



Unsolved Problems in Nanotechnology



Biographical sketch of Matthew Tirrell

Matthew Tirrell received his undergraduate education in Chemical Engineering at Northwestern University and his Ph.D. in 1977 in Polymer Science from the University of Massachusetts. He is currently Dean of the College of Engineering at the University of California, Santa Barbara. From 1977 to 1999 he was on the faculty of Chemical Engineering and Materials Science at the University of Minnesota, where he served as head of the department from 1995 to 1999. His research has been in polymer surface properties including adsorption, adhesion, surface treatment, friction, lubrication and biocompatibility. He has co-authored about 250 papers and one book and has supervised about 60 Ph.D. students. Professor Tirrell has been a Sloan and a Guggenheim Fellow, a recipient of the Camille and Henry Dreyfus Teacher-Scholar Award and has received the Allan P. Colburn, Charles Stine and the Professional Progress Awards from AIChE. He was elected to the National Academy of Engineering in 1997, became a Fellow of the American Institute of Medical and Biological Engineers in 1998, was elected Fellow of the American Association for the Advancement of Science in 2000 and was named Institute Lecturer for the American Institute of Chemical Engineers in 2001.

Unsolved Problems in Nanotechnology: Chemical Processing by Self-Assembly

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Abstract

The many impressive laboratory demonstrations of controllable self-assembly methods generate considerable hope and interest in self-assembly as a manufacturing method for nano-structured products. The practical realization of this hope will require several achievements in chemical engineering, including the precision manufacturing of precursors, expansion of our ideas of molecular chemistry to super-molecular chemistry from a bonding, kinetics and mechanistic point of view and a focus on self-assembly processes that can be scaled up to interesting levels. This leads to a rich array of research and process development issues for chemical engineers.

Chemical engineers are playing very significant roles in developing a new science base in phenomena, structures and potential applications where understanding at nanometer length scales is crucial. Synthesis and demonstration of new catalysts, new multi-component polymers and new biomaterials are all fine examples of areas to which chemical engineers are making major contributions to nanoscale science, in particular but not exclusively, via the self-assembly route that is the subject of this paper. Whether this new science base leads to important technological developments depends even more on chemical engineers. The thesis of this paper is that the opportunities for chemical engineers to advance nanotechnology demand an emphasis on developing suitably effective processing technologies. Treating self-assembly as a serious chemical process is rich with chemical engineering opportunities.

Self-assembly is a spontaneous process, guided by information content intrinsic to the assembling units, in which multiple levels of structural organization are built into a product (Kuhn and Ulman, 1995). Owing to the complexity of structures formed and the nominal ease of spontaneous organization, self-assembly is increasingly being examined as a practical chemical processing method. It is akin to crystallization except that the complexity of the structural elements involved is greater in self-assembly and length-scales beyond a single lattice constant emerge in the product. In some cases, self-assembly can result in intricate, interlocking, useful architectures of matter. The resultant structures are being actively explored as new materials, surface treatments, catalysts, membranes, photonic materials

and electronic devices, to name a few areas of current engineering exploration. Self-assembly is one of the key mechanisms by which nature builds products, from biological molecules such as proteins to larger structures such as cells and extracellular matrices, the spatial arrangement of atoms is determined, in large part, by information built into the assembling units. Complexity, in the sense of development of emergent properties of an assembly that cannot readily be envisioned from the constituents (Ottino, 2003), can arise spontaneously during self-assembly and often does, especially in biological systems. We are only beginning to develop sufficiently sophisticated synthetic assemblers to mimic biology in this way, as illustrated in Figure 1, from Simon, et al (2001).

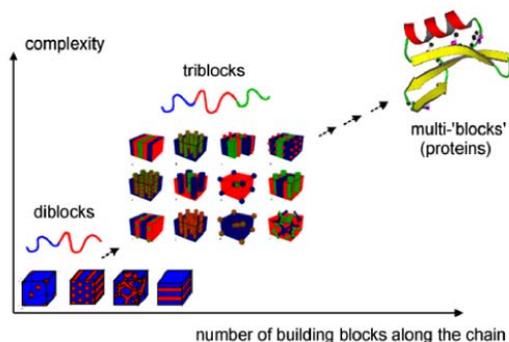


Figure 1. Schematic diagram showing how complexity of self-assembly may increase as the number of building blocks in a copolymer increases. (adapted from Simon, et al. 2001)

Indeed, other routes to self-organization, including those far from equilibrium (Ottino, 2003), may also be of interest for nanotechnology.

