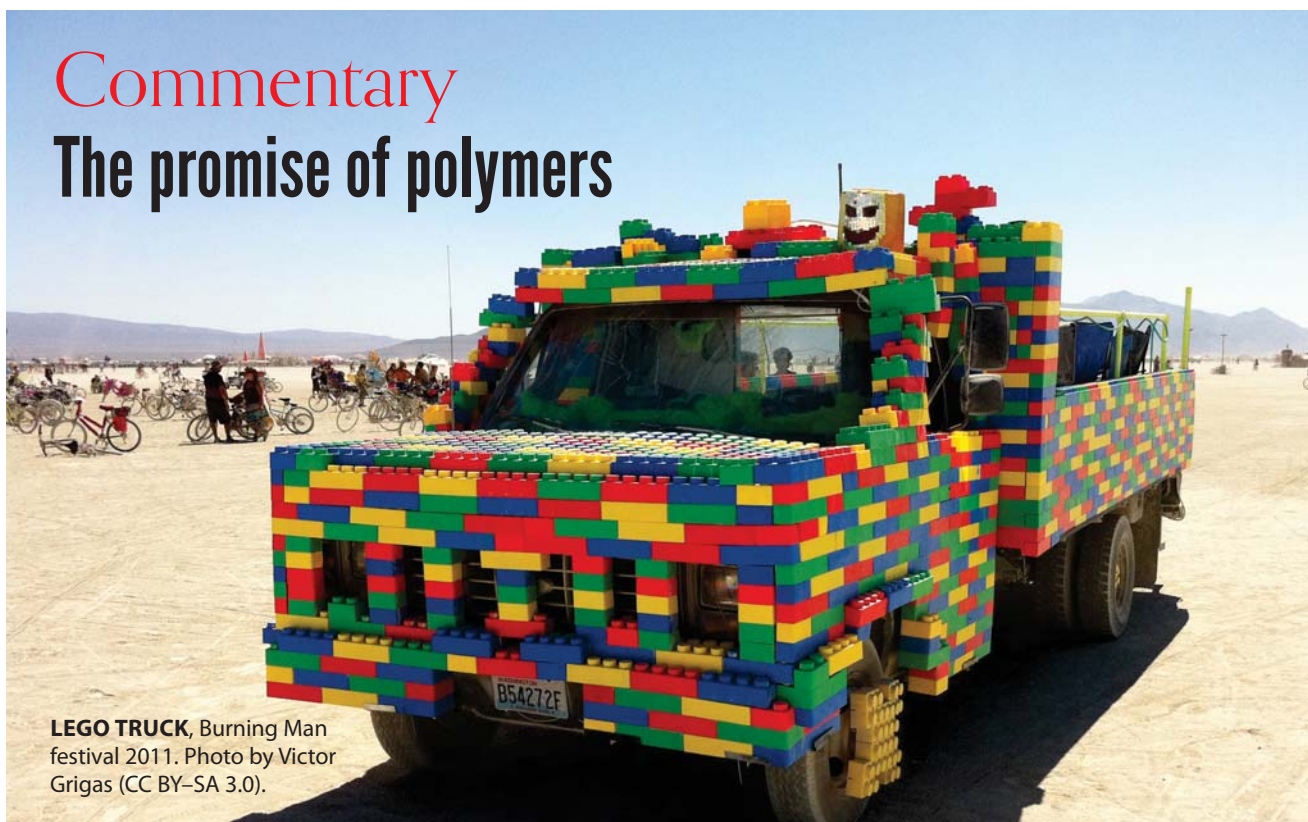


Commentary

The promise of polymers



LEGO TRUCK, Burning Man festival 2011. Photo by Victor Grigas (CC BY-SA 3.0).

This month marks the 50th anniversary of the release of *The Graduate*, a highly acclaimed and memorable movie. It included the sage advice offered to the title character, Benjamin Braddock, by his father's friend Mr McGuire: "I just want to say one word to you. Just one word. . . . Are you listening? . . . Plastics." Although the remark was intended as the humorous epitome of well-intentioned dorkiness, it was prescient in its selection of a growth area in which to build a business career.

The commercial polymer industry, which encompasses plastics, rubbers, fibers, adhesives, thermosets, and composites, is now approaching \$500 billion in global annual sales, well over an order of magnitude larger than global semiconductor sales. In the US, the polymer market sector has grown more rapidly than the GDP and is among only a handful of sectors with a consistently positive trade balance.

