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Supramolecular Polymers: From Scientific Curiosity to Technological Reality

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Summary: Supramolecular polymers[1] are introduced as a new approach to come to materials in which the repeating units are not connected by covalent bonds but by specific secondary interactions. Self-complementary quadruple hydrogen bonded structures with high association constants are presented as easy to synthesize fragments in supramolecular polymers. Some of the many possibilities of equilibrium polymers are discussed, while it is shown that these supramolecular polymers can obtain materials properties normally only obtained with macromolecules.

Keyword: equilibrium polymers, hydrogen bonding, macromolecules, supramolecular polymers, ureidopyrimidinone units

Introduction[1]

Synthetic polymeric materials are amongst the most important classes of new materials introduced in the previous century. They are primarily used for construction purposes, but also electronic and biomedical applications are at the forefront of science and technology. It was only after the pioneering work of Staudinger, that it became evident that polymeric properties in both solution and solid state are the result of the macromolecular nature of the molecules. A large number of repeating units are covalently linked into a long chain and the entanglements of the macromolecular chains are responsible for many of the typical polymer properties.[2] Before macromolecules were generally accepted, the majority of scientists was convinced that polymer properties were the result of the colloidal aggregation of small molecules or particles.

The impressive recent progress in supramolecular chemistry,[3] paved the way to design polymers and polymeric materials that lack the macromolecular structure. Instead, highly directional secondary interactions are used to assemble the many repeating units into a polymer array.[4]

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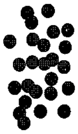
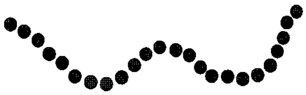
Polymers based on this concept hold promise as a unique class of novel materials, because they combine many of the attractive features of conventional polymers with properties that result from the reversibility of the bonds between monomeric units. Architectural and dynamic parameters that determine polymer properties, such as degree of polymerization, lifetime of the chain and its conformation are a function of the strength of the non-covalent interaction, which can reversibly be adjusted. This results in materials that are able to respond to external stimuli in a way that is not possible for traditional macromolecules.[1] These aspects of supramolecular polymers have led to a recent surge in attention for this promising class of compounds[5-7] and have stimulated our group to bring together materials science and supramolecular chemistry. The cartoon in Figure 1 shows the required directionality in the supramolecular interactions as compared with the historical and the current macromolecular view on polymers.



Colloidal Aggregate

Macromolecule



Supramolecular Polymer

Fig. 1. Supramolecular polymers as a redesign of the historical view of polymeric materials and compared to Staudinger's macromolecular concept.

The impressive recent progress in supramolecular chemistry,[8] paved the way to design polymers and polymeric materials that lack the macromolecular structure. Instead, highly directional secondary interactions are used to assemble the many repeating units into a polymer array.[9]

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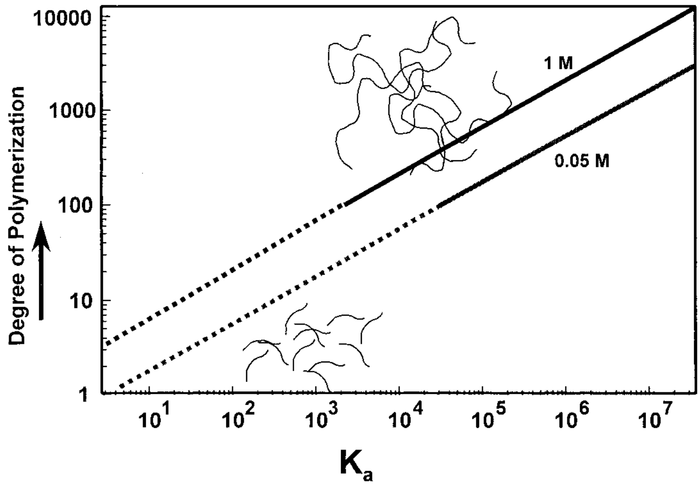

Fig. 2. A theoretical plot of the relation between association constant and degree of polymerization as a function of concentration of the bifunctional monomer using a simple isodesmic association function.

