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Macromolecular Engineering

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The science and industry dealing with synthetic polymers have been growing and developing with amazing vigor and speed. One may be astounded to remember that 100 years ago even the concept of a polymer, a long macromolecular chain, did not exist and one could not find a single chemical plant to synthesize even 1 kg of a polymer. Today, thousands of publications containing the word polymer in their title are published each year and around 2×10^8 tonnes of polymers are produced annually, i.e., 0.5 kg of polymer per capita worldwide every week!

Polymers are preferred materials in applications for industrial practice and we as a society use them daily. Their growth accompanied and pushed economic expansion and industrial revolutions throughout the 20th century, even during the dark and difficult years. Many modern-day technologies emerged due to polymer science and its rapid progress. The aircraft and space industries, movies and music with its superabundance of vinyl records, CDs and DVDs, sport and outdoor equipment and modern packaging are only a fraction of examples being used today. Adhesives are made from polymers and so are paints. Could you imagine life without polymer photoresists that enable lithography to produce all the tiny electric circuits in our laptops, cell phones, Ipods or Blackberries? The interior of every automobile is essentially entirely made from polymers, but they are also used for body parts and for under-the-hood applications. Although we could continue to cite and marvel over all of these practical achievements with polymers, the interested reader can refer to Volume IV of this book, which tells the story of the growth of many applications along with those that are expected to grow provided that critical scientific, industrial and economic bottlenecks and challenges are overcome. Indeed, the world of polymers results from a unique chain of knowledge which we call *macromolecular engineering*. The latter relies on and produces some very fundamental and sometimes even abstract science that finds its way to applications, but at the same time it more often refers to applications and processing for motivation and for inspiration. Many examples will be given throughout the four volumes of *Macromolecular Engineering: From Precise Macromolecular Synthesis to Macroscopic Materials Properties and Applications*.

Polymer science exhibits a typical frontier character by the pioneering nature of its development. Nourished from many areas of chemistry and physics, both fundamental and applied, polymer science generously contributes to these disciplines. For example, statistical physics and small-angle neutron scattering brought very firm and useful bases to build an understanding of polymer solutions, melts and self-assembly of macromolecular systems. At the same time, the Flory approximation, initially intended to predict the swelling of a macromolecule in a good solvent, and Edwards' replica trick introduced the understanding of rubber elasticity; both are now the bread and butter of statistical physicists to help solve many problems. De Gennes' reptation concept, the basis of polymer rheology, is a part of modern physics in its own right. In chemistry, the discovery of Ziegler–Natta catalysis fundamentally changed the nascent polymer industry of the 1950s, introducing novel polyolefin-based thermoplastic polymers through highly selective processes and laying the foundations of an industry of commodity plastics. To give an idea of the vitality of that industry, it took just 5 years to transfer isotactic polypropylene from the laboratory to industrial production. In the same decade, the development of living polymerization by Michael Szwarc provided a deeper insight into the structure and reactivity of ions, ion pairs, their aggregates and dormant species. Very efficient catalysts for ring-opening metathesis polymerization and atom-transfer radical polymerization are now being used by many organic chemists in the highly selective metathesis cyclization or atom-transfer radical addition reactions. In a similar way, metallocene and post-metallocene catalysts had a tremendous impact on coordination and organometallic chemistry. The entire field of dendrimers is shared by organic and polymer chemists, as also is the area of supramolecular chemistry.

During the first enthusiastic decades of polymer chemistry and industrial practice, various polymerization techniques were developed and an amazing number of new polymers, each made from different monomers, were introduced into the market to answer fast-growing and increasingly demanding applications. However, only a limited number of commodity polymers have proved themselves as workhorse materials since the 1960s, impossible to displace thanks to their low cost and versatility. During the last 20 years, these commodity polymers have mutated to truly high-tech materials, with marvelous science, both chemistry and physics, and technology contributing to this metamorphosis. Nevertheless, they are still called commodity because of their price and volume. In the 1970s, fashion, future projections and research efforts were focused on other polymers, with more noble pedigrees, but which often did not meet expectations. During the last 30 years not many new technical thermoplastics have been introduced and the production of those that did appear often ceased soon after their introduction. It is believed that the development of polymers for new classical applications will rely on better synthetic control of the molecular structure, stereoregularity and architecture of chains. It may also be supposed that better control of organization at various scales ranging from nanometers to millimeters will be a constant demand. Hence macromolecular engineering is

about obtaining such control on a laboratory, pilot or plant scale, and on designing new polymers for new applications in areas of today's concerns, such as biomedicine and energy economy.

