ADVANCES IN POLYMER SCIENCE 200

Volume Editors G. J. Vancso · G. Reiter

Ordered Polymeric Nanostructures at Surfaces

Springer

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Volume Editors: G. Julius Vancso, Günter Reiter

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Foreword to the 200th Volume

Advances in Polymer Science celebrates the 200th Volume of the Series. This asks for a moment of recollection and consideration, since *Advances in Polymer Science* is a true mirror of scientific progress, intellectual penetration and scholarly apprehension of one of the most successful fields of current research. Polymer Science is not only the fundament of the plastics industry but it has also gained reputation as an enabling factor of advanced technologies from microelectronics to bioengineering. Moreover, it has shown to be a unique challenge to theoretical and experimental physics. The bridging function to molecular biology is obvious. It is this context which is properly and meticulously mirrored by the last 100 Volumes of this Series. While the focus rests on concise descriptions of special topics, specialized and selected methods, careful discussion of synthetic and analytical approaches to new challenges in materials preparation and performance written by established experts in their respective sub-discipline, a complete picture of the state of the art emerges nevertheless when one draws the sum over the nearly 400 individual review papers published since 1991 in Volumes 101 to 200 of this Series. All of the contributions are critical reflections on the respective topic and give pertinent information not only to the expert but also to the newcomer to the field to whom guidance to the large and diverse body of available literature is provided. Emerging subfields or novel directions of research are discussed for the first time in a comprehensive manner. *Advances in Polymer Science* contributes with this style and dedication to the scientific fundament in an international context. While the first 100 Volumes were dominated by contributions from mainly Europe, and the classical languages of science of the last century, namely English, French and German were all represented, this has changed completely. Authors from all continents are well represented. English has become the sole medium of expression.

The strongest impact to the contributions for the last 100 Volumes had the disappearance of the east-west conflict. A large body of research experience and literature from Eastern Europe and Russia became suddenly available and has found its way into *Advances in Polymer Science* in the form of a considerable number of expert reviews. These reviews reflect the immense work performed over many years in research centres and institutes which were not accessible to the rest of the scientific world. The freshness and originality of the approach

to define and tackle research problems comes as a surprise to many of us who have experienced the times when such information was not available at all or only in a rudimentary form. These reviews are to be considered as an important widening of the horizon of polymer science.

Similarly we see a considerable increase of contributions from the US and Canada in the last 100 Volumes indicating both the cosmopolitan nature of polymer science and the appreciation which this Series receives internationally as a depository of pertinent information and expertise.

A few remarks concerning the subdisciplines covered by the last 100 Volumes may be of interest in so far as directions and currents in Polymer Science are pinpointed.

Contrary to the believe of many critical bystanders **Polymer Synthesis** is still strongly going ahead. This is demonstrated by the ca. 100 individual reviews published in this Series since 1991 devoted to progress in synthetic methods, catalysis of polymerisations, biogenic macromolecules and their synthetic modification. Many of these contributions cover novel developments in synthesis allowing precision synthesis of novel macromolecular structures not available before. The next important field concerns **analytical methods** including rheology and solution properties of polymers. Nearly 60 reviews are devoted to this context, and – as is typical for this sub-discipline – **polymer physics** aspects are integral components of the reviews.

While both of these areas are the classical realm of *Advances in Polymer Science* we see the strong emergence of another area in the last 100 Volumes: **biomedically relevant polymers**. This includes synthesis of biocompatible polymers, polymeric drugs, application and evaluation of polymers in the medical field and in bioengineering which are summarized in well over 40 reviews.

Application of polymers and polymer based **hybrid materials** including aspects of processing and processing related properties constitute the central theme of another group of reviews. This includes reviews on inorganic/organic and polymer-polymer blends as well as reviews on degradation of practically relevant polymer compositions. This group of ca. 40 reviews illuminates the crossover between fundamental science and application driven research that is so typical for many sub-disciplines of our field.

The same could be said for the group of review papers dealing with **complex polymer systems** such as networks, gels and similar complex macromolecular topologies characterized by an interplay of regularity and randomness. Physical properties and phenomena related to the complexibility of structure are highlighted as well, fracture behaviour, relaxation phenomena and elasticity are key words to describe the features which are discussed among others in this group of ca. 40 reviews.

