The Inception of Modern Polymer Science

Control of Molecular Structure and Function for Designer Polymers

Polymers are essential building blocks of both biological life and artificial everyday objects (Figure 1). Every polymer molecule consists of long chains of repeating units (mers) linked together either linearly or within a complex architecture. Building blocks may be nucleotides in DNA, aminoacids in proteins, or petroleum-based small molecules, such as ethylene, propylene or styrene in the case of synthetic polymers. Hermann Staudinger proposed almost exactly hundred years ago, that polymers are covalently bonded chain-like molecules. [1] To celebrate this discovery the year 2020 has been named the year of polymer science.

Although covalent bonds hold together the monomers in both natural and synthetic polymers, they are fundamentally different, and this difference is expressed in the structure of the polymer chains. Every single macromolecule of a given type of protein or DNA strand is essentially identical, as it comprises the same number of mers. Even more: the sequence of consecutive mers in the chain is strictly predefined in a biological macromolecule, which in turn is critical for its unique structure. These primary, secondary, tertiary and eventually quaternary structures define all biological functions of proteins and enzymes. The sequence control is the essence of complementary base pairing of DNA chains, responsible for both transferring genetic information and protein synthesis.
On the other hand, typical synthetic polymers consist of a mixture of chains of many possible lengths (i.e. molecular weights). This is because most polymers, of which we consume ~200 megatons a year, [1] are synthesized by coordination or by free radical polymerization. Radicals are extremely reactive species that within one second of a lifetime can react with thousands of monomers (i.e. polymerizable molecules containing a C=C double bond). After reaching the average one second lifetime, two radicals recombine or disproportionate, terminating the reaction. As these reactions occur at random, molecular
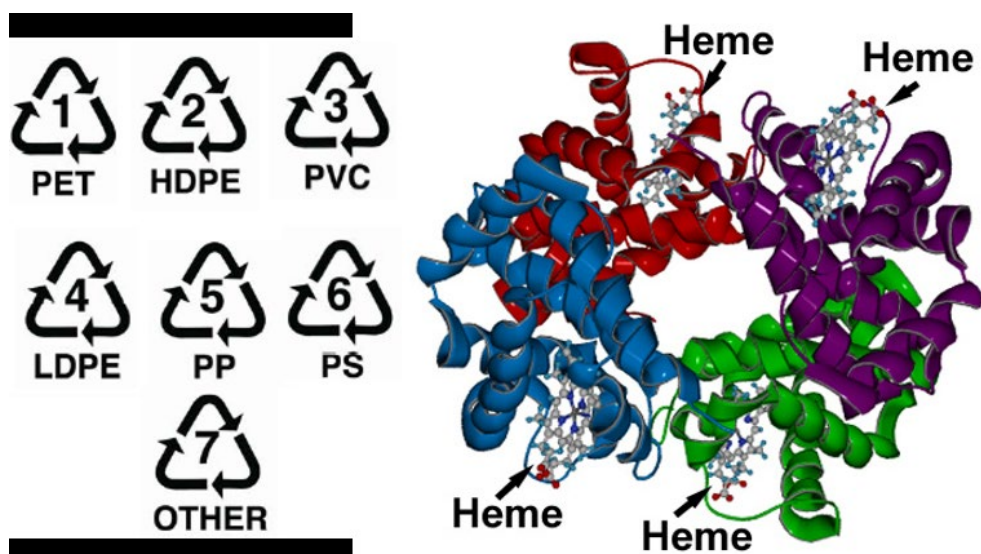
Figure 1. Synthetic polymers vs biopolymers. Left: Every day-use, commodity plastics consist of polymer chains of random molecular weights. Right: Hemoglobin contains four protein subunits; each protein has a strictly determined sequence of aminoacids, which gives rise to a unique way the protein folds. The folded structure enables specific function of the protein. (Image source: Wikipedia and Wikibooks)

weight distributions (MWD, also called dispersity, which is a measure for the spread of the distribution) is observed in synthetic polymers, as opposed to monodisperse biopolymers which display no distribution, i.e. each macromolecule is of the same chain length. [2] While plastics based on high dispersity polymers revolutionized the materials world in the 20th century, for many years polymer chemists have been trying to synthesize well-defined polymers with a level of control approaching those from nature to eventually approach the properties and sophisticated function of their natural counterparts.

