Novel polymers: Molecular to nanoscale order in three dimensions

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The assembly of polymer chains in solution is a powerful method that is leading to the preparation of interesting and unique macromolecular-based synthetic nanostructures. Specific control over the intramolecular and intermolecular physical interactions dictates either the folding of single chains or the aggregation and ordering of multiple chains. This control is provided through the selective placement of functional groups along the polymer backbone and the relative strengths of their attractive and repulsive interactions.

Over the past decade, polymer chemistry has attained the sophistication necessary to produce macromolecules with accurate control over their structure, composition, and properties over several length scales, from typical small molecule angstrom-scale resolution to nanometer dimensions and beyond. Most recently, methods that allow for the preparation of polymeric materials with elaborate structures and functions have been modeled from biological systems as so-called bioinspired materials. In biology, complex systems are constructed by the ordering of polymer components (e.g., polymers of amino acids, saccharides, nucleic acids) through a combination of covalent bonds and weak interactions (hydrophobic, hydrogen-bonding, and electrostatic interactions), with the process being elegantly controlled by the specific sequence compositions. An extension of these assembly concepts to synthetic macromolecules is primarily driven by the desire to create materials that resemble the structure and morphology of biological systems, but that possess the versatility in compositions and properties that exists for synthetic materials.

Advanced synthetic approaches, characterization of solution structures, study of the parameters that govern two- and three-dimensional ordering, determination of the fundamental behavior of the nanoscale structures that result, and evaluation of the ability to further manipulate the nanostructured materials have each contributed toward the development of complex nanostructured synthetic materials. An overriding theme of this session on "Novel Polymers" as addressed in two introductory discussions and two full presentations was the congruent use of modern synthesis methods to study solution order in macromolecules. Particular emphasis was placed on the synthetic strategies currently being developed to rapidly advance the numbers and types of nanostructured materials that are available for analytical characterization and eventual utilization.

The simplest polymers consist of a large number (poly) of repeating molecular units (mers) each connected through covalent bonds at two sites to create a linear chain. These linear chains are most often flexible and adopt a random coil conformation in solution. Although biology commonly exerts conformational restrictions on biopolymers, much less control has been exercised for synthetic materials. The first presentation described recent efforts to limit the conformational space that synthetic polymers (or shorter chain oligomers) can explore by placing segments that have different degrees of favorable interactions with the solvent and the polymer chain. The synthetically challenging task of preparing phenylacetylene oligomers of specific chain lengths (up to 18 molecular repeat units) of high purity and containing a tri(ethylene oxide) side-chain segment at each repeat unit was rewarded with the exciting finding that the conformation of the oligomeric chains could be precisely switched from random coil to helix by slight changes in the solvent composition. In a good solvent (chloroform), the chain adopts a random coil. However, in a solvent (acetonitrile) that poorly solvates the phenylacetylene backbone, weak attractive interactions between the polymer segments cause the phenylacetylene backbone to collapse on itself, whereas the solvated tri(ethylene oxide) side-chain segments maintain a molecular dispersion within the acetonitrile. This work represents the assembly of a single polymer chain through attractive intramolecular interactions (Fig. 1) (1, 2). The architecture of the polymer chain, having amphiphilic character present as hydrophobic backbone with extending side chains of hydrophilic character allows for the formation of helices on collapse of the backbone in a controlled manner. It was also found that at high concentrations of the tri(ethylene oxide)-substituted phenylacetylene chains, the helices formed multiple-chain aggregates in what appeared to be a lock-washer assembly, resulting from intermolecular interactions as well as the intramolecular conformational order. Ultimately, this led to gelation of the solution, which may indicate a use for these materials as stimuli-responsive polymer gels. Moreover, the central channel of the helix has been shown to bind metals and stereospecific molecules, which opens the way for the application of these structures in molecular recognition or investigation as protein mimics. Once the helix size and structure is known, then the faces can be engineered to control the intermolecular forces that will be important for helix–helix assembly, for example to mimic the helix bundles commonly found in protein structures.

The architectures of polymer chains can deviate greatly from the simplest linear polymer chains of a single composition (linear homopolymers), which broadens significantly the modes of order that can be investigated toward the preparation of complex nanostructured assemblies. Topologically, the two chain ends of linear polymers can be connected to yield macrocycles, several linear polymer chains can be coupled from one chain end to a single point to yield star polymers, or multiple chains can be attached through one of their chain ends to a linear polymer backbone to yield graft

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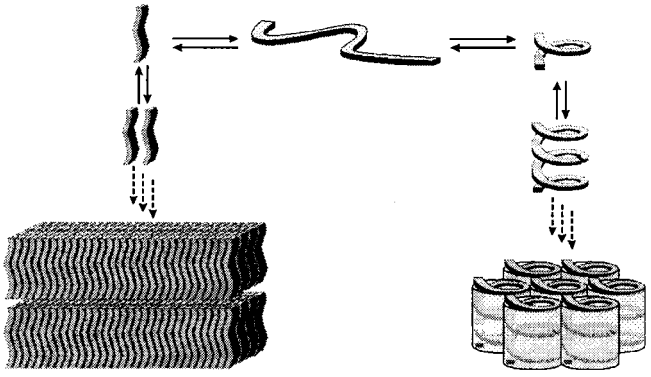