The ability to form structures spontaneously from the bottom up, using principles akin to biological assembly, has inspired considerable research among chemists, physicists and chemical engineers to develop useful products (Whitesides, et al. 1991). The high level of scientific activity in this field creates several kinds of major opportunities for chemical engineering research. The overall opportunity might be characterized as a shift from product to processing research in self-assembly. As self-assembly attempts to evolve from laboratory techniques and provocative demonstrations of structure, to practical, larger-scale, applied processing methods, a broad spectrum of important engineering research problems is being generated.

Opportunities for new chemical engineering research in self-assembly are the focus of this article. What this requires, among other matters, is taking self-assembly seriously as a processing method and asking, "What are the barriers to its development and widespread implementation in the commercial sector?" This review takes a processing perspective, appropriate to motivate this underdeveloped field of chemical engineering research. A recent review (Schreiber, 2000), from a surface science perspective, describes the current state of laboratory growth methods and structural characterization comprehensively, for the case of self-assembled monolayers. An up-to-date review on three-dimensional self-assembled structures has yet to be written. This article aims at processing two- and three-dimensional self-assembled structures.

An important characteristic of self-assembly processing, which changes both the chemistry and chemical engineering research perspective, is that the fundamental objects participating in the process are, more often than not, neither simple atoms nor simple molecules. Rather, they are modular, prefabricated, complex molecules or objects with internal structure and external size, shape and functionality. The structure, size, shape and functionality define the information content of the assembler. Colloidal crystallization of structured particles typifies the process of developing organized assembly of complex, multimolecular objects. The rules of chemical bonding (interaction potentials) and chemical kinetics for reactions among objects such as these to form stable, useful products remain to be thoroughly explored to form a good basis for process development.

Brief summary and critique of the state-of-the-art of self-assembly processing

Numerous processes for producing chemical products, surface layers or new materials by self-assembly have been developed. Table 1 gives a substantial but not exhaustive list. A short discussion of what is included, and what is omitted, and why, is warranted. Adsorption of polymers consisting of identical units, that is homopolymers (not on the list), is a widespread and effective practical method to modify materials surfaces. However, it is a random process without any particular guidance to the assembly coming from the molecular structure, and therefore it lacks an important ingredient (a trajectory guided by information content of the assemblers) in the definition of self-assembly. On the other hand, in the adsorption of multi-component polymers, such as block copolymers or hydrophobically modified polymers, some pieces of the molecule are driven by their chemical nature to stick to interfaces; others are not. The resulting molecular arrangement is directed by information (internal structure) in the adsorbing molecules. Amphiphilic molecules "know" which end is up when placed in a surface or interfacial region.

Table 1: Processes Incorporating self-assembly

Adsorption of multicomponent polymers
Cooperative supramolecular self-assembly of surfactant organic mesostructures
Grafting of polymers on interfaces
Langmuir-Blodgett deposition
Layer-by-layer deposition or sequential adsorption
Micellar control of reactions
Microcontact printing
Organizing colloids into arrays and crystals
Self-assembly of monolayers
Spin and dip coating of supramolecular solutions and dispersions
Surface directed ordering of molecules at interfaces (liquid crystals)
Surface modification by monolayer or multilayer deposition
Templating
Vesicle fusion

Some of the processes in Table 1 have been known for quite some time (e.g. Langmuir-Blodgett deposition); others have been developed in the last decade (e.g. microcontact printing). Note that by definition, in our parlance, a self-assembly process, while being largely controlled by the chemical architecture of the assemblers, may have elements that are neither spontaneous nor inherent in the assembling entities. That is, some of these are directed assembly processes,

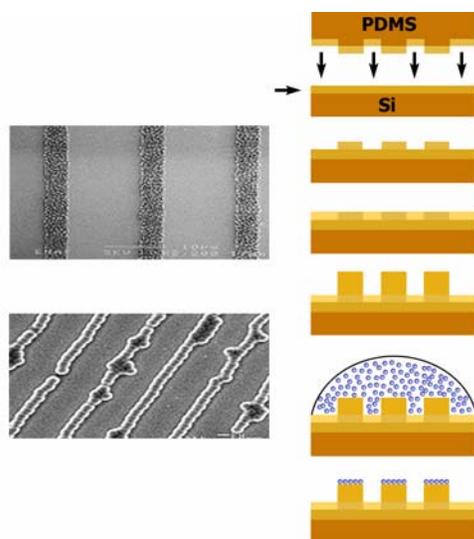


Figure 2. Extension from molecular to microscale systems. Selective self- organization of charged colloid particles using patterned multilayers as templates. Initial patterning done with microcontact printing, followed by layer-by-layer assembly, with the final step incorporating electrostatic assembly of nanoparticles. (adapted from Chen, et al. 2000)