This year also marks the 50th anniversary of the founding of the American Chemical Society journal *Macromolecules*, the world leader in publishing original research on the fundamental science of

large molecules. It covers advances in synthetic chemistry, physical properties and their characterization, analytical theory, and computer simulation. The launch of the journal coincided with the gradual emergence of a new respectability for macromolecular research in academia, while in industry the corresponding efforts in fundamental research would soon experience a substantial decline in support, which persists today.

Monomers in chains

The remarkable properties of polymers stem from their length—hundreds, thousands, and even millions of monomers, covalently linked into chains, with astronomical degrees of conformational freedom. By appropriate choice of monomers, chain length, and architecture (linear, branched, and other), lightweight and extremely cost-effective materials with impressive physical properties have been achieved. For example, some elastic materials can undergo repeated extensions by up to 1000% and fully recover, due to the entropic restoring force that results from distortion of the chains' random-walk conformations.

Other monomers lead to highly transparent glasses that do not undergo brittle fracture, including plexiglass, used, for example, to surround hockey rinks, and polycarbonate, used in CD-ROMs. In such polymer glasses, the individual molecules retain their random-walk conformations down to the nanometer scale, but most molecular motion is quenched by lack of available space.

Still other polymers can crystallize. In that process, the long chains fold back and forth through hundreds of unit cells to generate dense crystalline layers, typically 10–100 nm thick, which are impervious to moisture, oxygen, or carbon dioxide; have superior mechanical strength; and are remarkably tough. More recent innovations include polymers that are semiconductive, for use in photovoltaics, plastic electronics, and portable sensors. Polymers for biomedical applications such as implants, drug delivery, and gene therapy can be made both biocompatible and biodegradable over prescribed time scales.

A 2016 NSF workshop report, *Frontiers in Polymer Science and Engineering*, summarizes the challenges and opportu-

nities in the field from the collective wisdom of approximately 60 leading experts representing academia, industry, and national laboratories. One conclusion in the report is that polymers will be instrumental in solving almost all of society's grand challenges, especially in harvesting, storing, and distributing renewable energy; providing widely available and cost-effective medical therapies; and ensuring access to clean water. Unfortunately, the low cost of plastic materials also encourages inappropriate disposal, which, coupled with their chemical stability, creates a growing long-term environmental threat. Achieving a fully sustainable polymer industry is therefore another daunting challenge.

Block polymers

Tremendous progress has been made in the past 30 years in developing new strategies to synthesize polymers with well-defined length, end groups, and architectures; now even physical chemists and physicists can learn to prepare model materials. An exciting frontier in synthesis targets sequence-defined polymers, in analogy with proteins and DNA, which carry information in their exact sequence of monomers (amino acids or nucleotides, respectively). This emerging field could help us learn what properties could be achieved with such specificity in manmade materials, and how they could be prepared in large quantities and in reasonable times.

One class of macromolecules—block polymers—has enjoyed increasing attention ever since the first well-defined preparation of one¹ in 1956. Such polymers contain chemically incompatible blocks whose immiscibility drives the molecules to self-assemble into exquisite nanostructures, just like their small-molecule analogues—lipids and surfactants. In the past 40 years, a numerical self-consistent mean-field theory has been developed with which one can compute free energies of various ordered states with remarkable accuracy and discrimination. That ability makes block polymers the apotheosis of condensed-matter systems in which a mean-field approach quantitatively captures the phase diagram.

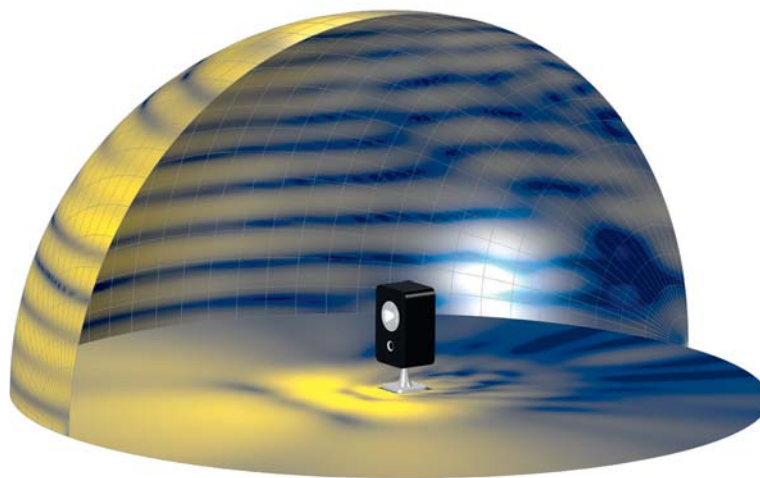
The theory is not yet a predictive one, however, since the lattice symmetry must be specified *a priori*. Notably, the design space for block polymers is almost immeasurably large: the number, length,

and sequence of blocks; monomer identity; and architecture. As with other emerging areas of polymer materials, advances in theoretical and computational design will be essential for researchers to bypass prohibitively time-consuming experimental exploration. In fact, the NSF report highlights the need to bring theory and simulation into a much closer partnership with experiment. Advances in both theoretical understanding and computer power offer the hope for experimental design and analysis in real time,

including the analysis of the reams of data generated by modern characterization tools such as synchrotron-based wide-angle, small-angle, near-resonant, and grazing-incidence x-ray scattering.

