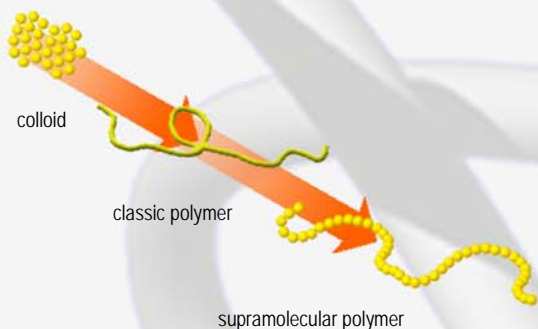




SupraPolix BV

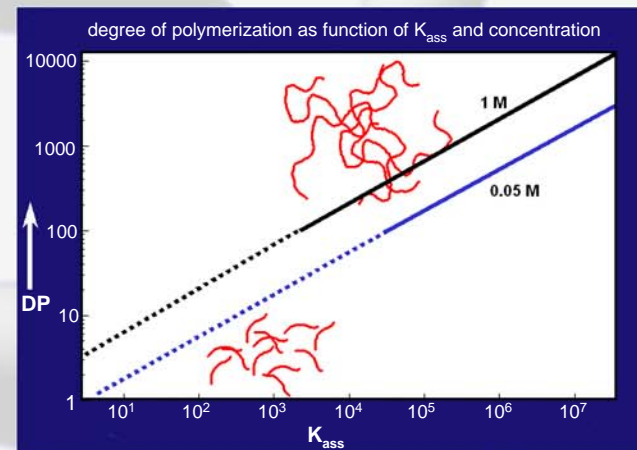
SupraPolix offers a new concept in the world of plastics by separating the processability demands from the material demands: incorporation of already a small amount of our product *SupraB*[®] in existing plastics makes it possible to use polymers of much lower molecular weights, resulting in favorable processing when desired. As a result, full exploitation of all the material properties of existing plastics is possible, deepening their use in many applications ranging from adhesives to biomaterials in which ease of processing is of utmost importance. This pamphlet gives a short overview of the scientific base of *SupraPolix* that has its origin in the group of Bert Meijer and Rint Sijbesma at the University of Technology in Eindhoven, the Netherlands.



Introduction to SupraMolecular Polymers

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. Before macromolecules were generally accepted, the majority of scientists were convinced that polymer properties were the result of the colloidal aggregation of small molecules or particles. It was only after the pioneering work of Staudinger (*Die Hochmolekulare Organische Verbindungen*, Springer, Berlin, 1932), 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. The impressive recent progress in supramolecular chemistry, 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. 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 the reversibility originating from the secondary interactions. Consequently, architectural and dynamic parameters that determine polymer properties, such as degree of polymerization, lifetime of the chain and its conformation, can reversibly be adjusted, resulting in unique materials that are able to respond to external stimuli. These aspects of supramolecular polymers have led to a recent surge in attention for this promising class of compounds and have stimulated the Meijer-group to bring together materials science and supramolecular chemistry. The cartoon on top shows the required directionality in the supramolecular interactions as compared with the historical and the current macromolecular view on polymers.

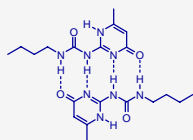


What defines a SupraMolecular polymer?

The term *supramolecular polymer* is rather popular and is used for a variety of different structures, utilizing secondary (or supramolecular) interactions between chains or for the construction of polymer chains. Hence, supramolecular polymers are defined as those polymeric materials 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. 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. 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.

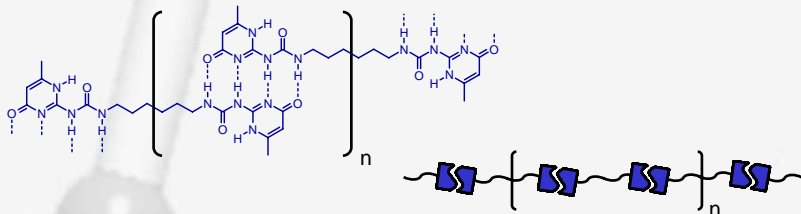
In supramolecular polymers, which are formed by the reversible association of bifunctional monomers, the average degree of polymerization (DP) is determined by the strength of the end group interaction and the concentration of the solution. To obtain polymers with a high molecular weight, a high association 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".



