Organic Materials Science

George M. Whitesides

Abstract
The following article is based on the presentation given by George M. Whitesides, recipient of the 2000 MRS Von Hippel Award, the Materials Research Society’s highest honor, at the 2000 MRS Fall Meeting in Boston on November 29, 2000. Whitesides was cited for “bringing fundamental concepts of organic chemistry and biology into materials science and engineering, through his pioneering research on surface modification, self-assembly, and soft lithography.” The article focuses on the growing role of organic chemistry in materials science. Historically, that role has been to provide organic polymers for use in structures, films, fibers, coatings, and so on. Organic chemistry is now emerging as a crucial part of three new areas in materials science. First, it provides materials with complex functionality. Second, it is the bridge between materials science and biology/medicine. Building an interface between biological systems and electronic or optical systems requires close attention to the molecular level of that interface. Third, organic chemistry provides a sophisticated synthetic entry into nanomaterials. Organic molecules are, in fact, exquisitely fabricated nanostructures, assembled with precision on the level of individual atoms. Colloids are a related set of nanostructures, and organic chemistry contributes importantly to their preparation as well.

Keywords: nanotechnology, PDMS [poly(dimethylsiloxane)], self-assembled monolayers, self-assembly, soft lithography.

Introduction
It is an enormous compliment to start one’s career in one field—in my case, physical-organic chemistry—and to have an entirely different field recognize research resulting from that career. It is a particular compliment to me (and to my colleagues who have actually done the research being recognized by the Von Hippel Award) because, when I started my career, materials science was just forming as a discipline; as a graduate student in chemistry in the early 1960s, I had never heard of it. It has since grown to become one of the most interesting fields in science and engineering: its place at the interface between engineering and physical science has allowed it to play an important role in some of the most exciting technology of the last century. Materials science, together with biology, has become a major focus for exploration in chemistry and for applications of physics. It has been enormously interesting and rewarding to be a part of these two fields—materials science and chemistry—as they have advanced together. It is a great honor for me and for the members of my group to receive this award in recognition of the growing part that organic chemistry, biological chemistry, and biology are now playing in materials science—both in the present and for the future.

Much of the work carried out in the early days of materials science concerned the traditional classes of materials—metals, ceramics, and to a smaller extent, organic polymers. The world of materials is, of course, now changing rapidly; organic materials, materials relevant to biology, and materials with complex new types of functionality and properties are all increasingly important to the future of technology (and therefore to the future of materials science).

While organic polymers have historically been the most important class of organic materials in materials science, these polymers have played, primarily, relatively simple roles as structural materials, coatings, and protective films; they have not been taken quite as seriously as metals, for example, which have multiple functions and complex electronic and optical properties.1 The view of organic polymers as materials with only narrow applications is now changing; it is increasingly clear that one should think of organic polymers—and indeed many other organic substances—as materials with many functions—from electrical conductivity and electroluminescence to biocompatibility and capacity for information storage. I believe that organic materials should now be considered in the same category as the historical pillars of materials science in terms of versatility in applications and in importance. They have an overall complexity in behavior—including structural, electronic, and optical behavior—that probably exceeds that of any other single class of materials. They have unique phases (elastomers, gels, liquid crystals). In addition, they bring a key new capability to materials science: the ability to bridge materials science and biology. This combination of materials science and biomedicine will offer, I firmly believe, some of the most important opportunities for materials science in the future.

Chemistry and materials science offer one another four opportunities. First, chemistry can design and synthesize new components (compounds, structures, polymers, composites) with which materials science can work. Second, materials science offers a range of targets and a sophisticated understanding of applications. Third, each field—in pursuing its activities—uncovers new phenomena and develops new techniques for measurement. Fourth, combining chemistry (which is normally concerned with molecules and small particles such as colloids) and materials science (which is normally concerned with meso- and macroscopic phenomena) has the potential to explore the transition between microscopic structure and macroscopic properties.