In many situations, nature has evolved remarkable materials properties by means of a hierarchical structure, such that the end result is much greater than the sum of the parts. Polymeric materials are inherently hierarchical themselves, in terms of both space and time. For example, a high-molar-mass polymer has three

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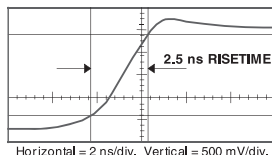
Noise: <100 e⁻ RMS (Room Temp.)

<20 e⁻ RMS (Cooled FET)

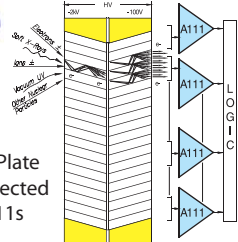
Gain-Bandwidth $f_T > 1.5$ GHz

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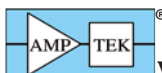


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characteristic length scales: a persistence length of order 1 nm, which represents the step size in the chain orientation's random walk; an overall radius of gyration, of order 10–100 nm, a measure of the polymer's average size; and an intermediate entanglement length scale, of order 5–10 nm, that dictates many aspects of the viscoelastic and flow properties of molten polymers. Similarly, when such a polymer crystallizes, the unit cell has dimensions of order 1 nm; the lamellar thickness, 10–100 nm; and the bulk spherulites, microns to millimeters. The two longer length scales are determined by processing and are therefore usually under kinetic control. Whether bioinspired or not, the ability to control structure on multiple length scales in a rational way represents an emerging intellectual frontier in polymer science.

Collaborators needed

The NSF report highlights the urgent need for new partnerships and modes of collaboration among industry, academia, and national laboratories. The constriction of industrial resources for long-term research means that industry has to rely on intellectual engagement with universities and national labs as never before. On the other hand, the intense competition for federal research funds suggests that academics in particular could benefit from deeper relations with company scientists and engineers, especially if new intellectual-property models can be implemented.

While *The Graduate* and *Macromolecules* are each marking their 50th anniversary, this year also represents the 100th anniversary of the macromolecular hypothesis, first publicly presented by Hermann Staudinger in a talk before the Swiss Chemical Society² in 1917. Staudinger

worked for years to overcome considerable opposition to the concept that polymers are long chains of smaller molecules connected by covalent bonds, as opposed to some unspecified kind of physically associated, colloidal structures.

By World War II, the macromolecular nature of polymers was generally accepted, and commercial examples such as nylon were widely hailed. The need for synthetic rubber during and after the war helped the polymer industry expand enormously. Based on today's commercial demand, the industry will continue to experience strong growth.

Although commodity plastics will likely remain the largest component of the market for the foreseeable future, the incorporation of advanced polymers into higher-value applications is more exciting. Examples include coatings on drug-eluting stents, patterning materials for nanometer-scale lithography, and fuel-efficient aircraft—the Boeing 787 Dreamliner is 80% plastic composite by volume. Even polyethylene, the world's largest-volume, least expensive, and chemically simplest polymer, can be processed into fibers 10 times as strong as steel; they are used in bulletproof vests, cables to anchor floating windmills, and other applications. Scientific advances in polymers open the door to even more interesting questions that involve molecular behavior and collective properties. So if someone suggests that you direct your future to plastics, pay attention!

References

1. M. Szwarc, M. Levy, R. Milkovich, *J. Am. Chem. Soc.* **78**, 2656 (1956).
2. H. Staudinger, *Ber. Dtsch. Chem. Ges. A/B* **53**, 1073 (1920).

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LETTERS

Trapping molecules for quantum chemistry

The Search and Discovery piece by Ashley Smart in the April 2017 issue of *PHYSICS TODAY* (page 18) reported the excellent work on magnetic stopping and trapping of methyl radicals by the group of Takamasa Momose (University of British Columbia). I am writing to pro-

vide a different perspective on the field than what was conveyed by the author. The very first sentence of Smart's article brings up a whole discussion: "By and large, physicists have succeeded in their quest to tame the atom."

The past few decades have seen re-