which may incorporate non-thermodynamic influences (dipping, printing, spinning, quenching, etc) or effects of external influences (templates, surfaces, fields, etc.). In fact, the effective use of these influences will be one of the most important issues in developing practical self-assembly processes. This article does not make a sharp distinction between purely self-assembly processes and directed assembly processes. In both, the information content of the assembling objects plays a major role.

The practical history of Langmuir-Blodgett (LB) deposition as a processing method (Swalen, et al. 1987) offers a sharp focus, and a sobering shadow, on the future of self-assembly processing. LB processing has never been an important practical technology, despite its wide-spread utility and unique capability of controlling structure in laboratory-scale materials assembly, owing among other things to the difficulty in scaling-up the process via continuous, parallel or repetitive processing. As we shall see, continuous processing has been achieved in few examples of self-assembly processing.

One promising self-assembly method that seems to lend itself to scale-up and to continuous processing, and also possesses great versatility in the range of components that can be used in the process, is Layer-by-Layer growth (LbL), pioneered by Decher and co-workers, and now being much more broadly explored (Decher, 1997). LbL works by successive dipping cycles of substrates into solutions of molecules with some

interactive complementarity (usually of opposite charge). Mohwald and co-workers have generalized this method to LbL on particle surfaces (Caruso, et al. 1998; Caruso and Mohwald, 1999) developing the capability, after destruction of the templating particle (usually by dissolution), to make self-assembled capsules with controlled structure, contents and wall properties (mechanical and transport). Destruction of an organic template to leave a self-assembled inorganic material has proven a very effective route to new porous materials for catalysts, sorbents and membranes (Asefa, et al. 1999; Melde et al. 1999; Freemantle, 2000).

Microcontact printing (MCP) is another burgeoning laboratory-scale method incorporating self-assembly (Kumar, et al. 1994). In the basic application of this methodology, a stamp is "inked" with a self-assembled layer. The stamp is then used in MCP processing to transfer the self-assembled material to another surface. The possibilities for making MCP an efficient, versatile, even continuous, process seem very achievable, based as it is on classical printing technology. Clearly, many of the processes in Table 1, MCP included, are not purely self-assembly, or even directed assembly processes but involve the intervention of some other processing technique in concert with self-assembly. Self-assembly used as one method in a multi-step process is a very likely outcome of much of current nanoscale processing research. This would characterize methods such as micellar or microemulsion controlled reactions, as well as a range of "hybrid" self-assembly processes. Figure 2 (Chen, et al. 2000) shows the product of a hybrid LbL-MCP process, followed by the deposition of a layer of colloidal particles.

Other hybrid processes include ink-jet printing followed by a self-assembly process such as vesicle fusion

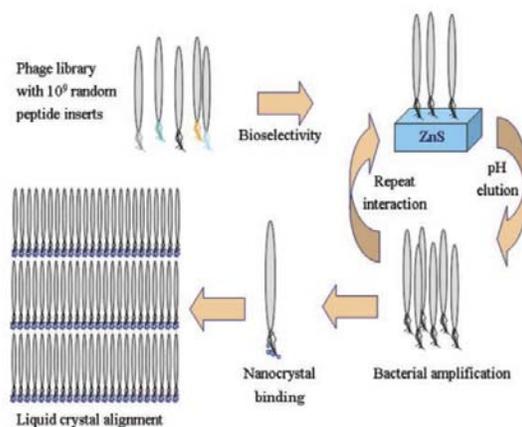


Figure 3. Schematic diagram of the process used to generate nano-crystal alignment by the phage display method. (Reprinted with permission from Science, Lee, et al. 296:892-895. Copyright 2002 AAAS.)

(Cremer and Boxer, 1999), and biological production of self-assembled products (Cha, et al. 2000; Belcher, et al. 2000; Seungju, et al. 2000; Wu, et al. 2002), one of which is illustrated in Figure 3.

