

Polymer Science with Synchrotron Radiation

Abstract

The advent of synchrotron radiation has revolutionised the structural studies of hard and soft condensed matter. In this paper we discuss the future potential of synchrotron radiation for the study of soft condensed matter with the emphasis on Polymer Science. The brilliance of third-generation synchrotron sources is such that time-resolved studies are feasible in the millisecond range, hence allowing studies of structural changes in polymer systems under processing conditions that involve fast kinetics. Microfocusing devices, the potential of nano-sized beams and the parallel development of fast counting devices in conjunction with adequate software offer new, unprecedented challenges for the structural polymer scientist.

Key words: polymer science, structural features, structural changes, synchrotron radiation.

Introduction

The use of polymer products has dramatically increased in recent decades, and has grown to be one of the largest economic motors in Europe. From the industrial point of view, standard polymers and engineering polymers are 99% of the market; specialty polymers are only 1%! The latter subdivision is of course rough; some of the so-called standard polymers like polyethylenes (homogeneous copolymers) can be considered to be specialties as well. Hence two trends of interest emerge. Mainly resulting from continuous efforts in the field of innovative polymer synthesis, there is considerable progress in the fine tuning of polymer properties at the molecular level, leading to new promising applications. Such systems comprise block copolymers, polyelectrolytes, conducting polymers, self-assembling systems for use in micro-electronics, photonic materials, liquid crystalline displays, medical and pharmaceutical applications (delivery systems, intelligent gels, etc.), which are the basis of potential new markets. On the other hand, rather than developing new polymers, one opts for improving existing materials and the development of multi-purpose materials by tuning the processing methods. Finally society requires us to consider the influence of human activities on the environment; hence the increasing need for recycling, biodegradable systems and biopolymers. In the broader context of chemistry, physics, biochemistry, biology and material sciences, polymer research is a young science with a continuous need for intensive basic research.

The rather recent development of high-brilliance synchrotron sources and the availability of sophisticated experimental techniques create unprecedented potential for exploring the structure-properties relations of (bio-) polymeric materials, much to the benefit of our basic understanding and the potentially wide field of applications. Here it will be shown that further developments in commodity and engineering polymers strongly depend on progress in our understanding of the relations between polymer chain microstructures, over polymer processing and (nano)-structure formation, to the ultimate final macroscopic properties (thermal, mechanical, optical, functional).

In Part I and Figure 1, we offer a schematic view on the state of the art in structural polymer research involving scattering experiments: synchrotron radiation, neutron scattering and light scattering. Next, in Part II, we focus on synchrotron radiation because of the unique ability to perform time-resolved studies.

The state of the art in scattering studies in polymer science

Macromolecules, like polymers, intrinsically have sizes in the nanometer range (radius of gyration, end-to-end distance), and their spatial arrangement (semi-crystalline morphology, phases induced by the separation of incompatible components in polymer mixtures, dispersed inorganic particles in a polymer matrix, (supra) molecular network linked by either chemical or (temporally) physical joints) often cov-

ers similar-length scales with occasional extensions to several μm (spherulitic arrangement of crystals, phase morphology after separation, processing induced skin-core structures, stacking of different polymers in multi-layer foils, etc.). Such nano-structured polymeric materials are used worldwide in huge amounts and in a large variety of applications (packaging, automotive, low weight and high performance applications, etc.).

The properties of polymer systems, such as mechanical and functional (thermal, optical, electronic) properties are largely defined by their nano-structured morphology, which is a manifestation of the chain microstructure and the processing step. It is crucial to monitor and understand the impact of realistic conditions, because polymer systems are very susceptible to changing conditions: they can adjust themselves to numerous metastable states and concomitant morphologies, usually of low order. For example, such conditions arise during injection moulding, film blowing and fibre spinning, and quite definitely in systems where part of the end-product's dimensions are on a sub-micrometer scale such as thin films and coatings; or where confinement in nano-scale environments occurs, such as polymer dispersions in a matrix or filled polymer systems; or when nano-scale phases are formed, as in the case of (block) copolymers. One must also assure predictability during a product's manufacture and stability during its lifespan against all kinds of changes, such as a function of time and temperature through recrystallisation, annealing, cold crystallisation and solid-solid transitions.

