

# Polymer Chemistry: Current Status and Perspective

by Krzysztof Matyjaszewski

**T**he last decades witnessed significant progress in the synthesis of macromolecules with precisely controlled architectures.

These polymers have been prepared by various chain-growth reactions predominantly using either vinyl or cyclic monomers [1]. Generally, well-defined polymers are prepared by reversible deactivation polymerization (RDP) with the concurrent growth of all polymer chains (fast initiation) and greatly diminished contribution of chain breaking reactions (transfer and termination). In this manner, low dispersity polymers, approaching Poisson distribution ( $\mathcal{D} = \bar{M}_w / \bar{M}_n \sim 1 + 1/\bar{X}_n$ ) are prepared. Originally, living polymerizations were developed for anionic polymerization of non-polar vinyl monomers such as dienes and styrene and required very stringent conditions, namely complete exclusion of moisture and air [2]. Nevertheless, such systems, from laboratory curiosity, were successfully transferred to industry, generating over \$1 billion in revenue for Kraton, and even more for other companies.

Living polymerizations were subsequently expanded to ionic ring-opening polymerization, coordination polymerization of both olefins and cycloolefins (ROMP), and eventually to radical polymerization (reversible

deactivation radical polymerization, RDRP). Classical living polymerization requires that all growing polymer chain ends are mediated by control agents that can be relatively expensive; e.g. metallocenes, post-metallocenes or stable free radicals. Recently, however, various catalysts that can be used at parts per million level have been developed for use in the presence of less expensive reagents, such as alkyl halides in atom transfer radical polymerization (ATRP), sulfur containing chain transfer agents in reversible addition-fragmentation (RAFT) polymerization, and alkylzinc or alkylaluminum compounds in degenerative transfer shuffling catalyst systems in olefin polymerization [3]. This approach has significantly reduced the cost of commercial synthesis of various block copolymers. The further reduction of the cost and development of more environmentally friendly conditions in these processes remains a challenge.

RDP permits precise control of the primary structure of polymer chains. These chains consist of carbon-carbon backbones formed in polymerization of vinyl monomers. In ring-opening polymerization, one can incorporate various heteroatoms to the backbone. It is also possible to copolymerize vinyl and cyclic comonomers facilitating their subsequent degradation. Currently, each particular polymerization method may have its own "preferred" monomers; coordination

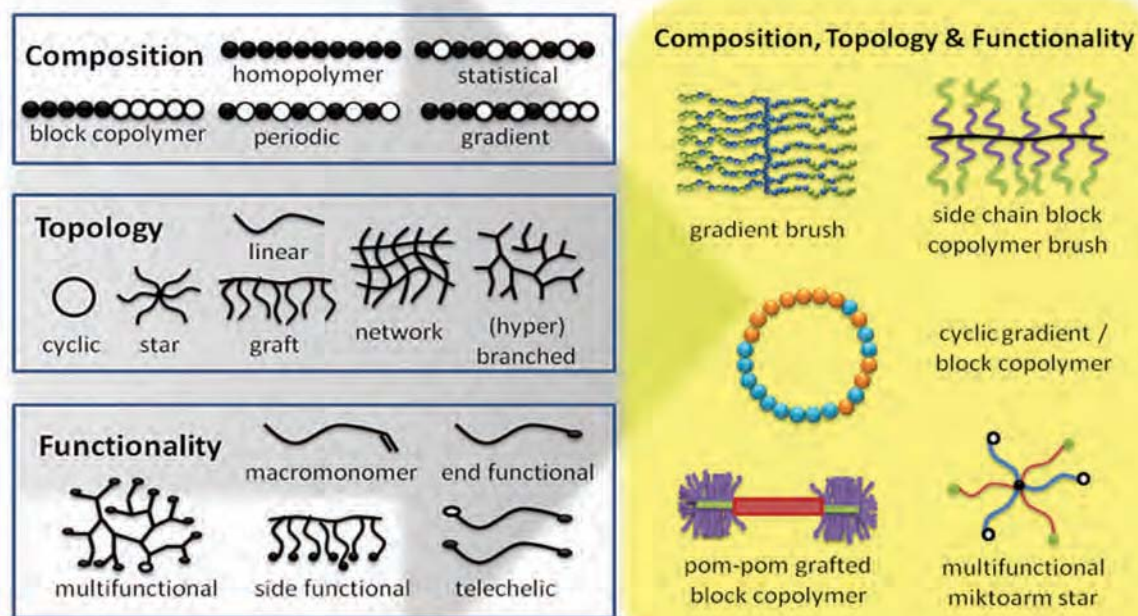


Fig. 1. Individual and combined basic elements of macromolecular architecture [4].

polymerization is used for ethylene and olefins, isobutylene for cationic polymerization and polar vinyl monomers for radical polymerization. However, there has been progress in using polar comonomers in coordination polymerization or olefins in radical polymerization. It is also important to extend the range of monomers from those that are “petroleum-based” to those from renewable resources thereby facilitating better control of polymer degradation and recycling. Nevertheless, the efficient copolymerization of “incompatible” monomers is still challenging.

