Chemistry has witnessed a remarkable transition in scales since the original discovery of the synthesis of urea in 1828 by Wöhler and that of Bakelite – a poly(phenol-formaldehyde) – in 1907 by Baekeland. Synthesis in the 19th and 20th century has mainly been focussed on the manipulation of individual chemical bonds using functional group transformations and a large variety of synthetic methods to prepare an almost unlimited number of complex (macro)molecules have been disclosed. At the end of the 20th century, chemistry witnessed the rise of supramolecular chemistry due to the seminal work on molecular recognition by Pedersen, Cram, and Lehn. Chemists learned to manipulate ensembles of molecules by the use of strong and directional non-covalent interactions, ultimately also leading to supramolecular polymers. These dynamic and living polymers represent a topic of increasing interest due to their enormous potential in a variety of applications.

Therefore, this special issue of the Australian Journal of Chemistry is focused on several aspects of supramolecular polymers. However, it escaped many scientists their attention that molecular polymerization via associative interactions between molecules was already proposed as an idea by Louis Henry in 1878\[1,2\]. It was at the same time that van der Waals proposed his famous equation of state that took intermolecular interactions in liquids into account and only 50 years after Berzelius coined his famous equation of state that took intermolecular interactions in liquids into account and only 50 years after Berzelius coined his famous equation of state that took intermolecular interactions in liquids into account. In 1907 by Baekeland. Synthesis in the 19th and 20th century has mainly been focussed on the manipulation of individual chemical bonds using functional group transformations and a large variety of synthetic methods to prepare an almost unlimited number of complex (macro)molecules have been disclosed. At the end of the 20th century, chemistry witnessed the rise of supramolecular chemistry due to the seminal work on molecular recognition by Pedersen, Cram, and Lehn. Chemists learned to manipulate ensembles of molecules by the use of strong and directional non-covalent interactions, ultimately also leading to supramolecular polymers. These dynamic and living polymers represent a topic of increasing interest due to their enormous potential in a variety of applications.

Today UPy-based polymers are marketed by e.g. SupraPolix and others, and they are produced at a 10 ton scale. Recently, also the self-healing properties of supramolecular polymers based on hydrogen bonding are receiving increasing attention. Besides hydrogen-bonding, chemists have used other non-covalent interactions such ionic and dipole-dipole interactions in creating one-dimensional supramolecular polymers from ditopic monomers.\[13\] Furthermore, supramolecular polymers based on shape-persistent monomers that self-assemble into ordered nanostructures and filaments are attracting considerable interest.

The formation of these ordered structures, however, often occurs via a different mechanism than the formation of supramolecular polymers from ditopic substituted monomers (vide infra).

The choice in mechanism of formation, the huge variety of self-assembling units and the stabilities of the structures formed, offer an enormous range of frequencies in the dynamic properties of these supramolecular polymers. This control yields unique processing capabilities of responsive materials, but also creates a modular approach to construct functional materials. Three major classes of functional supramolecular polymers can be discriminated (Fig. 1), where in recent years progress has been enormous: (1) functions based on excellent and unique mechanical properties with ease in processing due to the dynamic character of the bonding,\[11,12,14\] (2) electronic functions based on π-conjugated
repeating units leading to supramolecular electronics,[15] and (3) biomedical functions in regenerative medicine of biologically active supramolecular polymers.[16]

In spite of this success, in many cases the preparation of one-dimensional supramolecular polymers and nanostructures from their respective monomers is guided by serendipity as a complete understanding of the physical mechanisms of the self-assembly process is still lacking. In recent work, we have elaborated on the various growth mechanisms by which one-dimensional supramolecular polymers can grow.[17] For supramolecular polymers based on ditopic monomers and having intriguing mechanical properties, growth of the polymers occurs via an isodesmic mechanism and thermodynamically stable products are easily obtained. In contrast, the growth of shape-persistent monomers into ordered supramolecular polymers occurs in most cases via a nucleated or cooperative growth mechanism.[17d] Hence, kinetic factors and meta-stable traps can easily yield thermodynamically unstable materials. Although temperature dependent optical measurements are useful as a first diagnostic to establish whether a supramolecular polymerization occurs via a cooperative or nucleated or isodesmic growth mechanism, such equilibrium measurements fail to give any information on the nucleus size, or whether nucleation occurs via a homogeneous or heterogeneous pathway.[17d]

Based on the arguments above, an increasing number of kinetic studies on cooperative supramolecular polymerizations will be conducted in the years to come. Much can be learned from the field of protein assembly, notably the cooperative aggregation of shape-persistent amyloidal proteins, were kinetic studies[18] as a complete understanding of the physical mechanisms of the self-assembly process is still lacking. In recent work, we have elaborated on the various growth mechanisms by which one-dimensional supramolecular polymers can grow.[17] For supramolecular polymers based on ditopic monomers and having intriguing mechanical properties, growth of the polymers occurs via an isodesmic mechanism and thermodynamically stable products are easily obtained. In contrast, the growth of shape-persistent monomers into ordered supramolecular polymers occurs in most cases via a nucleated or cooperative growth mechanism.[17d] Hence, kinetic factors and meta-stable traps can easily yield thermodynamically unstable materials. Although temperature dependent optical measurements are useful as a first diagnostic to establish whether a supramolecular polymerization occurs via a cooperative or nucleated or isodesmic growth mechanism, such equilibrium measurements fail to give any information on the nucleus size, or whether nucleation occurs via a homogeneous or heterogeneous pathway.[17d]

In many areas of science, but supramolecular chemistry in particular, nature serves both as an inspiration and a challenge. It is tempting to compare one-dimensional supramolecular polymers with their natural counterparts: the cytoskeletal polymers such as actin and tubulin. However, in contrast to supramolecular polymers which are formed by self-assembly, the formation of cytoskeletal polymers occurs by self-organization via reaction-diffusion processes. As a result cytoskeletal structures display unique properties such as for example spatio-temporal synchronization between growing and shrinking individual cytoskeletal polymers. The design and characterization of artificial self-organizing supramolecular polymers will be a significant achievement in the years to come. In order to design these self-organizing supramolecular polymers, three goals will have to be met: (1) engineering of dissipative aspects to supramolecular polymerizations for example using light or chemical energy, (2) engineering of positive (autocatalytic) and negative (physico)chemical feedback cycles in the chemical self-assembly, and (3) understanding diffusion-driven instabilities in non-covalent systems. Although this seems a daunting task, a recent example in which inorganic self-organizing reactions are performed in a micro-heterogeneous medium has shown that even relatively simple chemistry can yield dynamic behaviour resembling that displayed by multicellular organisms.[20]

Although with some delay, the recognition of non-covalent forces as a tool to direct the ordering and function of molecules has now been widely acknowledged and respected. Currently supramolecular polymers are explored at the interface between chemistry, biology, physics, medicine, soft-condensed matter, and nanoscience. This multi-disciplinary approach will result in a better understanding of these systems through both experimental and theoretical studies, and undoubtedly will result in more innovative materials and new applications sought. During these advances, supramolecular materials will find their way into everyday life to enable technologies not previously possible.

References