Figure 1 is a more general schematic representation of how the different aspects of polymer science are interconnected. The central point is the chain microstructure of the polymer, which is defined by the synthetic step, either in the laboratory with or without the presence of a catalyst, or as defined by nature. Characterisation of the polymer requires NMR, FTIR, light scattering, fractionation methods, etc. Modelling or simulating the chain microstructure and its polydispersity in terms of chain length and branching is often needed for full understanding, and serves as input for predicting the thermal characteristics, crystallisability, mechanical performance, flow behaviour, etc. In practice, systems such as thermoplastics, elastomers, blockcopolymers, polymer blends or polymer composites will be handled by heating, cooling, pressure, flow, electric and magnetic fields, solvents, mechanical deformation, etc., resulting in the creation of order/disorder at the nanolevel or the micrometer level. Scattering studies are superior for the characterisation of the nano- and micrometer sizes and shapes of the macro-

molecular entities. On the other hand, it is convenient to have a number of sophisticated real-space experimental tools to characterise the morphologies: TEM, SEM, optical microscopy, AFM, STM. However, some of those need considerable sample handling, or they probe the surface only. Nevertheless they are crucial for the proper evaluation of the scattering information obtained in reciprocal space, as they are indispensable in the design of proper models for interpreting scattering data. The latter, in turn, provide highly quantitative information on the sample, without any of the inconveniences common to microscopic methods. Moreover, time-resolution is the crucial advantage of synchrotron radiation. Other interesting advantages of synchrotron radiation are in reflectivity studies of surfaces, grazing-incidence SAXS, microtomography, and local chemical speciation with microbeams. A very new development is X-ray photon correlation spectroscopy, which allows for the study of slow-mode chain dynamics. Many of the latter experimental tools are at the early development stage.

Clearly, understanding the origin and properties of nano-scale morphologies requires in the first instance *unparalleled understanding* of the process of their formation *under realistic conditions*, and secondly *in-depth studies of their (meta)-stability and morphology*. For all these aspects, techniques able to measure on a micro-down-to-nanometer scale, real-time and in-situ or while mimicking fast processing conditions or practical life, are crucial. Synchrotron radiation is key to this end.

However, there are a number of threats to this essential route: a potential lack of coordination among current European initiatives and existing or planned national sources, uncoordinated and mono-disciplinary research, the growing gap between researchers of industry & academia, and the lack of knowledgeable researchers.

Both the academic world and industry have their specific strengths and roles to play in elucidating the various aspects along the way from chain microstructure via processing to the end product. These