Several elements of macromolecular architecture can be controlled in RDP. They include chain topology, chain composition, chain functionality, chain stereostructure and chain uniformity. They can be also combined as illustrated in Fig. 1 (reproduced from [4]). These elements are based on chains with covalent bonds connecting monomeric units. In addition, dynamic non-covalent bonds can also form macromolecular chains with properties strongly affected by the dynamics of chain interactions (dynamers, vitrimers and many self-healing materials) [5-7]. Eventually polymer chains can be assembled to secondary or even higher order structures through various weak supramolecular interactions in bulk or in solution as in polymerization-induced self-assembly (PISA) [8].

Chain topology elements span from linear chains to cycles and various branching features. They can include long or short chain branching, loose or dense branching, or even hyperbranched systems and dendrimers. Branches can be distributed with a tunable density along the chain, typically in graft copolymers, or very densely as in bottlebrush copolymers. Branches can be limited to one focal point as in star polymers which can be formed by an arm-first or core-first approach. They can also be distributed in bulk material, forming networks of different uniformity, mesh size and composition. The type and degree of branching can tremendously affect mechanical or rheological properties of resulting polymers. For example, bottlebrush copolymers can form photonic materials with periods of hundreds of nanometres. Bottlebrush copolymers can become supersoft and superelastic with moduli lower than those of hydrogels. In contrast to hydrogels, which become hard after water evaporation, bottlebrushes can never dry out since their backbones are diluted by their short, unentangled side chains rather than by water [9,10]. By varying graft density, length of side chains, and crosslinking density, it is now possible to prepare elastomeric materials with thermomechanical properties mimicking various biological tissues. It remains a challenge to design



*Kris Matyjaszewski (right) with Michael Buback (IUPAC Polymer Division President 2012-15) at the banquet of MACRO 2014*

branching degree, uniformity, or location and correlate these elements with macroscopic properties and then precisely carry out synthesis of such materials.

Another important parameter is chain composition. Block copolymers and segmented copolymers revolutionized polymer science 60 years ago and have been the subject of very intense research both in academia and industry. In the chains of block copolymers, there are abrupt changes in composition on passing from one to another segment. This results in phase separation and formation of various nanostructured morphologies. Until recently, only diblock and triblock copolymers have been studied. In the latter case over 30 different morphologies were identified, greatly expanding upon the classical spherical, cylindrical, gyroidal and lamellar structures observed for binary systems. Recent progress in ATRP and RAFT has permitted synthesis of segmented copolymers with 20 or more blocks. The question remains: “what morphologies can they adopt?” Another important objective is to design and prepare gradient copolymers with a smooth change of composition along the

polymer chains. Such copolymers may have gradient with a linear, V-like, hyperbolic, exponential, or tapered shape. It is also possible to use gradient control not only in a binary system but also ternary, etc. systems. Recently, there is a strong interest in controlling sequence in polymer chains, decreasing dimensions from long to short segments and to individual monomeric units. This approach has been expanded from classical periodic sequence such as  $(AB)_n$  for alternating copolymers, to  $(ABC)_n$ ,  $(ABCD)_n$  and eventually to a programmed sequence that can be recorded and written back or even erased [11]. Such sequence control is inspired by biological systems, such as nucleic acids or proteins and is indispensable for passing from primary to secondary and eventually to the tertiary structures. It is not only a challenge to make materials with a particular sequence, including multiblock copolymers and gradient copolymers but also to predict how these copolymers will assemble to secondary and higher order structures and what kind of properties they will have.

Functional groups can be placed in various parts of macromolecules. They can be located with a pre-determined density along the polymer backbones, at the extreme position of chains, including chain ends in telechelics, chain centers, ends of arms in stars and bottlebrushes or in the cores of stars, or chain ends for hyperbranched or dendritic molecules. These groups should carry specific functions that can be used for further reactions, crosslinking or attachments of other moieties whether they be biomolecules, drugs, optoelectronic materials or other species. The site-specific functionalities can be of a singular type or based on several different functionalities. Some functional systems can form self-catalyzed structures that can provide additional control and even facilitate regeneration of formed products by concurrent or consecutive covalent and non-covalent polymerizations [12]. One challenge is to incorporate moieties in a specific position within macromolecules with reactive orthogonal functionalities for further reactions and synergistic effects.