Fig. 1. The figure schematically illustrates the various equilibria relevant to amphiphilic oligomers; both intramolecular conformational order and intermolecular assembly contribute to the final organization. Under dilute conditions, the amphiphilic oligomer can collapse because of intramolecular attractive forces, and if the proper conformation order is present based on the composition and structure, helical forms are generated. As the concentration of the solution is increased, the helical components may intermolecularly assemble to lengthen the helix axis. Further increases in concentration of the amphiphilic oligomers may allow for the preparation of multihelix bundles. Alternatively, an intermolecular assembly process that avoids the initial intramolecular conformational order leads to other types of solid-state order (5).

polymers. In each case, the composition can include one type of molecular repeat unit (homopolymer) or multiple types of repeat units (copolymer), and their connectivity arrangement can vary to give random, alternating, or block copolymers.

In an amphiphilic system similar to the tri(ethylene oxide)-substituted phenylacetylene oligomers of Moore, Wu has studied the assembly of a graft copolymer composed of a poly(*N*-isopropylacrylamide) backbone and grafted side chains of poly(ethylene oxide). This is a temperature-responsive system that reversibly gives collapse of the poly(*N*-isopropylacrylamide) backbone. In this case, the backbone does not contain the specificity for helix formation, rather the collapse leads to chain aggregation into nonordered spherical nanoparticles. Alternatively, the block segments of differing solubility can be attached at only one site to give a linear diblock copolymer (see for example Fig. 2), and their assembly produces micellar spheres,

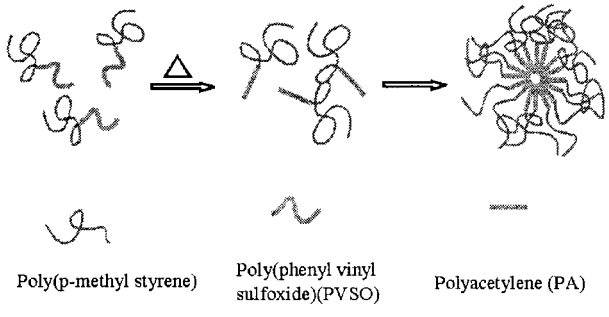
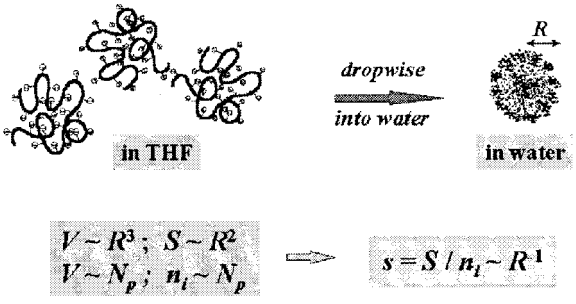


Fig. 2. Diblock copolymers assemble into polymer micelles when placed into a solvent system that solvates only one of the chain block segments. As shown here, the insoluble polyacetylene segment nucleates to form a core domain that is surrounded by the poly(*p*-methyl styrene). The nucleating core chains and the sterically repulsive interactions of the shell chains reach a balance to control the size and shape of the micellar assembly.



Therefore, the surface area (s) per stabilizer decreases as the particle size increases until it reaches a minimum value.

For polystyrene ionomers, we found that s ~ 3 nm².

Fig. 3. The microphase inversion method allows for the preparation of nanoparticles (>5-nm diameters) as stable aqueous dispersions with minimal amounts of surfactant added.

cylinders, or vesicles, depending on the diblock copolymer composition and the experimental conditions used during the assembly process. As outlined in Fig. 2, block copolymers consisting of poly(*p*-methyl styrene-*b*-phenylvinyl sulfoxide) can be converted to block copolymers of poly(*p*-methyl styrene-*b*-acetylene) by the application of heat. Self assembly then gives polymer micelles composed of polyacetylene as the insoluble core domains surrounded by poly(*p*-methyl styrene) (3). Therefore, the preparation of linear or graft block copolymers followed by their self assembly is a direct route for the formation of nanostructured materials having a core-shell morphology.

Although the approach described above is straightforward, the preparation of graft or block copolymers can be difficult and expensive. To further simplify the preparation of stabilized suspensions of individual synthetic polymeric nanoparticles in water, microphase inversion has been developed (4). As illustrated in Fig. 3, the dropwise addition of a polymer and surfactant mixture into water results in collapse of the entire polymer chain, and stabilization is provided by interaction with and coating by the added surfactant molecules. Importantly, the ratio of polymer to surfactant controls the size of the nanoparticles. Because the particle surface area decreases as the particle size increases, the particles grow until the point when the surface can be adequately stabilized by the amount of surfactant present. Ideally, nanoparticles of 5 nm or larger can be produced by the microphase inversion method.

This symposium session offered the participants information regarding the latest advances in chemical approaches for the preparation of nanometer-scale synthetic materials with controlled composition, structure, and morphology in three dimensions. Analogies can be made to several biological systems, and the synthetic models have shown interesting properties that suggest their applicability as biomedical detection devices or as vehicles for transport and delivery, among other applications.

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