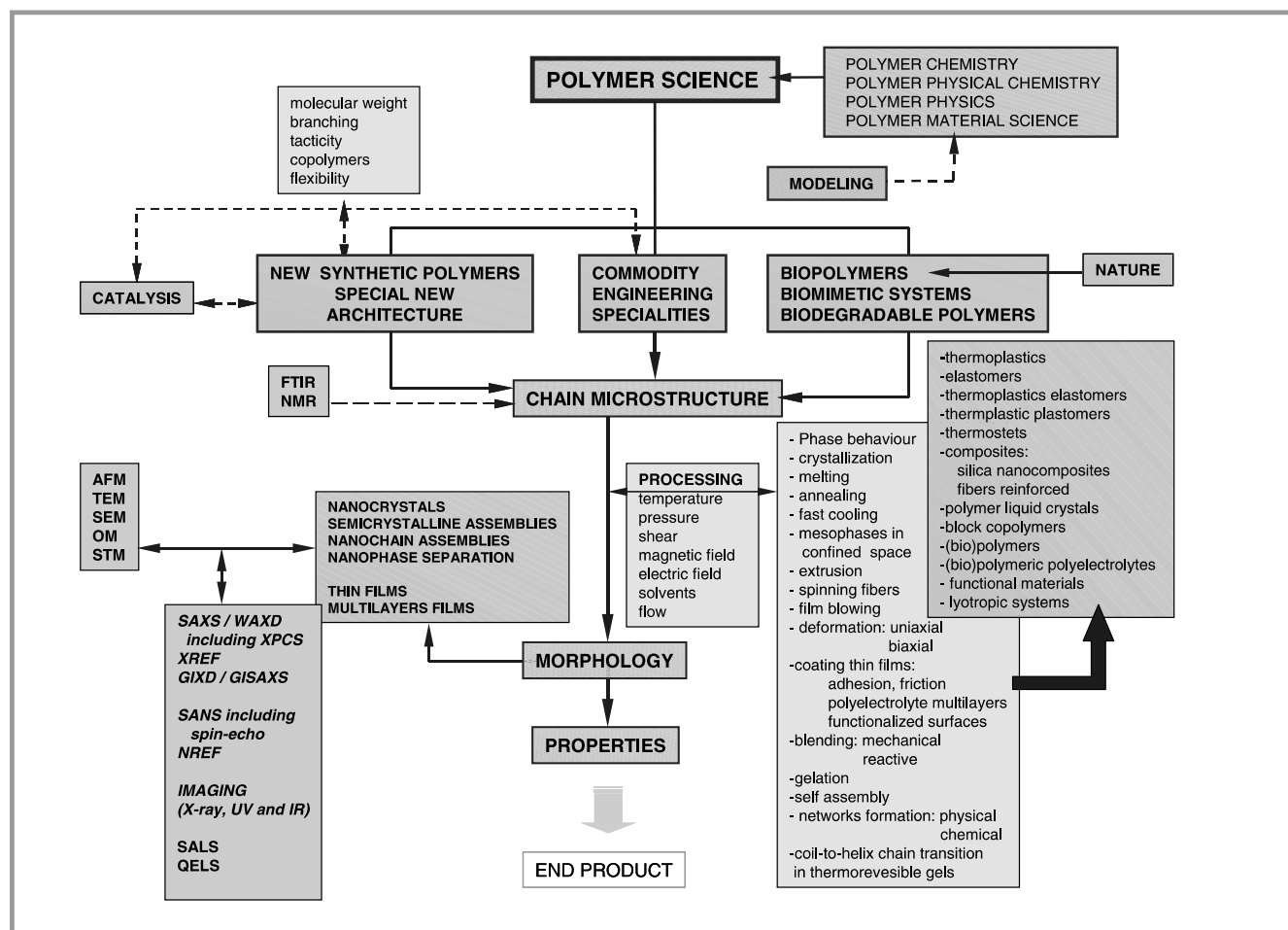


Figure 1. State of the art of polymer science with respect to scattering methods.