Achieving such precise control of every fragment of a macromolecule resembles in some respects the total synthesis of natural products. Thus, macromolecular synthesis often reaches an extremely high degree of chemoselectivity; in order to prepare ultra-high molecular weight polyethylene with $M_n > 20\,000\,000$, chemoselectivity of chain growth must exceed 99.9999%! The same is true for regioselectivity, which for many vinyl polymerizations leads to exclusive head-to-tail polymers (i.e. regioselectivity exceeds 99.99%). Also, stereoselectivity in some coordination polymerizations (albeit not in radical and carbocationic systems) may exceed 99%. These values are unmatched by most organic synthetic methodologies. Indeed, polymer chemistry often selects the best organic reactions and implements them to macromolecular synthesis. Thus, only reactions with selectivities $>90\%$ can be used in macromolecular synthesis. Then, by adopting protocols from physical organic chemistry, by adjusting the solvent, temperature, pressure, pH, ionic strength and many other parameters, the selectivities are further enhanced to yield precisely controlled high molecular weight polymers.

Macromolecular Engineering: From Precise Macromolecular Synthesis to Macroscopic Materials Properties and Applications is a book dedicated to these aspects and is organized in four volumes. *Volume I* presents essentially all of the synthetic techniques used to prepare well-defined macromolecules. They include carbanionic polymerization, which was the first process to provide living polymers, a pathway to nanostructured materials and many commercially important products. Other ionic processes based on carbocationic polymerization and ionic ring-opening polymerizations also afforded high molecular weight, well-defined (co)polymers with several commercial products.

Free radical polymerization, with the concurrent initiation, propagation and termination steps and thus its chaotic character, is totally unsuited to the preparation of complex architectures, although nearly 50% of all polymeric materials are currently obtained by this means. Recently, however, new controlled/living radical processes, such as atom-transfer radical polymerization (ATRP), stable free radical polymerization (SFRP) and degenerative transfer techniques (mediated by alkyl iodides or dithio esters, i.e. RAFT or MADIX), where the growing radicals are prevented from early termination, have been developed, opening up many avenues to well-defined (co)polymers with polar groups and functional moieties.

Coordination polymerization has industrial relevance similar to radical polymerization. New catalytic/initiating systems based on single-site catalysts expanded the range of polyolefin-based materials and opened up routes to specialty products. Ring-opening metathesis polymerization, recognized by the Nobel Prize awarded to Chauvin, Grubbs and Schrock in 2005, is another stellar example of the creation of a powerful tool of macromolecular engineering combining high levels of structural fidelity and functional group compatibility.

Chain growth addition polymerizations are not the only means available for the preparation of well-defined polymers. Recent advances in polycondensations have permitted the synthesis of low-polydispersity polymers and block copolymers. Enzymatic catalysis and protocols inspired by biotechnologies are two emerging techniques that afford uniform polymers, such as polypeptides, polysaccharides and nucleic acids. Another increasingly prevalent method of design of complex functional systems is through the accurate placement of non-covalent interactions at precise locations within self-assembling building blocks. Some monomers can be polymerized by only one mechanism, therefore a selective transformation between polymerization mechanisms opens up the possibility of preparing unusual polymers, including hybrid materials.

Many polymerizations are carried out under homogeneous conditions without any external stimuli. However, heterogeneous polymerization, especially in dispersed media that employ compartmentalization, provides an avenue to materials that cannot be prepared under homogeneous conditions. In a similar way, external stimuli can provide additional control and improve or alter selectivities in macromolecular synthesis.

Hence the chapters included in Volume I present the state-of-the-art in macromolecular synthesis and describe not only organic, but also inorganic polymers.

The main mission of *Volume II* is to describe various elements of macromolecular architecture. They include microstructure control, in terms of tacticity and composition, leading to statistical, alternating, gradient or block copolymers. Also, functionalities, especially end-functionalities, are very important since they provide unusual building blocks for macromolecular architecture.