Most of the current self-assembly processing methods function primarily to create surface and thin film structures (LB, LbL, multicomponent polymer adsorption.). This “two-dimensional” emphasis derives both from the many applications for surface modification and for the templating assistance that surfaces generally offer to self-assembly processes. Nevertheless, much more work is needed in the direction of three-dimensional self-assembly methods. As work in colloidal crystallization has shown, not only is three-dimensional assembly of pre-formed, supermolecular objects a route to materials with interesting new structures and properties (Velev, et al. 2000) but also, studying the crystallization of objects reveals considerable new insight into the inter-object potentials (Davis, et al. 1989).

Processes competitive with self-assembly

An issue that must be addressed is that of competing processes: What competitive processes are available to achieve similar targets? Structuring at the nanoscale is not available exclusively via self-assembly. While the “bottom-up”, additive approach embodied in self-assembly has much to recommend it, “top-down”, subtractive processes, such as nanolithography by x-ray, electron beam and UV also have considerable potential yet to be tapped. Furthermore, subtractive processes have a track record of past accomplishment. Direct-write processes, which are automated layer-by-layer depositions, including ink-jet printing (Sachs, et al. 1992), stereolithography or 3D printing (Griffith and Halloran, 1996), are also advancing rapidly, based in part on advances in robotics (Lewis, 2000). Nano-imprinting, a nano-scale throwback to the metal-stamping of, say, auto body parts or refrigerator housings, is also showing serious promise in electronic device fabrication. (Chou, et al. 2002) More conventional processes, such as lamination and multilayer extrusion (Cesarano and Calvert, 2000), are also achieving a greater degree of spatial control. Sol-gel processing and certain combustion/aerosol processes also are achieving some success in creating controlled nanostructured products.

Thus, there are serious competitors to self-assembly processing. Engineering research in self-assembly processing should be realistic about comparative advantages of alternative processes, and creative about

inventing combinations of new technologies for nanoscale processing.

New issues in self-assembly processing

There are several identifiable directions in which scientific and technological advances in the chemical sciences must be made in order for self-assembly processing to become an important, widely used processing tool. The directions discussed below are each important; a prioritized list is not possible in the current state of the field.

Precision synthesis of precursors.

The ability to form a desired state of organization spontaneously depends on the internal structure of the assemblers. It is then clear that information must be built into the assembling objects with some degree of fidelity. There are various avenues for achieving this. Size, shape (in rigid objects), conformation (in flexible objects), sequence (in multicomponent macromolecules), spatial relationships among subunits all can be “read” in molecular recognition interactions. In synthetic molecules, small amphiphiles such as surfactants or lipids are classes of molecules that can be synthesized with precision, that is, they can be made and isolated as pure compounds. The ability to make micellar and bilayer membrane structures by self-assembly is a direct consequence of the precise architectures of these molecules. Impurity in assembling molecular structure creates disorder or other degradation in quality in the self-assembled product.

Only biological systems currently achieve precise syntheses of molecules of more than a few hundred daltons. There are two broadly thought-provoking points in this realization for current self-assembly research. One is that precision synthesis and fidelity of information content is essential for effective self-assembly of intricate, functional systems. This should motivate a broad array of useful chemical synthesis and process research to produce the starting materials for non-biological self-assembly. Protein folding, the unimolecular self-assembly process by which proteins (multicomponent macromolecules with precise sequence distributions) take their functional forms, is far from fully understood. However, it is certain that the final state of a protein folding process is determined by the primary sequence of amino acids in the macromolecular backbone. Precision synthesis of the sequence controls the assembly. Folding processes of nucleic acids are also increasingly recognized to be functionally important, while information is built into polysaccharides by control of architectural features such as branching. Successful development of self-assembly

processes will place a premium on new chemical or directed biological routes to pure, precise macromolecular synthesis and production or particle formation. Furthermore, it will be fruitful to understand, in much more detail than we currently do, the sensitivity of various synthetic self-assembly processes to the lack of precision in the architecture of the assemblers.

A second lesson that may be extracted arising from consideration of biological self-assembly is understanding of how nature achieves precision synthesis. Biological systems do not synthesize perfectly; rather, considerable effort is expended in detecting and correcting errors en route to a pure product. The chemical processing analogs of this are on-line measurement, control and post-reaction separation processes. To achieve the necessary control over molecular architecture, it will be necessary to explore both chemical and biological synthesis routes with a realistic eye toward process efficiency.

Expanding the idea of the molecule.