At the interface between materials science and biology, there will also be important opportunities for the exchange of concepts. Figure 1 illustrates a simple example. This figure shows four fundamental types of materials: metallic, ceramic, polymeric, and biological. The combination of different components as alloys or composites has been a remarkably successful strategy in materials science for achieving and designing new properties. There are entire subfields devoted, for example, to the concept of “alloys.” Do these kinds of concepts—so useful in one area—carry over into another? There is probably no general answer to this question, but it is interesting that the glowing mice in Figure 1d can be considered a kind of biological “alloy.” These mice are a combination—that is, an “alloy”—of mouse and jellyfish.2 They combine certain genes taken from a jellyfish with the genome of the mouse. Gentle illumination of these mice with UV light produces the green fluorescence...
characteristic of a specific jellyfish protein. This type of biological alloy is becoming important in genomics. It also suggests that using the concepts familiar in one field to describe the phenomenon emerging in a second may provide stimuli to the imagination. Are there other ideas that can be taken from metallurgy that would suggest new approaches to genetics? Could the strategy used to create hybrid organisms stimulate new ways of designing or creating alloys?

Historically, materials science has played a strong role in issues related to national security. Materials science was, in a sense, invented by the U.S. Department of Defense (by DARPA, the Defense Advanced Research Projects Agency) to satisfy a need for a university-based style of research with the characteristics of some of the best industrial laboratories: that is, combining a wide range of talents from conventional disciplines to solve difficult interdisciplinary problems. Those problems were originally posed in terms of military systems, and metals and ceramics—as components of airframes and armor—were centrally important. Sensors and electronics also of airframes and armor—were centrally important. Sensors and electronics also.

The end of the Cold War changed the focus and pace of development of materials-based technologies. There is now intense competition in the commercial world, while the military world is less technologically dynamic and more cost-conscious. The economic competition extends across all economic sectors, but the major innovative foci in the United States have centered on information technology, computational equipment and communications, and—to a smaller, but very rapidly growing extent—biomedicine and the interface between materials science and biology. Industry has also been increasingly constrained to focus on product-development research and to leave longer-range research to the universities. Venture capital-backed startups now play a vital part of the process of commercialization of new technology. Materials science still sits at the base of this tumultuous change, but since it is often far removed from end products, it requires more effort to explain to nonscientists what the opportunities—both intellectual and practical—of materials research are than it does for biology or astronomy.

It is important for materials science to engage with fields in which opportunities are particularly rich, and to do so rapidly. The combination of chemistry—especially chemical synthesis—and materials science is one such area. The combination of biology/biomedicine and materials science is a second one. Nanoscience, a field that will have a very strong chemical component, is a third.

**Opportunities**

Organic chemistry is particularly important in three broad fields that overlap with materials science: biomaterials, information technology, and nanotechnology. Why? The central reason is the versatility of carbon as an atomic building block of molecules. Organic chemistry is, of course, fundamentally centered on the chemistry of carbon, as microelectronics is centered on silicon. The progression from diamond—the hardest material known, the best thermal conductor, and a good electrical insulator—through graphite (soft and electrically conductive) and buckytubes (which have astonishing electrical conductivity and stiffness) to polyethylene and methane illustrates the range of substances and properties that can be obtained in carbon-based compounds (Figure 2). This amazing collection of properties results from simply changing the ratio of hydrogen to carbon, and the bonding between carbon atoms. Very few elements have the versatility of carbon.

Why is it that this versatility is so important for the future of materials science? The answer is that ultimately, organic chemistry (or perhaps more generally, chemistry) offers both the ability to synthesize materials to design—that is, to convert atomic-level design to physical reality—and the opportunity to connect to the carbon-based molecular structures that make up life.

Chemistry has always excelled in synthesis and has historically solved problems through the synthesis of new molecules. I believe that one of the major impacts of organic chemistry on materials science will be to reintroduce the idea of exploratory synthesis—that is, the invention of new materials and processes—into materials science as a core discipline.

**Organic Surface Science and Self-Assembled Monolayers**

Our initial work in organic materials science, and our initial effort to connect molecular-level synthesis to microscopic properties, began with organic surface chemistry. We started with work on the surface chemistry of polyethylene. This work was technically fascinating, but unsatisfyingly complicated. As soon as self-assembled monolayers (SAMs) became...
available from the initial experiments of Nuzzo, Allara, and colleagues, we focused on this marvelous system for surface science. SAMs form on dipping a thin, supported film of gold into a solution of almost any organic compound that contains sulfur; this procedure works particularly well with alkanethiols [e.g., CH₃(CH₂)₁₇SH]: these compounds form monolayers that are highly ordered and relatively durable (Figure 3).

