



## Editorial

## Introduction to the special issue of *Polymer* on “Macromolecular Engineering” dedicated to Professor Krzysztof Matyjaszewski on the occasion of his 65th birthday



One cannot help but wonder at the extremely rapid maturing of polymer science, which started, as many scientific disciplines, as mere “collection” of curious facts and observations, and is currently at a level of development, which makes it possible to easily prepare unimaginable (until recently) materials, many of which imitate and even greatly surpass those provided by nature. Indeed, the accumulated discoveries and their critical analysis, have led to the development of macromolecular engineering – the subject of this special issue, which celebrates the accomplishments of polymer science and is dedicated to one particular polymer scientist – Krzysztof (Kris) Matyjaszewski – on the occasion of his 65th anniversary.

It is probably appropriate to begin by reflecting briefly on some of the important steps, which made it possible to speak of macromolecular engineering. The history of polymer, or macromolecular, science has been relatively brief but the number of unique materials it has given humanity is so impressive that many historians of science have been tempted to dub the newest era of human development the *Plastics Age* (read *Polymer Age*) in analogy to previous periods named after the most important and dominating materials (stone, bronze, iron, etc.) responsible for progress. Natural organic polymers (oligo- and polysaccharides, and proteins) have been used by humans in their daily lives since time immemorial. Although the number of these materials was comparatively limited, the number of their applications was extremely large and included building and clothing materials, materials employed in the creation of art objects, adhesives, etc. Yet, they suffered from many drawbacks, e.g., lack of stability and longevity. The situation was somewhat improved with the comparatively recent introduction of semisynthetic (chemically modified natural) polymers, such as nitrocellulose in 1846 [1,2]. The first purely synthetic (as opposed to chemically modified natural) polymers recorded in the scientific literature, including polyacrolein and poly(acrylic acid) [3], and polystyrene [4], were obtained in the same period (the 1840s) by accident, e.g., as side products of chemical transformations or by the unintentional thermal or photochemical polymerization of the pure monomers. It is interesting to note that even in the early report describing the polymerization of styrene, it was recognized that the polymeric product (dubbed “metastyrole”), might find useful applications in the field of optics due to its ability to strongly refract light [4]. By 1860, the isolation and polymerization of isoprene were also reported [5]. For decades, more precisely until 1920 when Staudinger published his seminal work [6], the

molecular structure of polymers was incomprehensible and was the subject of heated arguments. It was this lack of understanding that was partially responsible for the fact that very few synthetic methodologies emerged prior to the 1920s that led to useful materials (with the notable exception of bakelite, described in detail in 1909 [7]), and they were to a large degree the result of luck and careful (but more or less passive) observations rather than rational design. Within a century after the structure of macromolecules was accurately described, the number of papers, monographs, and patents dedicated to kinetic and mechanistic studies of polymerization reactions, synthesis of new monomers and polymers, structural characterization, and uses is truly stupendous. The properties and applications of polymeric materials are strongly dependent upon their chemical composition and macromolecular topology, architecture, and presence and position of functional groups, as well as molecular weight and molecular weight distribution. The search for new materials was one of the main driving forces that led to the development of synthetic methods allowing precise control over these parameters. Living polymerizations, in which the initiation is fast, and termination and transfer reactions are minimized to such a degree that they are virtually absent, have proved exceptionally useful. Historically, living anionic polymerizations were developed first [8,9], followed by cationic processes [10,11], but these methods suffer from several notable drawbacks, including sensitivity to various impurities, limited range of monomers and difficult copolymerizations, to mention but a few. Although some success was achieved in the 1980s with radical polymerizations using iniferters [12], it was not until the mid 1990s that highly robust controlled/living radical polymerizations (CRPs) were developed [13–15]. The most popular CRP methods are i) stable free radical polymerization (including iniferter- and nitroxide-mediated polymerization (NMP) [16–20], and organometallic radical polymerization [21–24]), ii) catalytic processes (including atom transfer radical polymerization (ATRP) [25–32] and reversible chain transfer catalyzed polymerizations [33]); and iii) degenerative transfer-based polymerization [34] (with reversible addition-fragmentation chain transfer (RAFT) polymerization [35–39] being the most widely used, but also including iodine-mediated polymerizations [40] and polymerizations in the presence of tellurium or antimony compounds [41]). These techniques and detailed mechanistic studies made it feasible to precisely design and rationally select the reaction conditions for the synthesis of well-defined

polymers with specific properties for targeted applications, or, in other words, these techniques made macromolecular engineering [10,42] possible.