Control of stereostructure is now essentially limited to coordination polymerization of vinyl and cyclic monomers, though some limited control can be achieved in anionic systems. Specially designed catalysts can provide excellent and programmable stereocontrol for polypropylene and other polyolefins, and can be even extended to the synthesis of stereoblock copolymers. Such control for cationic and radical polymerizations is very difficult to achieve, though there has been some success through complexation with

lanthanide cations in the polymerization of acrylamides, leading at first to stereoblock, and then stereo-gradient copolymers by a radical mechanism. Extending and improving such a control in radical polymerization to (meth)acrylates, acrylonitrile or styrenes is a challenge.

RDPs can provide polymers with very low dispersity. However, there is a growing interest in synthesis of polymers with higher dispersities and even those with intentionally programmed distributions. This can be accomplished by various exchange reactions including depropagation, transesterification or transacetalization reactions. However, a designed slow exchange reaction between active and dormant species that is slower than propagation, which can be accomplished by using a very low concentration of Cu catalysts in ATRP or using less efficient RAFT reagents (dithiocarbamate for methacrylates), has also proved to be effective. Another possible method of controlling molecular weight distribution is by slow feeding the initiators, or a continuous addition of terminating agents. Programmed feeding (constant rate, linear or nonlinear addition rate) can also be used to change the skew and asymmetry of distributions [13]. Block copolymers with broader distributions may have lower order-disorder transition temperature, form larger domains, generate new bicontinuous morphologies, and even exhibit photonic properties. Thus, controlled and predesigned heterogeneity, including molecular weight distribution, tacticity, composition (gradients), and shape (branching) can lead to new classes of materials with novel properties [14]. On the other hand, synthesis of block copolymers with short, precisely controlled segments may provide efficient phase separation at the scale below 5 nm, an important feature for ever-diminishing dimensions in microelectronics. It is a challenge to harness these parameters and prepare advanced materials with tunable processing windows, broader glass transition, higher critical micellar concentrations, and precisely controlled low molecular weight block copolymers with new morphological features.

Most RDPs are carried out under homogeneous conditions. However, some new opportunities arise from polymerization in confined spaces. For examples, in a tiny microemulsion droplet (10 nm), essentially only one very large macromolecule can grow by radical means and cannot terminate with another one, as they are separated by phase boundaries. This can lead to fast terminationless radical polymerization or dendrimer-like structures (*cf. infra*). Even more interesting opportunities arise from polymerization in small

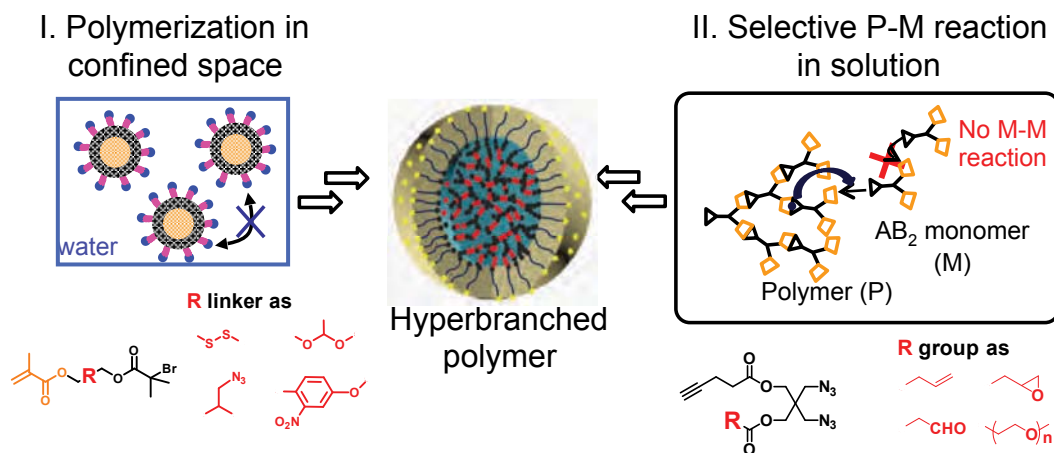


Fig 2. Two approaches to highly branched uniform polymers.

inclusion complexes: metal oxide frameworks (MOFs), zeolites or in the very small pores of mesoporous silica where tacticity control can be enhanced. Alternatively, templated polymerization can provide control of chain length, stereostructure and sequence. Cost-effective re-use of such confined/templated systems in preparing large quantities of materials in confined space remains a challenge.