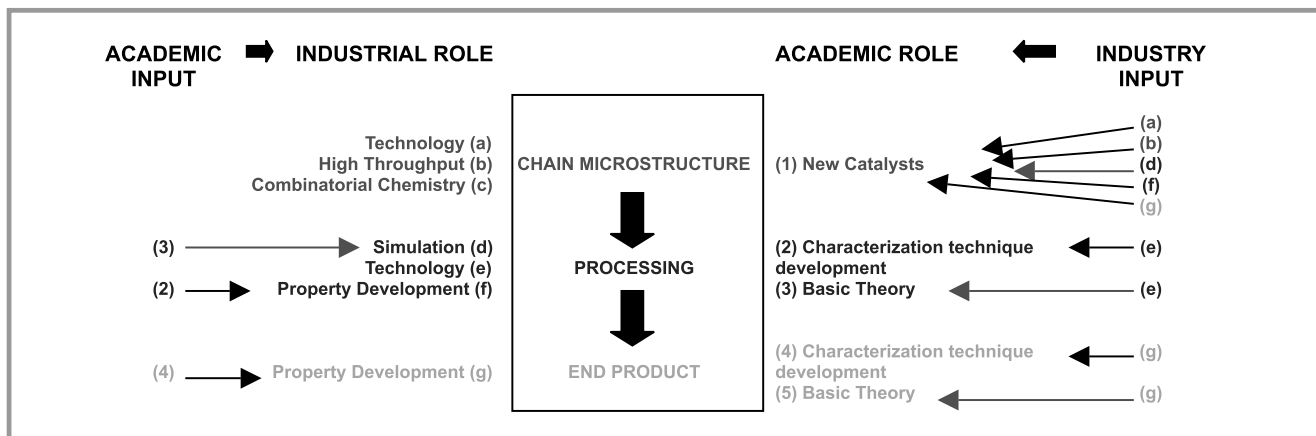


Figure 2. Illustration of the roles of academia and industry and the input needed from 'the other world' in order to bring relevant results into the field. Number and letters in the outer columns refer to the corresponding roles of academia and industry respectively. Black arrows: existing fruitful dialogue. Red arrows: missing links.

specific roles are listed in Figure 2. However, both worlds cannot proceed independently, and should communicate in order to deliver relevant contributions. Academia needs some industrial input, and vice versa. Quite often there is a fruitful dialogue (black arrows in Figure 2), but there are many necessary links missing (red arrows in Figure 2).

This is one of the reasons that control of the 'knowledge cycle' is still not possible. By this it is meant that it is not only important to relate polymerisation through processing to product properties with a minimum of trial and error, but that it is also crucial to master the reverse route; in other words, to translate non-optimal properties into a more appropriate processing method or even a more suitable macromolecular architecture, and ultimately to shorten lead times for development.

■ Synchrotron radiation

Synchrotron X-rays: the present status in polymer science

For most polymer systems, the collection of a typical X-ray scattering pattern with a conventional X-ray tube or a rotating anode easily takes 30 min or more. With the high-intensity beams now available at synchrotron sources, data can now routinely be collected in a few seconds or even much less time (milliseconds), allowing for the time-resolved study of rapidly changing structures as they occur, e.g. during polymer crystallisation, processing or deformation. The characterisation of weakly scattering systems becomes feasible, and the X-ray wavelength tunability is advantageous in systems where absorption is an item. X-rays probe the bulk of a structure,

in contrast to AFM, for example, where only surface information is obtained.

With the advent of highly defined synchrotron beams – high brilliance, high resolution, micro-focus – surfaces (grazing incidence experiments) and local features can now be studied, breaking the monopoly of the microscopic approach.

It is possible to combine property-related techniques with X-ray scattering experiments, such as DSC, temperature-modulated DSC, tensile testing equipment, the rheometer, AFM, light-scattering, all of which obviously allows for better elucidation of structure-property relations. In principle, the growth of polymers during synthesis can be characterised *in situ* as well. Such an approach is of particular interest in the case of difficult primary polymer structures, such as hyperbranched molecules, whose the shape and configuration can readily be described in terms of fractal dimensions, which are not accessible through chromatography, NMR, IR or mass spectrometry.

At synchrotron sources, in contrast to most laboratory setups, small-angle and wide-angle cameras are integrated, allowing for an accurate time correlation of structural development at different length scales. With the attachment of small-angle (laser) light scattering, this scale can even be extended to include μm features.

