

Structure-Property Relationships of Macromolecular Assemblies in Solution

The formation of macromolecular assemblies drastically changes their solution properties and it is important, therefore, to establish the relationship between the structure and the various solution properties of macromolecular assemblies. For example, hydrophobically modified (HM) polyelectrolytes (amphiphilic random copolymers) sharply increase the aqueous solution viscosity, as depicted in the graph on the right. Due to this property, they are used as viscosity enhancing reagents or gelators. It was found that these HM polyelectrolytes form star-like micelles in aqueous media, but not all hydrophobic moieties are included in the hydrophobic cores of the micelles. As a result, the micelles further associate to form a network structure in concentrated solutions by means of the hydrophobic interaction among bare hydrophobic moieties outside the cores. The viscosity-enhancing ability of the HM polyelectrolytes is thus governed by the micellar structure.



We have also investigated viscosity enhancement during the renaturation process of thermally denatured double-helical polysaccharides, the circular dichroism of helical aggregates of π-conjugate polymers, the thermal stability of the secondary and ternary structures of globular proteins after complexation with an ionic polysaccharide, and so on.

References (main papers in 2007)

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