In supramolecular polymers, which are formed by the reversible association of bifunctional monomers, the average degree of polymerization (DP) is determined by the strength of the end group interaction.[13] The degree of polymerization is obviously dependent on the concentration of the solution and the association constant and a theoretical relationship is given in Figure 2. To obtain polymers with a high molecular weight, a high association constant between the repeating units is a prerequisite. In analogy with covalent condensation polymers, the chain length of supramolecular polymers can be tuned by the addition of monofunctional "chain stoppers".[14] This also implies that impurities containing only one function will have a strong influence on the maximal DP, since they will act as chain stopper. Hence, as in traditional polymer synthesis, the purification of the monomers is extremely important to obtain high molecular weights.

What Defines a Supramolecular Polymer?

The term *supramolecular polymer* is rather popular and used for a variety of different structures, utilizing secondary (or supramolecular) interactions between chains or for the construction of polymer chains. In the following definition, the polymers that have secondary interactions between macromolecular chains only, are ignored, since all polymers possess either hydrogen bonding (nylons), dipole-dipole (polyesters) or London-dispersion interactions (polyethylene), that determine their materials properties. Hence, supramolecular polymers are defined as those polymers that are made out of repeating units held together by other bonds than just covalent bonds. In these supramolecular polymers, however, there is a strong interplay between intra- and interchain interactions and the cooperativity between the two has a large impact in overall strength of the bonding as well as in the ultimate properties (comparable to the cooperativity between the hydrogen bonding and base-pair stacking in DNA). In order to make a rather stable individual supramolecular polymer chain, the bonding within the chain should be significantly stronger than the interactions between the chains. If this requirement is not included in the definition, many structures that lack a covalent architecture can be called polymers. This is nicely demonstrated by looking at terephthalic acid; in its crystalline form the molecules are connected in a long chain by the dimerization of the carboxylic acids by hydrogen bonding. However, upon melting or dissolution these chains are disrupted, due to the lack of strength of the acid dimer under these conditions. Furthermore, it is evident that such crystals do not exhibit any useful polymeric materials properties and the supramolecular structure formed is not only the result of the hydrogen bond dimerization but also due to crystal packing. Many other examples of this kind can be found in the recent literature.

Consequently, the balance between strong unidirectional association and uncontrolled multidirectional association (or gelation) is one of the major aspects in the design of supramolecular polymers. There are three main categories of supramolecular polymers: coordination polymers, polymers using π-π interactions, and hydrogen-bonded polymers (see Figure 3). However, only the latter are able to yield polymeric materials with a large variety of interesting bulk properties, because of their general flexibility to tune the strength of the bonding by external stimuli. As a result of this progress in supramolecular polymers, it has been stated recently that "polymer chemistry comes full circle".[3]

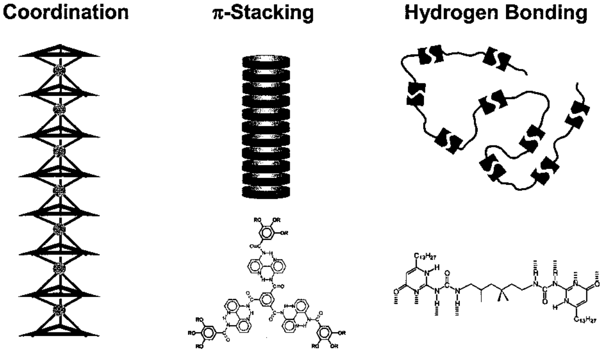
Coordination **π-Stacking** **Hydrogen Bonding**

Fig. 3. The three main categories of making polymers without covalent bonding between the repeating units, as subdivided on the type of secondary interaction.

Supramolecular Polymers Based on Hydrogen Bonding[15]

Although hydrogen bonds between neutral organic molecules are not among the strongest non-covalent interactions, they hold a prominent place in supramolecular chemistry due to their directionality and versatility.[16-18] The relationship between the degree of polymerization and the strength of the non-covalent interaction between monomers in a supramolecular polymer (see Figure 2) implies that multiple hydrogen bonds with a high association constant are required to obtain significant degrees of polymerization.