Polymer structure-property relations: some challenges for the future

Nanoparticles:

It is well known that the mechanical, thermal, optical and electric properties of bulk synthetic and oriented polymers can be considerably improved by the addition of

inorganic or organic filling materials. Recently, research in this very traditional field has started booming again as a result of new developments in nano-technology and the concomitant production of nano-sized particles of well-defined sizes and shapes, of different chemical natures, offering opportunities for selecting different types of physical and chemical interactions. Nano-particles with potentially promising interactions with polymer matrices involve clay particles and platelets, pure metals, inorganic crystals, silica spheres, carbon-tubes, fibres and rods. Recent experimental research and results are still of a highly explorative nature, and often lack the substantial structural support to provide a useful platform for further advances. There is a clear need for the fundamental understanding and predictability of polymer-nanoparticle composites. Of key interest is information on the structural order of (part of) the polymer chain in direct interaction with a well-defined nanoparticle surface and the description of the transition from surface ordering to the conformation of the polymer chain in the bulk network. Finally, it should be established whether or not the network structure imposes two- or three-dimensional organisation on the nano-particles. Under processing conditions, shear often strongly affects the preparation and final product properties of bulk and oriented (fibres, films) systems.

Intelligent materials:

Realising that structures and hence properties may change depending on external conditions, the challenge for the future is to optimise products towards controlled metastability. Here, «metastability» refers to the flexibility to change from one meta-

stable structure to another, rather than to true thermodynamic instability. At the very end of the line of the bulk properties controlled by nano-sized polymer assemblies are the small-scale sophisticated 'smart' materials designed to change their properties in a desired way in response to external changes. The degree of success defines the materials' 'intelligence'. Potential goals are the realisation of nano-scale devices such as optical switches, molecular pumps, polarity switches, etc. In this context, self-assembly, involving the association within or between dissimilar macromolecules, is a key issue, as one tries to avoid the creation of new polymeric molecules. From an experimental point of view, learning about structural changes imposed by external changes is similar to studying processing in real-time or conducting simultaneous quality evaluation.

Combined approaches

In the past, product properties were optimised towards stability and performance in as wide a range of environmental conditions as possible. The relations between structure and properties were deduced via the independent study of properties and morphology, essentially by microscopy and (room temperature) static scattering techniques. Nowadays, there is a definite and urgent need for product optimisation by considering the processing step, which involves the study of structural development and its inherent kinetics. Properties and structures should no longer be evaluated and studied independently, but measured simultaneously. The complex morphological changes occurring in a given system under mechanical loading, extrusion or during temperature excursions, for example, should be studied in real time. Hence, the availability of synchrotron X-ray sources is of primary importance, as is the development of lab-scale sample environments that mimic realistic environmental or processing conditions of flow, pressure, temperature, humidity, acidity, etc. This very demanding combined approach has as yet hardly entered polymer research – apart from a few pioneering groups – and as such still has a challenging future in the academic and industrial polymer community.

Instrumental challenges in synchrotron X-ray scattering based (polymer) research

- **Sample environment:** Observing structural developments during processing

via extrusion and injection moulding (among other possible methods), creates the need for X-ray transparent cells with controllable pressure, shear, temperature, temperature jumps, humidity and atmosphere, and/or combinations of these. Polymer orientation and crystallisation in strong magnetic and electric fields is a new experimental challenge. Devices have to be developed for following structural evolution during fast spinning processes. Experimental hutches at the synchrotron beam lines should be large enough to accommodate all the ancillary equipment needed.

- **Detectors:** Registration of fast structural development, such as that realised during fast cooling or in sharp phase transitions. Synchrotron X-rays are intrinsically strong, but the detectors are either too weak (dynamic range) or too slow to handle the rapidly evolving scattering patterns of the structural changes.

- **Data processing:** Structures are becoming increasingly sophisticated, and hence the scattering patterns are more difficult to describe in terms of physically relevant morphological parameters. The basic structures have to be revealed by microscopy first, before they can be built into a model that can describe the scattering patterns. In that respect, microscopy is truly complementary to X-ray work, and warrants continuous development for application under non-standard conditions of temperature (high and low temperature AFM), deformation, pressure, humidity, etc. Secondly, one may benefit from statistical approaches in which structures are created computationally: Molecular dynamics or Monte Carlo simulations may create such structures. Computational science, in conjunction with experimental validation possibly realised by (synchrotron) X-ray experiments, needs to be developed further.

General Conclusions

Our priority list of conclusions distinguishes between experimental priorities; user priorities; polymer science priorities; European industry and policy; education and publicity, collaboration and people.