The very strong evolution of **theory and simulation** is reflected in another group of review papers. Theory of polymer systems has evolved as a segment of theoretical physics and has had a very strong impact on how experiments are

conducted and data sets are explained and evaluated in many areas of polymer science. The development of simulation methods based on sound fundaments of theory have equally contributed to significant progress which is reviewed in 35 articles found among the nearly 400 reviews that appeared since 1991.

While this is certainly a more recent development properly reflected in this series a somewhat traditional field which is normally associated with polymer physics is still relevant and finds attention in form of review articles. It is the field of **crystallization of polymers** including phenomena of nucleation and crystal growth as well as studies into the crystallography of polymers and liquid crystal phases of polymers which finds attention by well over 20 reviewers. Nearly the same attention is given to polymers of particular chain architecture which in consequence create special supramolecular or hierarchical order phenomena. **Blockcopolymers**, micelle forming polymers, polymer based membranes and similar topologies are in focus. These areas are strongly associated with the current trend in materials science to emphasize the **nanoscale** characteristics of such structures which is also of central interest to the ca. 15 contributions dealing with polymers covalently or by physisorption attached to solid planar surfaces, the physical properties of the **brush-like structures** formed, and pattern production found in the interaction of polymers with surfaces.

It is somewhat sad to see that a classical field covered very well by the first 100 Volumes of this series has almost disappeared: the **kinetics** of polymerisation reactions is only covered by less than 10 review papers which sheds light onto the research situation where such studies have moved out of polymer science and into the field of chemical engineering.

In conclusion, *Advances in Polymer Science* has emerged as the prime source of relevant data and expertise presented in a critical form to all researchers in the field of polymer science. It has reflected the changes in research targets and research style in a precise and unambiguous manner and thus gives testimony of a very lively and quite progressive field in constant change and motion. We are anxious to see how the field will evolve as reflected in the next 100 Volumes of this series.

Mainz, March 2006 Gerhard Wegner

Preface

Modern technologies often demand access to functional structures, mostly at surfaces, at length-scales below 1 μm (1–100 nm). In various cases such structures must be ordered in a regular and tuneable fashion, while corresponding systems must also exhibit specific physical properties. The fabrication of hierarchically ordered structures at multiple length-scales, which serve as functional platforms, remains an experimental challenge. Such platforms, often based on polymers, are important both for fundamental studies investigating relationships between the nanostructures and the resulting physical properties, as well as for promising (potential) applications. Examples where such nanostructures are needed include faster and denser microelectronic systems, X-ray optics, nanolithography, and bioactive surfaces.

Structural order across many length-scales can be created by using self-organising materials, whose assembly is controlled and directed by various molecular interactions (and their combination) as well as by external constraints. Self-organisation occurs from nanoscopic to macroscopic scales, controlled by phenomena like microphase separation, adsorption or crystallisation. Ordered, nanoporous materials may be obtained in sol-gel processes or by aggregation (crystallisation) of colloidal particles. Competing factors controlling structure formation include chemical differences, conformational entropy, spatial constraints (molecular shape effects) and external (electric, magnetic, hydrodynamic flow) fields. Supramolecular materials built from highly regular, molecular nanostructures characterized by specific chemistries, like functional end-groups or molecular shape (flat objects, rods, spheres, tubules) may possess interesting viscoelastic, electrical, or optical properties and may sensitively respond to various external stimuli (sensors). Nanostructured surfaces may exhibit highly selective interactions with molecules in the environment and may act as biosensors.

Fundamental processes of nature work on the nanoscale rather than on the microscale. In order to study these processes (self-assembly, aggregation, ordering, etc.), as well as to mimic them, we must also perform our investigations on the nanometer scale, using well-defined, regular, tuneable and controllable systems. In corresponding mesoscopic devices we expect to encounter new physical phenomena (increasing importance of intermolecular forces, quantum effects, etc.), which may modify—or even govern—thermodynamic,

mechanical, electrical and optical properties. Employing such *molecular* phenomena may provide the following advantages for the fabrication of modern devices based on ordered polymeric nanostructures:

Simplicity, as the system has the tendency to create such patterns in a self-regulating way, based on intrinsic phenomena like self-assembly, microphase separation, or morphological instabilities induced by intermolecular interactions.

Accuracy, as the size of the molecules determines the characteristics of the nanoscopic features.

Speed, as on molecular length-scales intrinsic intermolecular interactions may be much more significant than external forces. Consequently, we expect faster motion towards the equilibrium states.