Figure 2 illustrates two approaches to highly uniform hyperbranched polymers from  $AB_2$  monomers or inimers (*i.e.* monomers and initiators combined within one molecule) prepared in dispersed media. Polymerized inimers can reach high degrees of branching (DB ~ 0.5) but are typically characterized by low molar mass and very broad molecular weight distributions that arise from a unique combination of a chain-growth and a step-growth mechanism. However, confinement of inimers into a discrete nanospace, (typically micro-emulsion micelles), permits complete inimer conversion while preventing inter-micellar reaction [15]. Thus, at the end of polymerization, each micelle contains only one hyperbranched polymer with the molecular weight directly determined by the micelle dimensions. The synthesized hyperbranched polymers were further used as multifunctional macroinitiators for a subsequent polymerization of a second monomer to produce core-shell structured hyperbranched polymers in one pot. An alternative approach to similar materials, but in solution, employs  $AB_2$  monomers with 1 alkyne and 2 azide moieties in a highly efficient Cu-catalyzed azide-alkyne cycloaddition (CuAAC) [16]. Due to complexation between the Cu catalyst and the triazole product, all added  $Cu^I$  catalysts are quickly bound to the formed functional groups and confined in the polytriazole polymers at low conversion and the free

Cu catalysts in the solution are depleted. Thereafter, monomer-monomer reaction in solution (step-growth) becomes suppressed and all monomers have to diffuse to the proximity of the polytriazoles units, where they interact with the Cu catalysts and react with the locally abundant azido groups on polymer molecules (chain-growth). In this manner, hyperbranched polymers with very high DB ~ 1.0, predetermined molecular weight, and low dispersity ( $\overline{M}_w/\overline{M}_n < 1.05$ ) are formed in a one-pot reaction within hours.

RDPs are typically carried out under constant temperature or pressure. However, it is advantageous to use several external triggers to control polymerization rates and loci. Such temporal and spatial control can be accomplished using light, electrical current, mechanical force, or chemistry (*e.g.* pH variation) [17]. Generally, development of more selective, more efficient, and less expensive, recyclable polymerization catalysts is very important. These can be metal free and responsive to external stimuli leading to new classes of smart or intelligent materials which can respond to light, pH, solvent or gas vapor, mechanical forces and can change shape, exhibit shape memory, self-heal, repair, and perhaps even self-replicate. The challenge is how to use them together and provide dual control, start and stop polymerization at will, and perhaps switch from one to another mechanism of polymerization, expanding the range of accessible elements of polymer architectures.

New RDPs, especially proceeding by radical mechanisms, have opened avenues to prepare hybrid materials. They include organic/inorganic hybrids based on grafting from nanoparticles, nanotubes and flat surfaces but also bioconjugates formed by the covalent linking of natural products (proteins, nucleic acids, carbohydrates) with synthetic polymers. Covalent grafting

of polymers from inorganic surfaces provides access to very densely grafted brushes that affect many properties, including enhanced lubrication, antifouling, or antimicrobial properties [18]. Nanoparticles, nanorods or nanotubes with densely grafted polymers do not aggregate and disperse very well in either solvents or polymer matrices. Proteins with grafted polymer chains can circulate for a longer time in the human body, can survive at low pH, can be dispersed in organic solvents, and be used as catalysts at higher temperatures or as therapeutics [19,20]. Nucleic acids combined with polymers can self-assemble and pass efficiently through cell membranes and can form various polyplexes. They can be loaded with dyes forming very bright fluorescent probes which can target specific cells after linking with antibodies or aptamers. It is interesting to extend such bioconjugation to larger objects such as living cells or tissue. Designing the most efficient materials and carrying out their precise synthesis is a challenge.

All these areas can be significantly aided by computational methods at ab initio level for better understanding mechanisms [21] and catalyst design, at mesoscopic and macroscopic level through various reaction kinetic and materials properties simulations. This can guide polymer chemists to develop comprehensive structure-reactivity and structure-properties relationships and to prepare a range of polymeric materials with new superior properties.

This short article attempted to illustrate the complexities of modern and post-modern polymerization chemistry. As these new processes take hold and new polymeric materials evolve, IUPAC must continue its historic purpose in the development of nomenclature and terminology, appropriate to these methods and materials and transcending the confines of the subject and national boundaries. 

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