Combining several hydrogen bonds in a functional unit is a valuable tool to increase the strength of this interaction. Moreover, employing a particular arrangement of the hydrogen bonding sites enhances its specificity. The strength of single hydrogen bonds basically depends on the nature of donor and acceptor, although it is influenced to a large extent by the solvent. Association strength between multiple hydrogen bonding units obviously depends on the same factors, as well as on the number of hydrogen bonds. It has also been shown that the particular arrangement of neighboring donor and acceptor sites is an additional factor, which significantly affects the strength of the complexation. This phenomenon was first recognized for the association of linear arrays of 3 hydrogen bonding sites: whereas complexes between the common ADA-DAD motif exhibits an association constant of around 10^2 M^{-1} in chloroform, this value is around 10^4 M^{-1} in complexes with a DAA-DDA motif, while AAA and DDD arrays exhibit association constants exceeding 10^5 M^{-1}. Detailed calculations by Jorgenson[19,20] showed that this effect is due to differences in secondary interactions between these motifs. In the complexes, diagonally opposed sites repel each other electrostatically when they are of the same kind (both donor or both acceptor), while disparate sites attract each other. In the DDD-AAA motif the number of attractive secondary interactions is maximized, while in the ADA-DAD motif the number of repulsive interactions is at its largest.

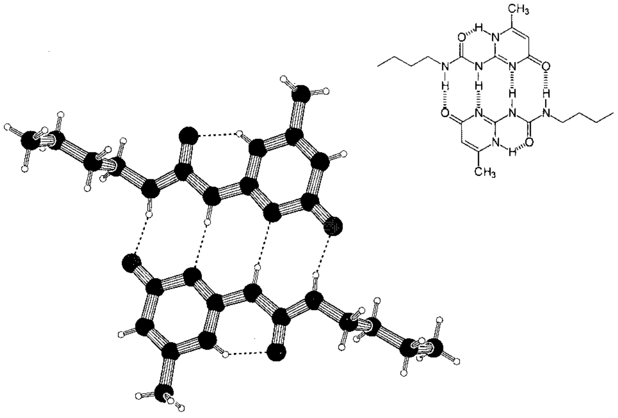

Fig. 4. X-ray structure showing the H-bonding pattern between two ureidopyrimidinone units.

Very stable complexes can be obtained when quadruple hydrogen bonding units are employed.[21-25] Aspects of multiple hydrogen bonding units that are of special importance with respect to application in supramolecular polymers are the self-complementarity of DADA and DDAA arrays, and the possibility of tautomerism. The latter may lead to loss of complexation when complementarity is lost, or when a DDAA array tautomerizes to a DADA array with a higher number of repulsive secondary interactions. We have reported on self-complementary quadruple

H-bonding units based on mono-ureido derivatives of diamino-triazines[24] (DADA-array) with a dimerization constant of $K_{\mathrm{dim}} = 2\times10^4\ \mathrm{M}^{-1}$ and hydrogen bonding units based on 2-ureido-4[1H]-pyrimidinones (DDAA, see Figure 4), that dimerize in chloroform with an association constant of $K_{\mathrm{dim}}=6\times10^7\ \mathrm{M}^{-1}$.[25,26]

Application of hydrogen bonding units as associating end-groups in difunctional or multifunctional molecules results in the formation of supramolecular polymers with varying degrees of polymerization (DP). The early examples of hydrogen bonded supramolecular polymers rely on units, that associate using single, double or triple hydrogen bonds all having association constants below $10^3\ \mathrm{M}^{-1}$. In isotropic solutions, the DP of these polymers is expected to be low. The development of the ureidopyrimidinone functionality (UPy), a synthetically very accessible quadruple hydrogen bonding unit with a very high association constant, has helped enormously to open the way for the exploration of all aspects of supramolecular polymers.

The ureidopyrimidinone unit can be made in a one-step procedure from commercially available compounds,[24,26] and dimerizes with an association constant of $6 \times 10^7\ \mathrm{M}^{-1}$ in $CDCl_3$. Difunctional compound (7), possessing two of these ureidopyrimidinone units forms a stable and long polymer chain in solution as well as in the bulk (Figure 5).[27,28]

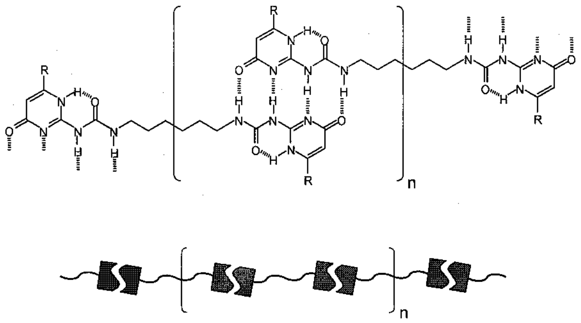

Fig. 5. Polymeric assembly of a bifunctional ureidopyrimidinone derivative.