Since self-assembly often, even usually, involves the spontaneous organization of objects considerably larger than molecules, it is useful to begin to think about larger assembling objects in self-assembly processes as we do about molecules in chemical reactions. The atomic and molecular notions of valence, bond strength, etc., have inexact but pragmatic counterparts when applied to interactions among structured macromolecules, nanotubes, particles and other important self-assembly constituents. Figure 4 (from Manoharan, et al. 2003) shows that composite, or structured, colloidal nanoparticles can be formed by the controlled consolidation of primary particles. The symmetry of these structured particles endows them with the potential for directional bonding, the molecular analog of the symmetry of electronic wavefunctions.

Another relevant example of an enlarged definition of

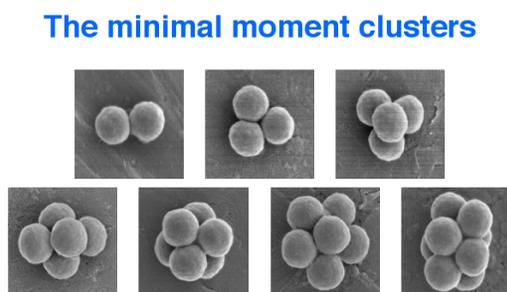


Figure 4. Composite particles formed by association of spheres confined within emulsion droplets. The precisely formed aggregates confer a selectable series of symmetries on the composite particles (adapted from Manoharan, et al. 2003)

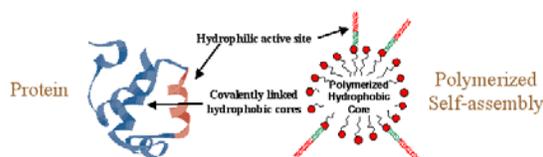


Figure 5. Micelles of peptide amphiphiles bear many similarities to protein macromolecules. They have hydrophobic cores, hydrophilic bio-active exteriors, globular shapes, and sizes in the tens if nanometer range. Connectivity can be introduced via polymerizable lipid tails.

the molecule is shown in Figure 5. In our group, we have been exploring the properties and applications of synthetic peptide-lipid conjugate molecules (Tirrell, et al. 2003). The idea of these molecules is to confer on unstructured, short, potentially biologically active peptide chains, some self-assembly character that will organize and present the functional peptide in an effective way. We have found that micelles formed from these peptide amphiphiles resemble proteins in several significant, and possible useful ways, enumerated in Figure 5. We now know (Yu, et al, 1998) how to use this self-assembly character to drive the peptide into ordered secondary structures as they are found in intact protein macromolecules. Protein analogous micelles are objects that can mimic protein molecules and, in this way, expand the notion of how to use protein functionality in self-assembly.

Scale-up of self-assembly processes.

As mentioned earlier in the context of Langmuir-Blodgett deposition, scale-up of self-assembly processes to technological significant scales has not been pursued to an appreciable degree. That is perhaps natural given the state of development of the field. Nevertheless, lack of ways to scale-up can be the demise of a promising processing route in a technological arena. Some of the most innovative developments in self-assembly processing to date have been achieved by chemists, where advances in assembly on non-planar surfaces have led to the ability to assemble macroscopic, three-dimensional structures spontaneously (Jacoby, 2000; Gracias, et al. 2000; Whitesides and Grzybowski, 2002). A great opportunity exists for some tools of process systems research to be applied to self-assembly processing, and nanoscale engineering in general. Success in enlarging the capacity of self-assembly processes by continuous, parallel or repetitive processing would be very valuable.

Kinetics and mechanisms of self-assembly processes.

Another important issue is the matter of kinetics. Self-assembly science is grounded in processes that tend

toward desirable equilibrium structures. Chemical processes generally should go as fast as possible, consistent with product quality. It is difficult to envision the processing research called for above proceeding fruitfully without data on the rates of self-assembly processes. Our view is that, for design and development purposes, we need to understand fully the trajectories, through time and structural intermediates, of self-assembly processes.

This need for research in self-assembly kinetics, and the related issue of mechanisms, has several facets. The acquisition of such data will stretch and eventually expand the tools we have to observe self-assembly in progress. Research on self-assembly kinetics requires data in real-time, pushing the field toward methods that are faster and more highly time-resolved. Accurate kinetic data are a necessary prelude to predictive models of the evolution of self-assembly processes. As the complexity and number of components in these processes increase, predictive models will become more important tools in process and product design. We believe it is fair to make the analogy between self-assembly and chemical reaction processes. Thorough understanding of chemical bonding, reaction mechanisms, pathways and kinetics are crucial to reactor design. Analogs in self-assembly are intermolecular or interparticle potentials, trajectories and rates of assembly.