Prevent Termination

A typical chain growth polymerization process consists of three main reactions: initiation (i.e. formation of active species), propagation (i.e. chain growth by repetitive addition of monomers) and termination (deactivation of active species). Very poor control over the polymer structure in conventional free radical polymerization usually arises from the continuous slow initiation, short radical lifetime and fast biradical termination.

The ground-breaking discovery to overcome this limitation was made by the Polish-American chemist Michael Szwarc
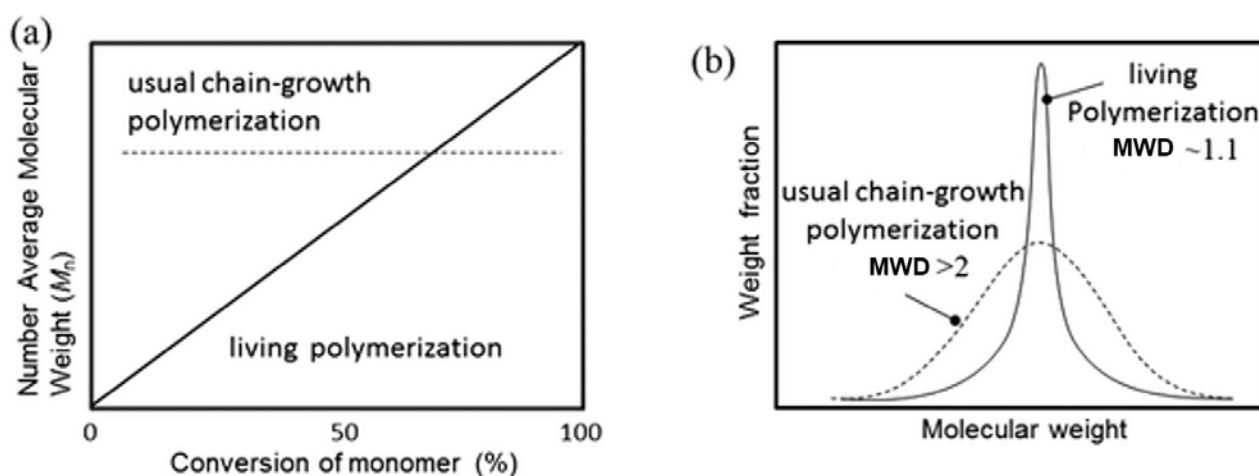

Figure 2. Free radical vs 'living' polymerization. (a) Average molecular weight in free radical polymerization stays constant throughout the reaction, whereas in living polymerization the molecular weight increases linearly since all the chains grow simultaneously. (b) MWD is broad in free radical polymerization and approaches 1 in anionic polymerization. (Adapted from ref. [4] with permission from Royal Society of Chemistry)
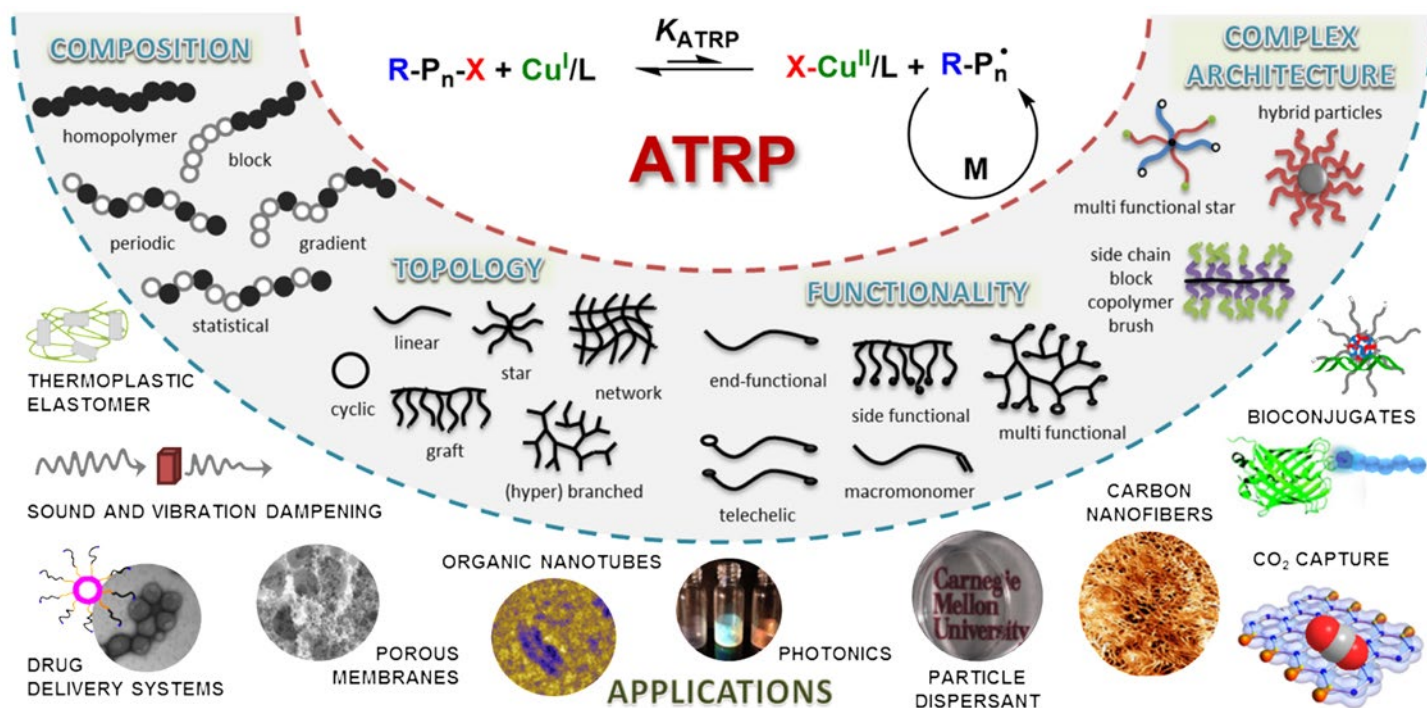
Figure 3. Top: Mechanism of ATRP. Halogen (X) is transferred between the initiator/growing chain (R-Pn-X) and the copper catalyst (Cu/L) forming a radical (R-Pn·). This radical can add monomers (M), or terminate, however termination is minimized due to the equilibrium (K_{ATRP}) being strongly shifted towards the left side of the reaction. Bottom: Schematic overview of polymer microstructures enabled by controlling the radical polymerization process and examples of applications of these materials. (Adapted from ref. [7] with permission from American Chemical Society)