Dissolving a small amount of this low molecular weight compound in chloroform, results in solutions with a high viscosity. It can be calculated that polymers with chain lengths of the order of 10^6 Dalton can be formed when highly purified monomers are used. The presence of monofunctional impurities is expected to lead to a dramatic reduction in DP, because they will act as "chain stoppers". In fact, deliberate addition of small amounts of monofunctional compounds results in a sharp drop in viscosity, proving the reversibility and unidirectionality of association. The reversibility of the linkages between the building blocks is instrumental in the development of materials that change their properties in response to environmental changes, so called 'smart materials'. Application of a light sensitive monofunctional compound yielded a material from which the degree of polymerization in solution could be tuned by UV-irradiation.[29]

Although the supramolecular polymers based on bifunctional ureidopyrimidinone derivatives in many ways behave like conventional polymers, the strong temperature dependence of their mechanical properties really sets them apart from macromolecular polymers. At room temperature, the supramolecular polymers show polymer-like viscoelastic behavior in bulk and solution, whereas at elevated temperatures liquid-like properties are observed. These changes are due to a three-fold effect of temperature on the reversible polymer chain. Due to the temperature dependence of the K_a value of UPy association, the average DP of the chains is drastically reduced at elevated temperatures. Simultaneously, faster dynamics of the scission-recombination process leads to faster stress relaxation in an entangled system. These two effects occur in addition to the temperature dependent stress relaxation processes that are also operative in melts or solutions of conventional polymers.

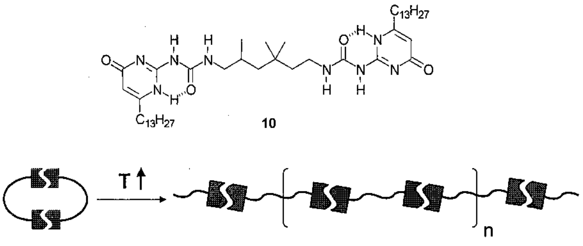

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Fig. 6. Entropy driven ring-opening polymerization of the cyclic dimer of **10**.

Similar to the behavior in the melt, solution viscosities of UPy-based supramolecular polymers are also strongly temperature dependent. Recently a very surprising inversion of the normal temperature dependence of the solution viscosity was observed in solutions of preorganized difunctional compounds (**10**), which form a mixture of linear polymer chains and cyclic dimers (Figure 6).[30] The thermodynamic parameters of this equilibrium are such that polymerization is favored at higher temperatures. As a result, the viscosity of a 145 mM chloroform solution of the compound was observed to increase by a factor of 3.9 when the temperature was increased from 255 to 323 K. Entropy-driven polymerizations are rare, and the unexpected effect in this system is the first time it was observed in a reversible synthetic system.