As mentioned, this special issue of *Polymer* is comprised of papers dealing with various aspects of macromolecular engineering and is dedicated to Professor Kris Matyjaszewski on occasion of his 65th birthday, which he celebrated in April 2015. An immensely inquisitive and knowledgeable, dedicated, hard-working, and productive chemist, and – importantly – an outstanding educator, Kris has been an inspiration to an inestimable number of students and researchers from all over the globe for several decades. He grew up near Lodz – at the time the second and currently the third largest city in Poland. Surprisingly, chemistry was not a childhood love for Kris (who was rather interested in sports in his early years), but when he closely encountered the science, to which he would dedicate his life, the excitement was quick and intense. After two years as an undergraduate student at the university in Lodz, he had the opportunity to complete his studies at the Technical University of Moscow in the USSR. Soon after coming back home, he had two important tasks ahead of him – marry his college sweetheart Malgorzata (Malgosia), and apply for a graduate student position at the Polish Academy of Sciences in Lodz. His first interview in 1972 was conducted by a young polymer chemistry professor, Stanislaw Penczek, who had, several years earlier, worked as a postdoctoral fellow at Syracuse, NY, in the laboratories of Professor Michael Szwarc. Szwarc had recently published a book [9] on the reactivity of carbanions and living anionic polymerizations, so Kris' first assignment was to read the book and get back to Professor Penczek to tell him (during the continuation of the interview) what he had learned. The following was first presented to me as an apocryphal story by a friend, but it was later narrated in detail by both Kris and Malgosia, which certainly legitimized it. Apparently, the newly-wed Kris spent his honeymoon reading Szwarc' book (Malgosia has told a number of witty jokes about that episode of her life) and as soon as he returned to Lodz, he went to see Professor Penczek for his interview. The Professor asked Kris if he read the book and if he liked it, and to both questions Kris gave brief positive responses, which was sufficient to get hired. So, in 1972, Kris Matyjaszewski began his studies in Stanislaw Penczek's labs. He investigated a number of problems related to the cationic polymerization of heterocyclic compounds (such as 1,3-dioxolane and 1,3,5-trioxane [43], and THF [44]), for instance the reactivity of free ions compared to ion pairs, as well as the equilibria between ionic and covalent reactive species in the polymerizations. One can see how this early work on cationic polymerization as well as the earlier work by Szwarc and others on living anionic polymerization served as inspiration for the development of ATRP, for which Kris would ultimately become widely recognized. After receiving his doctoral degree in 1976, Kris worked as a postdoctoral fellow in George Butler's lab at the University of Florida (1977–8). Finally, after a visiting professorship at the University of Paris (1984), Kris whose work had already attracted attention, interviewed for a permanent position at the Department of Chemistry at Carnegie Mellon University, where he was hired and has been a faculty member since 1985. During the period 1994–8, he served as the Department head and is currently the J. C. Warner University Professor of Natural Sciences. The culmination of Kris' interest in living radical polymerization was undoubtedly the discovery of ATRP, which he reported in 1995 [25], and which has become one of the most powerful synthetic techniques in polymer science that yielded a plethora of well-defined polymeric materials with very complex molecular architectures and high degrees of functionalization, some of which were previously inaccessible. Incidentally, 2015 marks the 20<sup>th</sup> anniversary since the publication of Kris' first paper on ATRP. The impact of ATRP on both academic research and