SAMs of terminally functionalized alkanethiolates on gold provide what is probably the most flexible system in materials science for tailoring the surface properties of materials because it is so easy to change the functional groups that are in the terminal position of the poly(methylene) chain. By changing that single functional group, it is possible to determine many of the properties of the surface. For example, if the terminal functional group is a methyl group, the surfaces are very hydrophobic; if the surfaces are populated by carboxylic acid groups, they are very hydrophilic. Extension of the idea of rational design of surface properties from simple examples (wettability) to the complex systems required in biology has been one of the accomplishments of biomaterials science in the last decade.17,18

The study of SAMs has clearly demonstrated the connection between the atomic- and molecular-level structures of surfaces and the properties of materials. Because the number of different types of organic groups that can be introduced onto a surface by synthesis is very large, it is possible to prepare a wide range of different types of surfaces by design.19

Figure 4 demonstrates the application of SAMs in biology and provides an example of a type of contribution that materials science can make to this field. This figure shows two images of bovine capillary endothelial cells (the cells lining the interiors of the blood vessels of cows). The fact that these cells are square (cells on surfaces are normally irregular in shape) reflects patterning of the surface using SAMs.20 Accomplishing this type of patterning requires a combination of two types of surfaces. One lies directly underneath the cells. In this instance, this surface is hydrophobic. It adsorbs proteins strongly from solution and allows the cells to attach and spread on the surface. The surrounding regions present a SAM designed in such a way that the structure of its surface prevents the adsorption of proteins. Since cells require intermediate proteins to act as “glue,” the cell is unable to spread onto the protein-free surface. Developing SAMs that provide the correct surface functionality to achieve the patterning of cells re-
Emerged from this work, soft lithography is one technology that has ties used in microelectronics. So-called soft rooms and expensive instrumental facilities without requiring access to the clean materials scientists—to carry out microfabrication. We have been very interested in developing methods of microfabrication that make straightforward for nonexperts in this field—chemists, biologists, and most materials scientists—to carry out microfabrication at the present time. Soft lithography is one technology that has emerged from this work. Soft lithography relies on printing, molding, and embossing using a stamp whose surface is patterned in a base-relief structure. The adjective “soft” in soft lithography comes both from the fact that the stamp—commonly made of poly(dimethylsiloxane) (PDMS), an elastomer that readily deforms (i.e., is soft)—and from the fact that the organic materials being patterned are often called “soft” by physicists. Soft lithography—in the instance of the patterning shown in Figure 5, microcontact printing—makes it possible to generate small patterns with sophisticated control over surface properties using remarkably straightforward experimental procedures.

In soft lithography, we begin with a pattern in a CAD file and print this pattern onto a transparency using a high-resolution printer (Figure 5). This process provides patterns with a linewidth down to approximately 20 µm. This feature size is not particularly useful for high-performance microelectronics, but it is sufficient for most applications in biology. The transparency is used as a photomask in 1:1 photolithography: it is placed on top of a wafer supporting a thin film of photoresist and exposed to UV light. After development, what remains is a base-relief pattern in developed photoresist. A liquid prepolymer of PDMS is poured over that pattern, cured, and then removed simply by peeling it away. The PDMS stamp can be used in a wide range of types of microfabrication.

The largest area of application of soft lithography at the present time is in the fabrication of microfluidic systems for bioanalysis (particularly genomics, cell biology, and high-throughput screening of drugs). Figure 6 shows channels in a microfluidic device that are approximately 50 µm wide, made by soft lithography. Sophisticated microfluidic devices can be made rapidly using soft lithography. This figure shows one example—a central channel surrounded by a helical, three-dimensional (3D) cooling channel. This technology is proving remarkably useful in rapid prototyping and in producing small lots of devices and systems for bioanalysis.