As an example of work in this direction, we offer our group's work on vesicle fusion. The essential steps of this physico-chemical reaction are depicted in Figure 6a. Vesicle fusion, just as LB deposition, is an increasingly useful laboratory method to coat surfaces with monolayers of lipid molecules. We have been interested

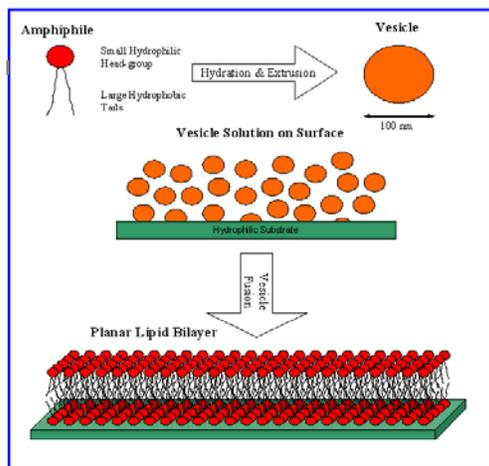


Figure 6(a) Schematic diagram of vesicle fusion. Attractive forces between vesicle and surface cause distortion of vesicle shape, eventual rupture of the vesicle and ultimately deposition of a nearly complete bilayer.

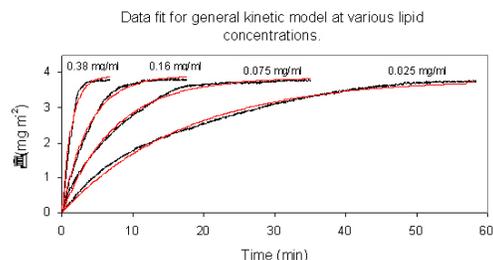


Figure 6(b) Kinetics of bilayer deposition via vesicle fusion as studied by ellipsometry. (A. Parra, D. Stroupoulis and M. Tirrell, unpublished data)

in its technological applications, particularly selective coating of the surfaces of microfabricated devices. For this we felt we needed kinetic data and a mechanistic interpretation so that we could extrapolate to new situations such as deposition on textured surfaces, in corners, etc. Phase-modulated ellipsometry has proven to be a useful tool in kinetic studies (Parra, et al. 2003). Figure 6b shows data on the accumulation of monolayers (we have proven that the plateau deposition is in fact a monolayer) fit to a model where we have considered both the diffusive rate of supply to the surface and surface reorganization as important potentially rate-controlling steps. Our unambiguous conclusion is that surface reorganization dominates in this case. These kinds of studies are very important to the advancement of this field.

Rates of self-assembly processes.

Chemical engineers are seldom satisfied with the rates of uncatalyzed chemical reactions for technological purposes. Biological self-assembly is, in some situations, promoted or directed by protein or templates. The fact that self-assembly proceeds down a free energy gradient to a thermodynamically determined endpoint is reassuring in some respects. However, metastable states of varying duration may intervene. Equilibration is unhurried; chemical manufacturing is not. It is challenging to think of how one might design a catalyst for a self-assembly process. Physical or chemical templating, for example, a type of epitaxial growth, is one possible route, which in self-assembly has been explored more for its effect on structure than on rate (Ball, 1997). External fields can profoundly affect the rates of self-assembly processes (Koppi, et al. 1993) and should be explored more extensively in this vein. Perhaps more than in simpler chemical reaction processes, the size and complexity of objects involved in self-assembly are such that diffusion limitations are more the rule than the exception, motivating a need for new research in transport phenomena applied to this field.

Characterization and process control.

Practical processes must be controlled to produce valuable products; in the case of self-assembly, these are products of intricate internal structure. Real-time structural analyses present instrumental challenges that must be addressed. Since self-assembly often produces structured products over several length- and time-scales, techniques capable of measuring, with resolution, over multiple length- and time-scales are needed. Informative, on-line measurement is a prerequisite for process control. Characterization of defects is particularly important for the applications envisioned. Furthermore, self-assembly processing of nanostructured products is a driver for new research in control of distributed processes (Christofides, 2001). Control of distributed systems such as self-assembly will also rely heavily on the development of tractable, predictive models.

Concluding remarks

It has been remarked that new directions in science are launched by new tools more often than by new concepts (Dyson, 1997). Self-assembly is a blend of concepts and tools; the field will advance more rapidly as we turn concepts into techniques. Research in the chemical sciences and technology over the next few years, pursued with a clear view to the barriers and competition facing self-assembly, is likely to produce important new progress, not only for self-assembly processing but for the optimum processing routes to nanostructured chemical products.

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