industrial product development is easy to illustrate by the very large number of publications (well over 15,000) and patents on the subject that have appeared during the past two decades. In this relatively short time, the mechanism of ATRP has been studied intimately, which made it possible to carry out the reactions using extremely low (often single digit ppm) amounts of catalyst. Kris' first paper on ATRP has been cited more than 3500 times (more than what many very successful scientists would be proud to receive for all their publications over their entire careers). The total number of Kris' citations exceeds 73,000 and his current *h* index is 134, which makes him one of the most cited chemists in the world. He has been the recipient of a plethora of prestigious awards, including the Carl S. Marvel award for creative polymer chemistry (1995), the Annual Prize of the Foundation of Polish Science, often referred to as the “Polish Nobel Prize” (2004), the Macro Group Medal (2005), the Hermann F. Mark Senior Scholar Award (2007), the Presidential Green Chemistry Award (2009), the Wolf Prize in Chemistry (2011), and most recently – the Charles G. Overberger Award and the Dreyfus Prize in the Chemical Sciences (to be formally awarded shortly). Several institutions proudly list Kris Matyjaszewski among their honorary members. Estimating the number of conferences and meetings organized and chaired by Kris is a challenging task. One can mention his chairing a Gordon Research Conference on Polymers (East, as it was named at the time) in 2005 and many others, remembered by many of the readers of this special issue. However, one meeting that most researchers working in the field of polymer synthesis and characterization can recognize is that on Controlled/living radical polymerization, which takes place every 3 or 4 years at the Fall National ACS Meeting and lasts 4–5 days with a very large number of presentations (well exceeding 100). The first CRP meeting took place in San Francisco in 1997, just two years after the announcement of ATRP, and was followed by meetings in New Orleans (1999), Boston (2002), Washington, DC (2005), Philadelphia (2008), Denver (2011), to eventually “complete a full circle” and return to San Francisco in 2014. So many ideas have been generated and so many new friendships have been kindled at these meetings, and organizing them and keeping the tradition alive is a community service, for which Kris is greatly appreciated.

One of the best ways to evaluate the impact of scientists and educators is to look at their legacy, expressed not merely as the number but also the accomplishments of their students and trainees. Over 40 doctoral students have already received their Ph.D. degree under Kris' supervision and countless undergraduate students, postdoctoral researchers, and visiting scholars have been trained in his labs in Mellon Institute. A number of these students and associates have moved on to start their own independent careers in academia, industry, national labs, research institutes, etc.

The enormous size and the accomplishments of the group of people that interacted with Kris through the years became apparent at a recent special symposium, supported by the Carnegie Mellon University Department of Chemistry and Mellon College of Science, which was organized in Kris' honor, and which took place in Pittsburgh in March 2015. The “family reunion”, which was attended by over 100 of his current and former graduate and undergraduate students, postdoctoral fellows, exchange students and visiting researchers, as well as colleagues from Carnegie Mellon University, was an exciting event and, on the eve of Kris' 65th birthday, brought back many memories. In addition to poster presentations given by Kris' current group members, twenty lectures were delivered by former group members, who now have their independent academic or industrial careers and are either just starting to make or have already made important scientific contributions. The entire meeting clearly illustrated Kris' impact on polymer science and his legacy (Fig. 1).



**Fig. 1.** Kris and Malgosia Matyjaszewski (center) surrounded by former and current students, postdoctoral fellows, colleagues, and friends, on the steps of Mellon Institute, March 2015. (Courtesy of Ken Andreyo.)

This special issue consists of 33 papers written mostly by former Maty group members (1 former undergraduate student, 8 graduate students, 16 postdoctoral fellows or visiting scholars) but also by 8 long-term collaborators and friends. One is tempted to name it the “Matyjaszewski legacy issue”, for it clearly illustrates how much original and inspiring research is being carried out by scientists influenced by Kris. Obviously, if everybody who closely interacted with Kris over the past several decades and who does polymer-related research was to write a paper, the issue would be the size of an encyclopedia. The 33 papers collected here will, however, do a nice job in affirming Kris’ impact on macromolecular science and will undoubtedly serve as inspiration to many. The first several papers describe mechanistic studies that are important in order to rationally select the reaction conditions needed for a polymerization reaction with desired outcome. The first two papers, by Balazs [45] and by Kowalewski [46], describe fundamental aspects of polymerization reactions. The paper by Gennaro [47] deals with Cu-mediated polymerization, studied by electrochemical methods and sheds light specifically on the mechanism of polymerizations taking place in the presence of metallic copper. Pintauer [48] discusses the role of the ligand in Cu-complex-catalyzed reactions that are closely related to ATRP, namely atom transfer radical addition. In his work, Kajiwara [49] describes the use of ESR spectroscopy combined with ATRP in understanding how chain length (controlled by ATRP) affects the structures of propagating radicals. The next section of the issue is comprised of papers describing primarily various synthetic methodologies. The section starts with Fossum’s paper [50] which provides examples of reactivity ratio-controlled polycondensation reactions and their use in the synthesis of functional polyethers. In