The strength of hydrogen bonds

Hydrogen bonds hold a prominent place in supramolecular chemistry due to their directionality and versatility, although hydrogen bonds are not among the strongest non-covalent interactions. Cooperativity holds the answer to this problem, and consequently several systems have been designed that combine multiple hydrogen bonds in a row. Indeed, this increases the strength of the interaction, and moreover, enhances its specificity. Very stable complexes can be obtained when quadruple hydrogen bonding units are employed. Therefore, it was not until the development of the quadruple hydrogen bond unit by Meijer and Sijbesma, that H-bonding systems were developed with high enough association constants to allow the formation of supramolecular polymers with

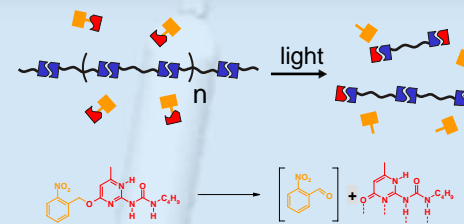
significant degrees of polymerization. These self-complementary quadruple H-bonding units based on 2-ureido-4[1H]-pyrimidinone dimerize in toluene with an association constant of $K_{dim}=6 \cdot 10^8 \text{ M}^{-1}$ and a lifetime of 1.7 s. Application of these hydrogen bonding units as associating end-groups in difunctional or multifunctional molecules resulted in the formation of supramolecular polymers with high degrees of polymerization (DP). 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.



SupraMolecular Ureidopyrimidinone-based polymers

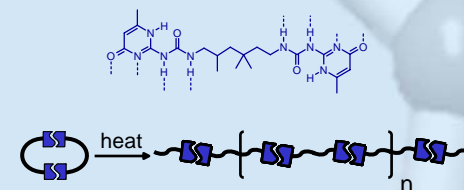
The difunctional ureidopyrimidinone compound shown above can easily be made in a one-step procedure from commercially available compounds (hexyldiisocyanate and methylisocytosine). The high association constant of the UPy's combined with the difunctional nature of this compound, results in the formation of a stable and long polymer chain in solution as well as in the bulk. Dissolving a small amount of this low molecular weight compound in chloroform, gives solutions with high viscosities. 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. 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.



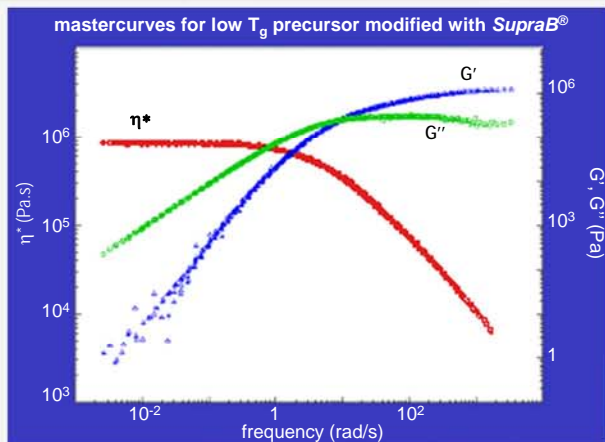
SupraMolecular smart material

The presence of monofunctional impurities is expected to lead to a dramatic reduction in the DP of supramolecular polymers, 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, as is shown in this cartoon.



SupraMolecular ROP

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 compound shown above, which forms a mixture of linear polymer chains and cyclic dimers. 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.



SupraMolecular materials

The quadruple hydrogen bonded unit has been further employed in the chain extension of telechelic polysiloxanes, poly(ethylene/butylenes), polyethers, polyesters and polycarbonates. In these compounds, the material properties were shown to improve dramatically upon functionalization, resulting in materials that combine many of the mechanical properties of conventional macromolecules with the low melt viscosity of organic compounds. This is not only obvious from their physical appearances as reflected in these pictures but was also eminent from their visco-elastic behavior as evidenced with rheological experiments.



Conclusions and outlook

Ten years ago, the first supra-molecular polymers were seen as scientific curiosities. Nowadays, this field of research is generating several technologically important applications. Progress in supra-molecular 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 supra-molecular polymers are under thermodynamic equilibrium and their properties can be adjusted by external stimuli. 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’ supra-molecular network can

reassemble to form the thermodynamically most favorable state, thus forming denser networks. Hydrogen bonded systems have shown to become of technological relevance and have surpassed the state of being scientific curiosities only. A large variety of applications is feasible, especially since the chosen approach can also be used for the modification of existing polymers by post-modification or changing the monomer feed. This generates the possibility to tune the properties by changing the relative ratio of UPy-monomer in the copolymer feed or the possibility to make new hybrids between blocks of macromolecules and supra-molecular polymers. Therefore, novel thermoplastic elastomers, superglues, hot-melts and tunable polymeric materials are within reach.



SupraMolecular electronics

The field of plastic electronics is rapidly expanding in a wide range of daily-life applications. A critical issue in all these applications is the high definition of the conducting polymer, which basically is only attainable for oligomeric species. Supra-molecular polymers can hold the answer to this problem by closing the gap between polymers and oligomers using the best of both worlds: the well-defined character of π -conjugated oligomers combined with the material properties of (supra-molecular) polymers.

Acknowledgments

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