in 1956. Instead of employing radicals as active chain carriers, he used carbanions. [3] Unlike radicals, carbanions do not react with each other and thus do not terminate. Importantly, all chains could be initiated at the same time and propagate concurrently.

The phrase 'living' was proposed for such an anionic polymerization, as all chains grow simultaneously without any termination, affording well-defined polymers with dispersity < 1.10 (Figure 2). The process has been used in industry, for example in the production of thermoplastic elastomers, i.e. physically crosslinked and recyclable rubbers, such as Kraton.

Trick the Termination: A Radical Idea

Despite the successful commercialization, anionic polymerization suffers from several drawbacks. Namely, carbanions are very sensitive to traces of moisture or impurities and require stringent conditions and special equipment. Additionally, only a limited number of

monomers can be polymerized via the anionic mechanism, as opposed to the radical one. Thus, methods to control radical polymerization to the extent of a typical living anionic polymerization have attracted tremendous interest.

This goal was ultimately achieved in the 1990s with the development of the reversible deactivation radical polymerization (RDRP) techniques, such as atom transfer radical polymerization (ATRP). [5,6] In conventional radical polymerization, in order to suppress biradical termination a very low concentration of free radicals (parts per billion vs. monomer) is used to permit a radical lifetime of ca. 1 second to grow chains to MW in the range of 100,000. This is accomplished by very slow dosing radicals to the system (slow initiation) and stays in a stark contrast to living anionic polymerization, when all chains are initiated fast and grow simultaneously. Thus, RDRP was developed in which all chains start growing concurrently (fast initiation), but, in a 'magic' way, 1 s lifetime of growing chains was extended to hours or even days. This was accomplished