Non-linear topologies include cyclic polymers and various degrees of branching, including hyperbranched polymers, stars, microgels, molecular brushes and – ultimately – dendrimers. Advances in polymer synthesis allow the preparation of previously unavailable materials, namely organic–inorganic hybrids, core–shell particles and very dense brushes with compositionally different compressibilities, lubricities and other properties.

Another approach is to combine synthetic polymers with natural products, yielding alternative hybrids or chimera materials. Other approaches using bio-inspired synthesis, including polyelectrolytes, along with a combination of various synthetic techniques yield functional macromolecules with complex shapes and architecture.

The properties of polymeric materials, although encoded in molecular structure, also depend on how they self-assemble to morphologies of the size of micrometers rather than nanometers. The organization on mesoscopic scales is governed by both thermodynamics and processing conditions. Self-assembly can be used to impart original macroscopic properties to the systems, including optical, electrical and transport through polymer matrices. These processes, including formulations and processing and techniques used to characterize polymers, are covered in *Volume III*.

The basis of polymer self-assembly is treated, including developments in simulations and modeling and the means to characterize the assembly features of nanostructured polymer materials are described. These characterization methods include proximal probe techniques such as atomic force microscopy, but also various scattering methods and microscopy.

Since the nanostructured morphologies are not static, dynamic phenomena, i.e. processing, are critically important in many cases and are discussed in Volume III. Further, because many properties will depend on thermal history, mechanical stresses, solvent removal, etc., the polymeric materials need to be precisely characterized at different stages by calorimetric techniques, chromatography or NMR spectroscopy. High-throughput screening allows the use of smaller amounts of polymers to obtain relevant information.

Some polymeric materials are eventually converted to polymer networks; they can be used as various sealants and adhesives and can be designed to react further during a blending process.

The ultimate goals of macromolecular engineering are to target special applications and some of the most important among them are described in *Volume IV*.

Perhaps the most stellar example of products prepared by macromolecular engineering is Kraton[®], a landmark material made by living anionic polymerization. This thermoplastic elastomer was originally designed to be used in the tire industry, but the first applications came in footwear and later in other compounding applications, including automotive, wire and cable, medical, soft touch overmolding, cushions, thermoplastic vulcanizates, lubricants, gels, coatings and in flexographic printing and road marking. It is anticipated that materials made by other controlled/living processes will lead to more applications, with an even larger market impact.

However, many other materials benefiting from macromolecular engineering are already commercially available. They include nanocomposites, especially based on layered structures, but also dispersants and surfactants.

It is anticipated that the electronics industry, constantly moving to smaller dimensions and nanometer precision, will present a great need for well-defined polymers. They include many conjugated polymers for molecular electronics, but also many other polymers for microelectronics, including dielectrics and resists. They often require special hierarchical organization and can find applications in soft lithography, magnetic and optoelectronic areas and even as materials for membranes and fuel cells.

Equally important are well-defined copolymers for biomedical applications. The 21st century will be a century of polymeric drugs which will deliver, at a programmed rate, a drug to a specific location and release it at the desired rate. Biomedical applications also include gels for tissue and bone engineering. The concept of biomineralization is expanding to the synthesis of new inorganic crystals with tunable nanostructured morphology. Covalent bonding of well-defined organic polymers with natural polymers can dramatically alter the action of enzymes and other natural products.

The promise of accurately controlling every facet of polymeric architectures through very selective processes and the diversity of available tools – including the programmed inter- and intramolecular assembly of building blocks – holds considerable potential and heralds limitless sophistication in macromolecular design. For this potential to be efficiently harnessed and translated into applications, understanding and optimizing the properties of the (nano)structures formed are instrumental.

Summarizing, the main objectives of this four-volume book. *Macromolecular Engineering: From Precise Macromolecular Synthesis to Macroscopic Materials Properties and Applications*, are to provide a state-of-the-art description of:

- synthetic tools used to control precisely various aspects of macromolecular structure, including chain composition, microstructure, functionality and topology;
- modern characterization techniques at molecular and macroscopic levels used to determine quantitatively various properties of well-defined (co)polymers in solution, bulk and at surfaces;
- correlation of molecular structure with macroscopic properties which can be additionally affected by processing;
- some emerging applications for the (co)polymers.

The book is directed towards chemists and polymer scientists interested in affecting macroscopic properties via precisely designed macromolecular structure and controlled processing. Each chapter provides background information, comparative advantages and limitations and the most recent advances of various synthetic approaches, characterization techniques and intended applications.