The ability to fabricate microchannel systems makes it possible to explore a range of new ideas in microfluidics. Figure 7 provides an example. This figure shows a simple microfluidic system—a crow’s foot microchannel structure—used to regulate the flow of fluids in the vicinity of mammalian cells. The flow of liquids in the microfluidic systems is typically laminar: because of the small lateral dimensions of the channels, there is no turbulence, and Reynolds numbers are low. In this application, by regulating the flow of liquids into the three inlets, it is possible to position a liquid stream containing a dye over the one portion of a cell attached to the bottom of the main channels, while leaving an adjacent part of the cell isolated from that dye. By relatively straightforward manipulation of the rates of flow, using channels that are a few hundred micrometers wide, it is straightforward to position the interface between fluid streams over the cell with an accuracy of a few micrometers. Figure 7b is a single cell in which the mitochondria of the cell have been dyed red to the left of the nucleus, and green to the right of the nucleus. This simple device illustrates the ability of soft lithography to fabricate tailored microfluidic devices for a wide range of uses in biotechnology and biomedicine.

Organic polymers have largely displaced silicon as the preferred material for the fabrication of microfluidic systems and will, in due course, probably also replace glass. Polymers are optically transparent (and thus allow optical detection), durable, easily fabricated, biocompatible, and, above all, inexpensive.

Near-Field Optics

In another application of organic materials in lithography, we embedded small, transparent, polymeric microspheres in a transparent membrane of PDMS; the spheres have an index of refraction higher than that of the PDMS. When these
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spheres are embedded at a distance from the surface of the PDMS that is approximately equal to their diameter, they act, on illumination, as ball lenses (Figure 8). Thus, by illuminating an array of microspheres in an appropriate membrane placed in contact with a film of photoresist, it is possible to project multiple microscopic copies of the pattern of the illuminating aperture into the photoresist. This procedure provides a simple method of patterning large areas of photoresist in parallel with relatively simple, repetitive figures using an experimentally straightforward system. It relies on the transparency of the PDMS membrane and its ability to conform exactly to the surface of the photoresist, as well as to hold the spheres embedded in it at the correct distance to focus into the photoresist. It is practical to achieve submicrometer features and 1000:1 size reductions in a single step using this technique (albeit with distortions in the dimensions of the patterns). We believe that this type of system—while not competitive with conventional photolithography for the production of the complex, multilevel patterns required for circuits—may be useful for simpler types of photolithography. Examples might include optical filters and inexpensive circuits.

Future Opportunities: Nanoscience

Nanoscience and nanotechnology are exciting, emerging subfields of materials science. They are also a part of chemistry, since molecules are the prototypical nanostructures. Nanomaterials are among the first new systems to emerge from nanoscience. Quantum dots, buckytubes, and iron/platinum colloids are examples of important new materials that have emerged from explorations of nanoscience (Figure 9). The semiconductor quantum dots studied by Brus et al. (Figure 9a) are rapidly becoming important as nonbleaching dyes in biotechnology; buckytubes (Figure 9b) have attracted wide attention for their remarkable properties—electrical conductivity, stiffness, and size. The iron/platinum colloids (Figure 9c) developed by Murray represent an example of components composed of ordered, self-assembled arrays that have substantial promise as magnetic materials. The development of new classes of materials based on colloid science and related areas represents a new opportunity both for materials science and for chemistry. Colloid synthesis is a sophisticated and highly developed area, but one that has not seen enormous growth or popularity within chemistry for a number of years. It is increasingly evident now that colloid science is once again moving to the center of the stage. It provides direct synthetic access to structures having dimensions in the range of 1–100 nm. As such, it provides the best present approach to “bottom-up” nanotechnology. Understanding how to connect the synthetic capabilities of the colloid community with the understanding of opportunities and measurements present in materials science is a new opportunity in nanoscience.

Organic electronics is another area of materials science that is rapidly emerging. Electronically functional structures are the core of all devices that manipulate information, and as such, they are unarguably
important. The current technology for fabricating microelectronic devices is based on a relatively small set of materials—silicon, metals, and ceramics. This technology has largely been optimized for high speed and durability, while cost has been a secondary characteristic. There are, however, applications for which different properties may be required. Electronic analogues of bar codes provide one example (Figure 10). The systems—which would replace printed bar codes and optical scanners with small, externally powered circuits—have the characteristic that the speed of operation of the microelectronic device can be low, but its cost must be even lower than currently available technology (because it will be used only once).