by introducing a large pool of dormant (inactive) species that exchange dynamically with minute amounts of growing radicals, which are deactivated back to dormant species after addition of a few monomers before they can terminate. Thus, by inserting ca. 1 min dormancy state after 1 ms activity, the overall life of growing chains can be extended to hours or days. This would be like extending human life from 100 years to 3000 years, if after each 1 day of activity we could be dormant for 1 month. In ATRP, a halogen atom is transferred between dormant alkyl halides and parts per million of Cu catalysts (see the reaction scheme in Figure 3), extending the lifetime of growing chains from 1 s to several days. This enables synthesis of well-defined, essentially tailor-made polymers with complex architectures such as stars, brushes, combs as well as controlled composition, functionality, chain topology etc., giving rise to a multitude of materials as summarized in Figure 3. [7]
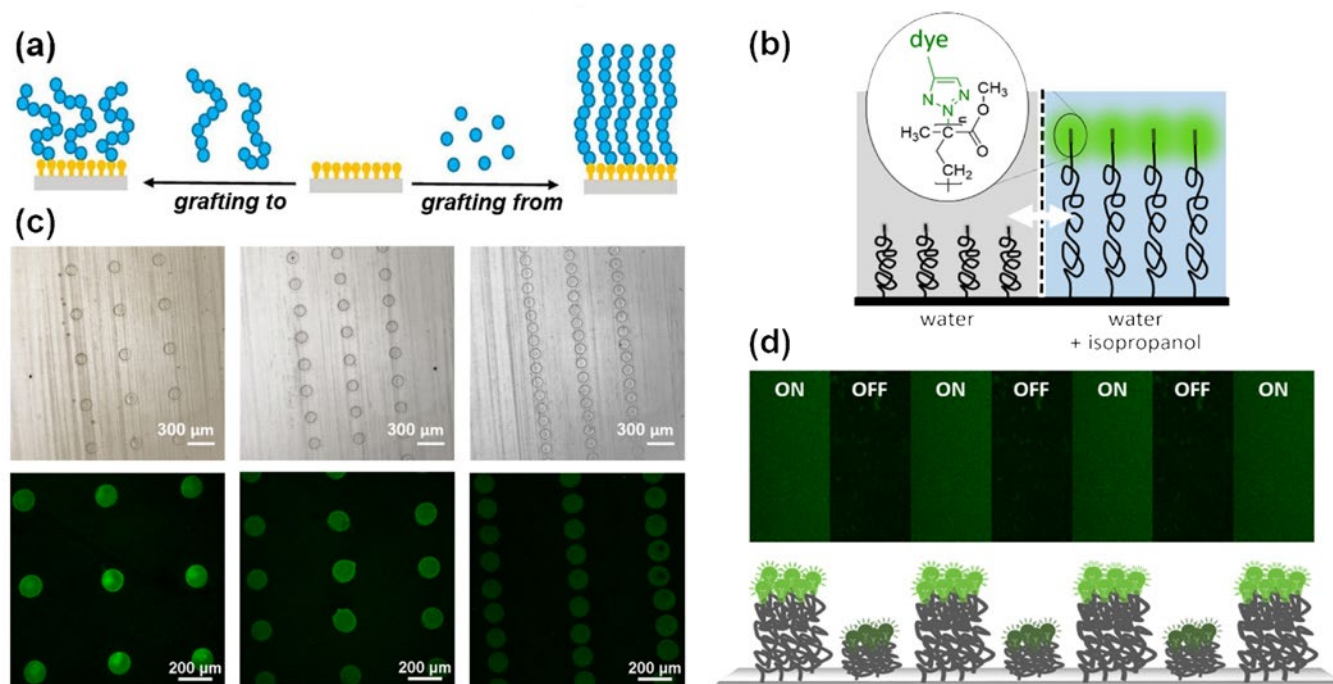
Figure 4. (a) Two main approaches to synthesize polymer brushes: grafting pre-synthesized functional polymer chains onto a functionalized surface; or grafting polymer chains directly from initiator-modified substrate. (b) Idealized, schematic representation of surface-anchored polymer chains in brushes, end-functionalized with a fluorescent dye, and their behaviour in different solvents. (c) Fluorescent patterns obtained by inkjet-printed surfaces employing the grafting-to approach. (d) Responsive, switchable behaviour of end-functionalized fluorescent brushes prepared by the grafting-from approach. Adapted from refs. [8-10] with permission from American Chemical Society and John Wiley and Sons

'God Made the Bulk; Surfaces Were Invented by the Devil'

In this famous quote, Wolfgang Pauli referred to the complexity of the surface properties of materials. The development of ATRP enabled macromolecular engineering of designer polymers and their applications in many fields including, for example, nanotechnology. One major class of hybrid nanomaterials synthesized by ATRP are so-called polymer brushes. They are polymer chains anchored with one end to a given surface, either two-dimensional (e.g. planar substrates) or 3D (nanoparticles, proteins). The ability to functionalize surfaces by attaching macromolecules, and thus tune their properties, have made polymer brushes a very intensely investigated field in polymer science. Polymer brushes can be synthesized by two main approaches: grafting-to, where functionalized polymer chains are anchored to a surface; or grafting-from, where polymers are 'grown' directly from the initiator-functionalized surface (Figure 4a). [8] Both approaches have been used to prepare 'smart' surfaces from fluorescently-labelled polymers, namely polymethyl methacrylate (PMMA) synthesized by ATRP and functionalized at the chain end with a single fluorescein molecule. Interestingly, PMMA displays solvent-responsive properties, making these brushes collapsed and non-fluorescent in water, but stretched and emissive in water/alcohol mixtures (Figure 4b).