What do we mean when we speak of *nanostructures*? Besides random (non-ordered) structures (e.g., nanoporous surfaces) that are built up from nanometer objects (crystallites, elements of microphase-separated block copolymer morphologies, etc.) we mainly consider ordered (symmetric, periodic, regular) structures exhibiting structural hierarchy on multiple length-scales containing sub-micrometer (molecular) features and order on a longer (e.g., micrometer) length-scale. Accurate control of lateral position and orientation of these structures with nanometer precision is of crucial importance. A combination of several processes (microphase separation, crystallisation, surface induced effects, spontaneous formation of organised surface structures at nanometer scales, hydrodynamic flow patterns, dewetting, etc.) guided by additional parameters (patterned substrates, temperature and field gradients) presents a highly promising approach to obtain nanostructures. As we demonstrate in this volume, interdisciplinary investigations carried out by physicists and chemists, in close collaboration with applied research, represent feasible pathways to reach this goal.

An intensive search is underway for new, simple, fast and versatile routes to create nanoscopically ordered patterns on surfaces. Several approaches have been explored and many of them are based on polymers. The molecular structure and functionality, hence also intermolecular (interchain) interactions of polymers, can be "tailored", which are essential factors guiding the self-assembly process at the molecular level. The size of a polymer (its molecular weight) can be varied, which provides a tuneable length-scale. Block copolymers allow one to combine different properties (stiff and flexible blocks, amorphous and crystalline (crystallisable) blocks, electrically conducting and insulating blocks, etc.) in a single molecule, thus introducing diversity at a molecular level. Accordingly, polymeric nanostructures are precise at the nanometer-level (size of the molecules), are flexible (different shapes such as spherical or lamellar morphologies, as well as more complex architectures are possible), allowing one to obtain various geometries (two-dimensional versus three-dimensional structures, circular versus linear patterns, assembly on flat or curved substrates, etc.). Corresponding platforms can be fabricated in

a highly reproducible fashion, encompassing fast processes. Other classes of materials can be incorporated as well, e.g. a build up of metallic structures (decoration) on patterned polymer surfaces by external means like evaporation can be achieved.

Diblock copolymers composed of two chemically different molecules, chemically linked together via one end, exhibit various morphologies (spheres, cylinders, lamellae) at a molecular level, controlled by the size of the two blocks and by their chemical nature. At surfaces, these morphologies are usually "masked" by the preferential segregation of one component to the surface resulting in uniform surface properties and microdomains aligned parallel to the surface. In order to nonetheless achieve patterning of the surface by block copolymers, the substrate should be prepatterned on the length-scale of the polymer, or coated with a thin layer of anchored random copolymers to provide a neutral surface, equally attractive for both blocks. Application of, e.g. high electric fields (or other orienting effects) allows one to also overcome the surface effect and to align block copolymer morphologies perpendicular to the surface. The use of more sophisticated architectures (such as triblock copolymers, miktoarm star copolymers, etc.) can yield fascinating, novel and complex morphologies. Mixtures of block copolymers and homopolymers may also provide interesting micro- and nanostructures, and thus offer additional routes for patterning. In addition, block copolymers allowing for selective decomposition (either via oxidation, sputtering, ion beam etching or appropriate temperature treatment) open possibilities to modify or to enhance the intrinsic nanostructures. Deposition of other materials (e.g. evaporating metals or semiconducting materials) onto such modified structures open new pathways towards the fabrication of organic–inorganic nanostructures.

Making use of nanoscale phenomena such as self-assembly, we can build designer systems with tailored, purpose-oriented properties, effectively combining mesoscopic sciences with supramolecular chemistry. Employing these phenomena in an "intelligent" way presents a highly promising approach for putting together useful, modern and "smart" devices in inexpensive and accurate ways. In addition to structuring, we must also consider the kinetics of the corresponding fabrication processes. Depending on how fast the molecules order, they may not be able to reach the thermodynamically predicted state and instead get "trapped" in metastable states. It is not obvious if kinetic aspects favour order or rather produce disorder. As an additional step, polymeric structures can be modified or treated using approaches like selective degradation, as mentioned. This way the polymer patterns can be sensitively changed in the vertical direction without modifying its lateral distribution.

Obviously, besides the attempt to answer fundamental questions, we are also interested in taking advantage of the acquired knowledge in various applications. Thus, the use of engineered, nanostructured polymeric platform

surfaces in the context of application-motivated problems in biomedicine, biology, materials science and nanotechnology is treated by various contributions in this collection of articles.

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