These and related systems will probably be made of organic materials, either pre-dominantly or exclusively. Organic materials for electronic systems—conductors, semiconductors, and insulators—represent a new class of challenges for materials science. In these systems, performance may be low relative to the standards of the most highly developed silicon-based microelectronics, but the underlying technology represents new and challenging problems. Obtaining reproducible results with these new organic materials, understanding how to fabricate and pattern them (probably by printing), and learning how to package them will require developing an entirely new technology base. The successful development of organic electronics will not threaten the high-performance microprocessor industry, but it will offer the opportunity to make many objects that we use every day—paper, shipping labels, hospital patient records—more responsive and information-rich than they are at present. Organic electronics will also provide the foundation for electronic paper, displays (using organic light-emitting diodes), and memory, and ultimately, perhaps, for organic molecular electronics.

A simple example from our laboratory of a new materials system with potential application in information technology is based on a relatively unexplored class of materials: electrets. An electret is a material in which an electrostatic potential can be induced. Figure 11 shows a film of poly(methyl methacrylate) (PMMA) that has been patterned with stored electrostatic charge by contacting it with a stamp—the same type of stamp used in soft lithography, but coated with a thin film of gold—and then subjected to a current pulse. By mechanisms that are not well understood, this process generates a persistent electrostatic potential at the surface of the PMMA. We have begun to explore this type of process for information storage.
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storage and for replication procedures such as micro-xerography.

This application is interesting, but even more interesting is the realization that although organic electrets are a very familiar class of materials, they are barely exploited, and our understanding of them is sufficiently poor that it is not possible to design (or even convincingly rationalize) their properties. The ability to pattern electrostatic potential has wide application in materials science; the potential to design organic materials that would serve as electrets with a range of different types of properties, and to find new types of applications for these electrets, is large. Fundamentally new discoveries may not be required to develop this type of material fully, but it will be necessary to combine the perspectives of materials scientists, chemists, and physicists to develop a complete and predictive understanding of organic electrets.

Self-Assembly

A third area at the border between chemistry and materials science in which, I believe, there will be rapid progress will be self-assembly. Figure 12 shows a set of self-assembled structures—SAMs, colloidal crystals, millimeter-scale self-assembled arrays (held together by capillary forces), and a prototype structure for a self-assembling electrical network. Self-assembly offers the ability to make highly ordered, symmetrical arrays (and perhaps, in the future, asymmetrical arrays) without the intervention of humans (or their surrogates, e.g., robots). Particularly in the area of assembly of nanometer-scale structures, the strategies now used for fabrication at larger scales fail. If nanotechnology is to be successful, it will require the development of new strategies and new techniques for the assembly of nanometer-scale components into final, functional materials or structures. Self-assembly offers this potential.

Self-assembly is probably closer in philosophy to crystallization than to conventional fabrication. The components are designed in such a fashion that interactions between them cause the direct formation of correctly aggregated structures. Thus, the information required for fabrication is, in a sense, encoded in the structures of the starting components. As in crystallization, the spontaneous formation of defects is a challenging problem in all forms of self-assembly.

Despite the challenges to its implementation, self-assembly is being widely explored as a route to photonic-bandgap structures, as a method for distributing components for use in a large-area electronic system, as a method of making ordered arrays of molecules, and for a range of other purposes.

“Impossible” Materials

Materials science, like every field of science, suffers from unexamined beliefs. We “know” the limits of many materials
properties, and often no longer think seriously of moving beyond those limits. As the need for new materials has increased, remarkably imaginative experiments are beginning to generate classes of materials that would, in the past, have been considered highly unlikely or even impossible. Figure 13 shows one example. This marvelous structure, designed and fabricated by Schultz and colleagues, has an index of refraction that is negative in certain frequency regions. This structure is not an intuitive one, and its design required a sophisticated understanding of the factors that determine index of refraction. This material may or may not ultimately prove to be practically important. It represents, however, the demonstration of an important potential in current materials science: that is, to reconsider the limits of important classes of materials and to inquire if materials now thought to be inaccessible might, in fact, be achievable with appropriate designs. A wide range of materials are emerging that have remarkable and stimulating properties—high-temperature superconductors, high-

temperature organic ferromagnets, aerogels, Bose–Einstein condensates, optical matter—all are examples. These successes lead naturally to the question of what other types of materials it might be possible to make. What about moldable organic polymers with very high indices of refraction? What about liquid ferromagnets? We obviously do not know what can be made until it has been made. Chemistry, with its remarkable capacity to synthesize new structures, will be an important partner with materials science in developing important new classes of materials.