By employing inkjet printing, patterns consisting of specific functional molecules were prepared on glass slides. Then, using simple dip coating of these slides in a solution of the fluorescently-labelled PMMA, a selective deposition of polymer chains on the printed drops was achieved, resulting in ordered emissive molecular arrays at the surface (Figure 4c). [9]

Alternatively, PMMA brushes grafted from glass slides using surface-initiated ATRP and subjected to similar chain-end modification were used to demonstrate the responsive behaviour (Figure 4d). Upon exchanging the solvent from isopropanol/water (ON state) to pure water (OFF state), a clear change in emission was observed by fluorescent microscopy (Figure 4d). [10] Collapse of the brushes in water forced them to aggregate, quenching the fluorescence of the chain ends. Both studies show applicability of polymer brushes in the design of patterned, smart surfaces with potential applications such as sensors, or in organic electronics.

The Second Century

In the last two decades we have witnessed an immense progress in controlling the microstructure of polymers, driven mainly by the development of precision synthetic tools, such as ATRP. While not aiming at replacing traditional polymerizations in the production of commodities, these chemistries have enabled new applications by employing designer macromolecules. However, controlled polymerization techniques are still being improved to make them more environmentally friendly, oxygen-tolerant, easier to use and industry-relevant. Control

of the monomer sequence in synthetic polymers is still far from the level of sophistication achieved by nature but holds the promise of creating macromolecules with yet difficult to predict properties. With the growing need for advanced materials, we can be sure that precision polymerizations will be at the forefront of materials development when polymer science enters its second century.

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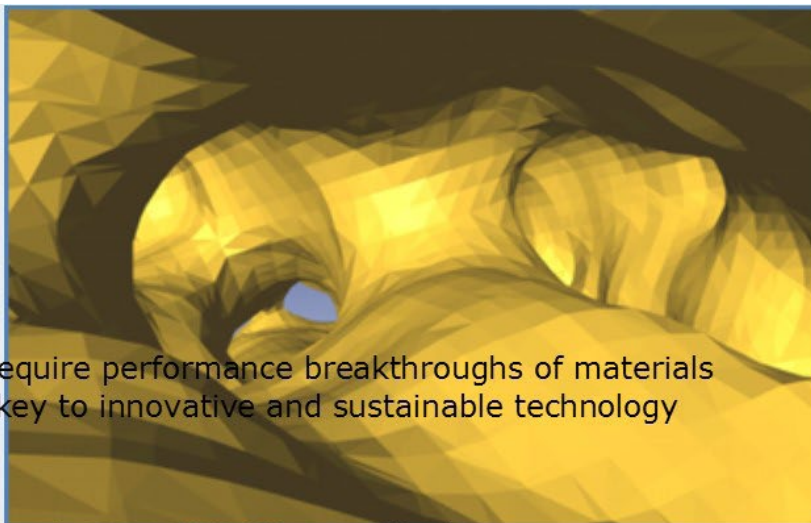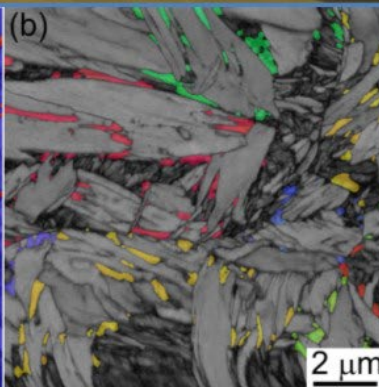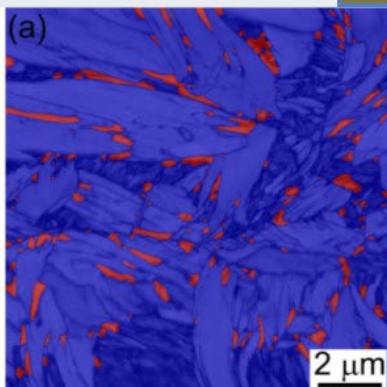
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