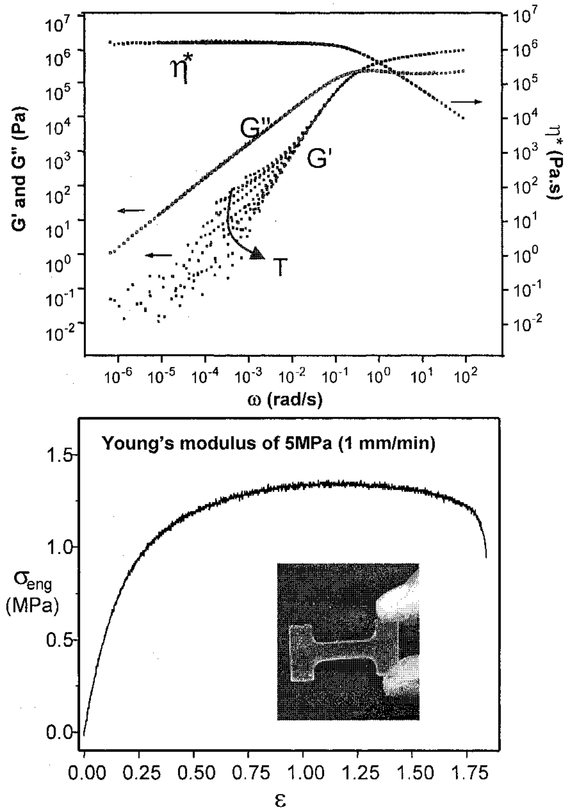

Fig. 7. Mechanical spectra of the supramolecular polymer based on a poly(ethylene/butylene). Top: master curves of the storage (G') and loss modulus (G'') are obtained by the superposition of curves obtained at different temperatures, with 40 °C as a reference temperature; the complex viscosity (η^*) versus frequency is given as well. Bottom: stress-strain measurement revealing the soft-rubberlike behavior.

The quadruple hydrogen bonded unit has been further employed in the chain extension of telechelic polysiloxanes,[31] poly(ethylene/butylenes), polyethers, polyesters and polycarbonates.[32] In these compounds, the material properties were shown to improve dramatically upon functionalization, and materials were obtained that combine many of the mechanical properties of conventional macromolecules with the low melt viscosity of organic compounds (Figure 7). Consequently, in this strategy the gap is closed between polymers and oligomers using the best of both worlds. Especially in the field of conjugated polymers for plastic electronic devices, expectations for future applications of this strategy are high.[33] Recently, Coates et al. used a vinyl-substituted UPy-unit to be part of an olefin polymerization using the Brookhart catalyst. With small amounts of UPy-units incorporated, the polyolefins showed thermoplastic elastomeric properties.[34]

The reversibility of supramolecular polymers adds new aspects to many of the principles that are known from condensation polymerizations. For example, a mixture of different supramolecular monomers will yield copolymers, but it is extremely simple to adjust the copolymer composition instantaneously by adding an additional monomer. Moreover, the use of monomers with a functionality of three or more, will give rise to network formation. However, in contrast to condensation networks, the 'self-healing' supramolecular network can reassemble to form the thermodynamically most favorable state, thus forming denser networks.[35]

Although the 'virtual' molecular weight and lifetime of supramolecular polymers and networks based on strong hydrogen bonding functionalities is extremely high, low creep resistance is an intrinsic property of these materials. Strong inter-chain interactions, especially in crystalline domains can be employed to reduce creep, leading to thermoplastic elastomers with enhanced processability. With the facile synthetic accessibility of these self-complementary UPy-units at hand, it is expected that many novel material properties can be obtained.

Conclusions and Outlook

Ten years ago, the first supramolecular polymers were seen a scientific curiosities. Nowadays, this field of research is generating several technologically important applications. Progress in supramolecular chemistry has made it possible to assemble small molecules into polymer arrays, and the created structures possess many of the well-known properties of "traditional" macromolecules. Due to the reversibility in the bonding, these supramolecular polymers are under thermodynamic equilibrium and their properties can be adjusted by external stimuli. Hydrogen bonded systems have shown to become of technological relevance and surpass the state of being scientific curiosities only. A large variety of applications are feasible, especially since the chosen approach can also be used for the modification of telechelic oligomers or to modify existing polymers. Moreover, the possibility to tune the properties by changing the relative ratio of UPy-monomer in the copolymer feed seems very attractive, while hybrids between blocks of macromolecules and supramolecular polymers are easy to prepare. Therefore, novel thermoplastic elastomers, superglues, hotmelts and tunable polymeric materials are within reach (Figure 8).

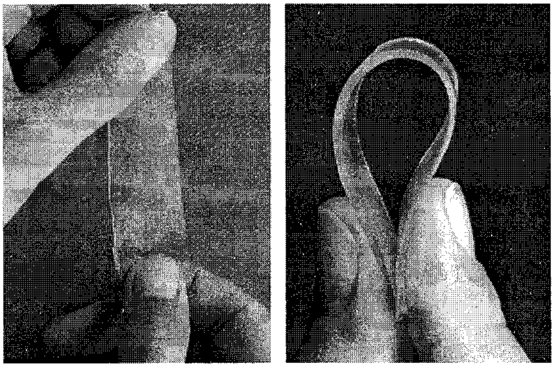

Fig. 8. Supramolecular polymer materials created with the ureidopyrimidone unit.

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