A. Experimental priorities:

1. Detector development: improve spatial and time resolution, so as to obtain very fast systems for simultaneous

SAXS/WAXS; create uniform standard procedures for fast and automatic primary data analysis.

2. Development of new experimental techniques:

- a. develop and/or improve (multi-) coupled experimental approaches such as SAXS/WAXS/SALS/DSC (including temperature-modulated DSC); SAXS/WAXS/RHEOLOGY; SAXS/AFM;
- b. material investigation *in situ* on relevant industrial polymer-processing equipment: extrusion, injection moulding, mechanical deformation (fibre-spinning, 2D-deformation (films), film blowing), polymer orientation in magnetic and electric fields; *in situ* use of nano-sized beams,
- c. scanning X-ray scattering with micro-beams, d-X-ray imaging techniques (eventually coupled with chemical speciation),

B. User-oriented priorities:

- a. make SR scattering facilities more available and attractive for the non-specialised user communities (polymer chemists, materials scientists, engineers, biologists) and organise teaching sessions for beginners as well as the more advanced user community;
- b. create fast access for test experiments;
- c. provide user-friendly sample environment and automatic data analysis procedures.

C. Polymer science priorities:

- a. basic research in polymer science should remain a top priority of the European research area;
- b. polymer synthesis: new catalysts and new synthetic paths;
- c. research towards biodegradable systems, optimal use of natural resources of biopolymers, recycling of polymeric materials.

D. European Science Policy and Industry:

- a. basic research involving synchrotron radiation should be a top priority in European research planning;
- b. improve the funding situation for European sources;
- c. coordinate European efforts for the large facilities;
- d. stimulate the European polymer industry to take full advantage of the

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For further information please contact:

Prof. Andrzej Włochowicz Ph. D., D. Sc.

UNIVERSITY OF BIELSKO-BIAŁA
Faculty of Textile Engineering
and Environmental Protection
Institute of Textile Engineering and Polymer Materials
ul. Willowa 2, 43-309 Bielsko-Biała
tel. +48 33 8279 114, fax. +48 33 8279 100
e-mail: awlochowicz@ath.bielsko.pl

or

Prof. Janicki Jarosław Ph. D., D. Sc.

UNIVERSITY OF BIELSKO-BIAŁA
Faculty of Textile Engineering
and Environmental Protection
Institute of Textile Engineering and Polymer Materials
ul. Willowa 2, 43-309 Bielsko-Biała
tel. +48 33 8279 114, fax. +48 33 8279 100
e-mail: jjanicki@ath.bielsko.pl



existing skills at the large European SR-facilities.

E. Education and publicity:

Combined experimental approaches, such as can be realised at synchrotron sources, are crucial for the further success of European polymer science. Many groups in the basic polymer science, the polymer material sciences and polymer chemistry are unaware of the potential for scattering experiments, or do not enter competition for access to the large-scale facilities because of their lack of education in the basic physical principles of scattering, and a lack of attractively advertised introductory courses by synchrotron specialist groups.

F. People: Science develops fast, and the knowledge levels needed to operate according to international competitive standards, are rising rapidly. In spite of the definite need for more skilful scientists, the evolution at the European level is in proceeding in the opposite direction. Young people, facing the efforts of becoming an established scientist, prefer an easier way by selecting studies leading to jobs that quite often are better paid and have higher social esteem. European action is needed to stimulate a positive attitude towards the sciences in our societies.

G. Collaboration: Polymer science and materials research & development need a multidisciplinary approach requiring knowledge about material properties as well as experimental approaches for characterisation. Due to ongoing scientific progress, the load in each separate sub-discipline is becoming increasingly large. All-round scientists are scarce. Nowadays progress can only be made when different people with different backgrounds join forces. Quite often this approach is hampered, not by the lack of common interests, but by the absence of collaboration promoters and discussion moderators (project leaders), and by the lack of substantial long-term financial support.



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