Coda

Organic materials offer two very important capabilities to materials science. The first is the ability to synthesize fundamentally new classes of materials. The second is the potential to bridge materials science and biology/medicine. The opportunities for new science and for new technology in both of these areas is enormous. What is required to exploit these opportunities?

Probably the most important need is for researchers—especially young researchers—who can speak the language of all of the interacting disciplines. Figure 14 illustrates the problem. This figure simply reproduces diagrams of the sorts used in these various disciplines on a day-to-day basis. In an ideal education, researchers would be able to read all of these diagrams and work with the science that underlies them. Armed with a working knowledge of the language of each discipline, the imagination to identify important problems, and the courage (and support) needed to attack them, it is hard to imagine that important new science and technology would not emerge.

Is it, in practice, practical for a single individual to know enough about multiple fields to be able to use the information in these fields fluently in his or her own research? Can one be both an effective generalist and a proficient specialist at the same time? Perhaps, perhaps not. As an alternative, the interdisciplinary research group—a social entity that has always been at the core of materials science—provides a good start. No single person may know everything that is required to solve a problem, but the group as a whole may. Even with interdisciplinary groups, however, it will still be critically important to have “translators,” that is, individuals who can speak enough of the languages to help each member of the group to understand the others. Producing materials scientists and engineers with sufficient breadth in their backgrounds to serve as translators among disciplines is one of the many challenges for the field.
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Acknowledgment

The work for our group described here had been carried out by an extremely talented group of graduate students, postdoctoral fellows, undergraduates, and faculty collaborators. Some are mentioned in the references, some are not, but all share in the success of the research. Most of the work was supported by the Defense Advanced Research Projects Agency (DARPA), and a series of DARPA program managers have also made important conceptual contributions to the research.

Figure 14. Various languages used in different scientific disciplines. (a) The photonic energy-band structure of a periodic dielectric array under two different polarized modes, transverse magnetic and transverse electric. The wave vector $k$ (x axis) varies across the irreducible Brillouin zone, from $\Gamma$ to X to M, then back to $\Gamma$. (b) Phase diagram of a uranium-plutonium alloy. Various polymorphic crystals ($\alpha$, $\beta$, $\gamma$, $\epsilon$, $\eta$, and $\zeta$) of U and Pu as well as coexisting phases are represented, depending on the composition of alloys and temperature. (c) Retrosynthetic scheme of cobyric acid, a precursor of vitamin B-12. (d) Complex biochemical pathways. See text for discussion.
References

George M. Whitesides is the Mallinkrodt Professor of Chemistry at Harvard University. His present research interests include materials science, biophysics, complexity, surface science, microfluidics, self-assembly, micro- and nanotechnology, and cell-surface biochemistry.

He received an AB degree from Harvard University in 1960 and a PhD degree from the California Institute of Technology in 1964. He was a member of the faculty of the Massachusetts Institute of Technology from 1963 to 1982 and then joined Harvard University’s Department of Chemistry. Whitesides has received a number of awards including the American Chemical Society Award in Pure Chemistry in 1975, the James Flack Norris Award (ACS, New England Section) in 1994, the Arthur C. Cope Award (ACS) in 1995, the Defense Advanced Research Projects Agency Award for Significant Technical Achievement in 1996, the National Medal of Science in 1998, the Sierra Nevada Distinguished Chemist Award (ACS, Sierra Nevada Section), and in 1999, the Wallace Oy Innovation Award in High-Throughput Screening (the Society for Biomolecular Screening) and the Award for Excellence in Surface Science (the Surfaces in Biomaterials Foundation). He is a member of the American Academy of Arts and Sciences, the National Academy of Sciences, and the American Philosophical Society.

He has served on advisory groups to the National Research Council, the National Science Foundation, the National Institutes of Health, the Department of Defense, and the Department of Commerce. Whitesides can be reached by e-mail at GWhitesides@gmwgroup.harvard.edu.

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