his paper, Siegwart [51] demonstrates the utility of sequential thio-butylolactone aminolysis and thiol-ene reactions in the preparation of biodegradable polymers with applications in nucleic acid delivery. Peng’s paper [52] describes novel aluminum complexes that mediate stereoselective ring-opening polymerizations. Control over chain-end functionality is an important facet of CRP reactions. The high degree of chain end functionalization of polymers prepared by such techniques is essential for the preparation of segmented copolymers. Of particular importance is the ability to prepare large systematic “libraries” of polymeric materials in order to rapidly screen their behavior and identify compositions suitable for specific applications. A series of double hydrophilic block copolymers containing a segment with functional groups able to complex to various metal ions, are described by Destarac [53]. The work by Costanzo [54] demonstrates the use of well-defined block copolymers for the dispersion of carbon nanotubes. Triblock copolymers with a polyester-type middle block and side segments containing reactive epoxide pendant functionalities are described by Plichta [55]. Di- and triblock copolymers with liquid crystalline behavior, synthesized by chain extension reactions using conjugated polymeric macroinitiators, are the subject of the paper by Stefan [56]. Block copolymers with a phosphine-containing segment, and the formation of core-crosslinked micelles via chain extension with a divinyl crosslinker, as well as the use of the formed nanoparticles as nanoreactors for catalysis is described by Poli [57]. End groups in well-defined polymers are not only useful in chain extension reactions, but also in other post-polymerization modifications. In his work, Lee [58] discusses the coupling reactions involving amine-terminated well-defined polymers. Sometimes, chain end functionalities, which are generated

during CRP reactions, e.g. alkyl halide in ATRP, may need to be removed for certain applications, and Lutz [59] shows the utility of dehalogenation reactions of polymers prepared by ATRP. Hybrid materials are a special class of (usually) end-functionalized polymeric materials. A well-defined synthetic polymer may be combined with inorganic natural material, as shown in the papers by Pietrasik [60], which discusses hydroxyapatite-based hybrids, and by Kruk [61], which deals with silica-based hybrids and their pyrolysis. Core-shell inorganic nanoparticles with well-defined polymer chains attached to their surface are the subject of the paper by Gao [62]. Carbon nanotubes can also be a component of composite materials, for instance, after modification with the appropriate polymerization initiating sites, as shown by Mosnacek [63]. In addition, a number of synthetic polymer – biomacromolecule hybrid materials have been prepared in recent years and have already attracted significant attention. The synthesis of peptide- or protein-containing hybrid materials and their applications is the subject of the papers by Di Lena [64] and Konkolewicz [65]. Cellulose-derived conjugates are described by Oh [66] and Huang [67], and hybrids containing another material isolated from plants, lignin, are the subject of Washburn's work [68]. In addition to control over functionality, CRP techniques allow for unprecedented ability to prepare macromolecules with complex architectures. A review paper by Neugebauer [69] summarizes important features of densely grafted copolymers, typically dubbed molecular brushes. The synthesis and characterization of polymer brushes is the subject of the papers by Boerner [70] (using ATRP) and Tang [71] (using a combination of ring-opening metathesis polymerization and RAFT polymerization). With the advent of macromolecular engineering methodologies, not only graft copolymers but also polymers with other complex architectures have become accessible. The synthesis of hyperbranched polymers by ring-opening copolymerization is the subject of the paper by Frey [72]. The work by Paik [73] demonstrates that the powerful combination of ATRP and azide-alkyne click chemistry is very useful in the synthesis of cyclic macromolecules. The main focus of the papers in the next section of this special issue is the preparation of advanced materials, their characterization, and fundamental structure-properties studies. The paper by Silverstein [74] describes the preparation of materials with hierarchical porous structures and the effect of reaction conditions on the porosity. Sheiko [75] presents a methodology that leads to materials with triple shape memory, in which various shapes may be encoded at the same temperature. The paper by Beers [76] discusses the swelling behavior of extended polymer brushes and provides a method to determine graft density based on solvation thermodynamics. Mueller [77] offers detailed fundamental studies of the morphological behavior (phase separation in the bulk phase) of a series of triblock copolymers, in which the block sizes are systematically varied. In summary, the work presented in this special issue addresses practically all important facets of macromolecular engineering – from fundamental studies of reactivity and reaction mechanisms to development of new synthetic strategies, to new materials and their applications but also various types of characterization and fundamental studies that enrich our understanding of how structure determines physical properties of polymers.

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On behalf of all the authors and innumerable members of the polymer community who have had the chance to interact with him, I wish Kris happiness and continued success! Thank you for many years of mentorship, support, and friendship!

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