Self-Complementary Quadruple Hydrogen-Bonding Motifs as a Functional Principle: From Dimeric Supramolecules to Supramolecular Polymers

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The self-association of individual molecules can lead to the formation of highly complex and fascinating supramolecular aggregates. However, for binding motifs which rely only on hydrogen bonds, a combination of several such weak interactions is necessary to observe self-association in solution. Systems based on four hydrogen bonds in a linear array can be obtained which efficiently aggregate at least in chloroform. Besides the physical-organic characterization of these aggregates and the factors influencing their stability, such quadruple hydrogen-bonding motifs can also be used in the field of materials science to synthesize, for the first time, supramolecular polymers through the self-association of self-complementary monomers. As the formation of noncovalent interactions is reversible and their strength depends significantly on the chemical environment (for example, solvent, temperature), the macroscopic properties of such polymers can be controlled by variation of these parameters; hence a first step towards intelligent materials with tailor-made properties is made.

1. Introduction

Hydrogen bonds[1] play an important role in determining the three-dimensional structure of chemical and biological systems[2] as a consequence of their specificity and directionality. The formation of one or multiple hydrogen bonds, especially in combination with other noncovalent forces, such as ionic or hydrophobic interactions, can lead to a dramatic change in the micro- and macroscopic properties of the resulting supramolecular assemblies.[3] In contrast to covalent bonds, which once formed are stable under normal conditions and can only be broken by providing sufficient energy, the formation of hydrogen bonds is reversible and their strength depends on the chemical environment, such as the solvent or temperature. Through a variation of the external parameters, this reversibility allows for the direct control of those physical properties of supramolecular assemblies[4] which are determined by the hydrogen bonds. The main drawback of hydrogen bonds is their limited strength; the more polar the solvent is, the weaker the hydrogen bonds are because of the increasing competitive solvation of donor and acceptor sites by solvent molecules.[5] Therefore, a single hydrogen bond possesses a considerable binding energy only in unpolar, aprotic solvents (hexane, toluene). However, stable supramolecular assemblies can also be obtained in more polar solvents, such as chloroform or acetonitrile, by a combination of several such weak interactions in binding motifs with multiple hydrogen bonds.[6]

Besides the well-known self-association of molecules with a centrosymmetric AD–DA array of hydrogen-bonding donor (D) and acceptor (A) sites, triple hydrogen-bonding motifs have been studied extensively in the past by the research groups of Whitesides,[7] Zimmermann,[8] and Meijer.[9] Association processes of such triple hydrogen-bonding motifs can only be used for heterodimerization, which requires the synthesis of two different, and yet complementary, molecules. Hence, in recent years research has focused on the exploration of quadruple hydrogen-bonding motifs, which in addition to several arrays that lead only to heterodimerization[10] also give rise to two arrays capable of homodimerization: the ADAD–DADA and AADD–DDAA array.[8] The additional hydrogen bond should also lead to an increased stability of such self-assembled dimers relative to those formed from the triple hydrogen-bonding motifs.[11]

2. The ADAD Binding Motif

Meijer and co-workers were among the first to synthesize self-complementary quadruple hydrogen-bonding motifs with an ADAD array by acylation of diaminotriazines and diaminopyrimidines (Scheme 1).[12] Crystal structure determination of these compounds confirmed the existence of centrosymmetric dimers with the expected ADAD–DADA binding motif. These compounds exhibited pronounced self-association even when dissolved in chloroform. The quantitative determination of the corresponding binding constants for these dimerizations were possible by following the

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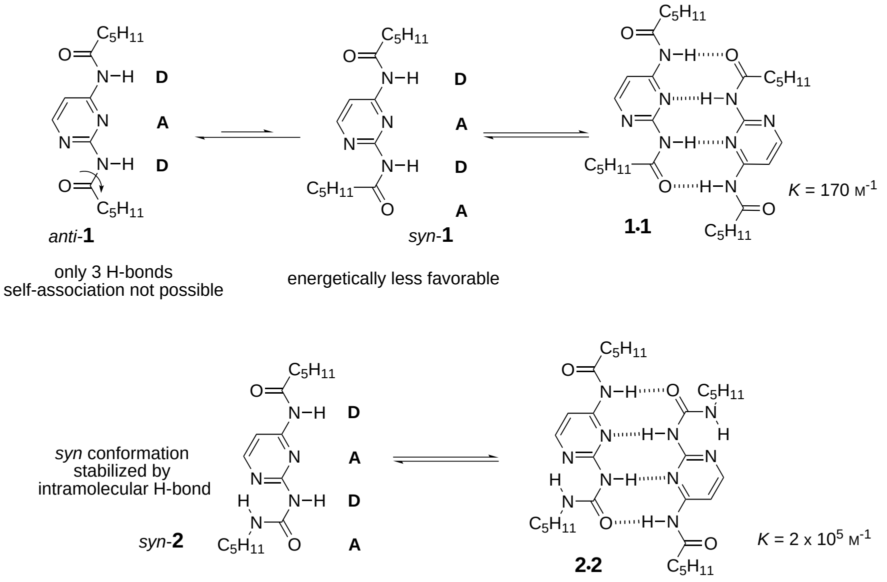
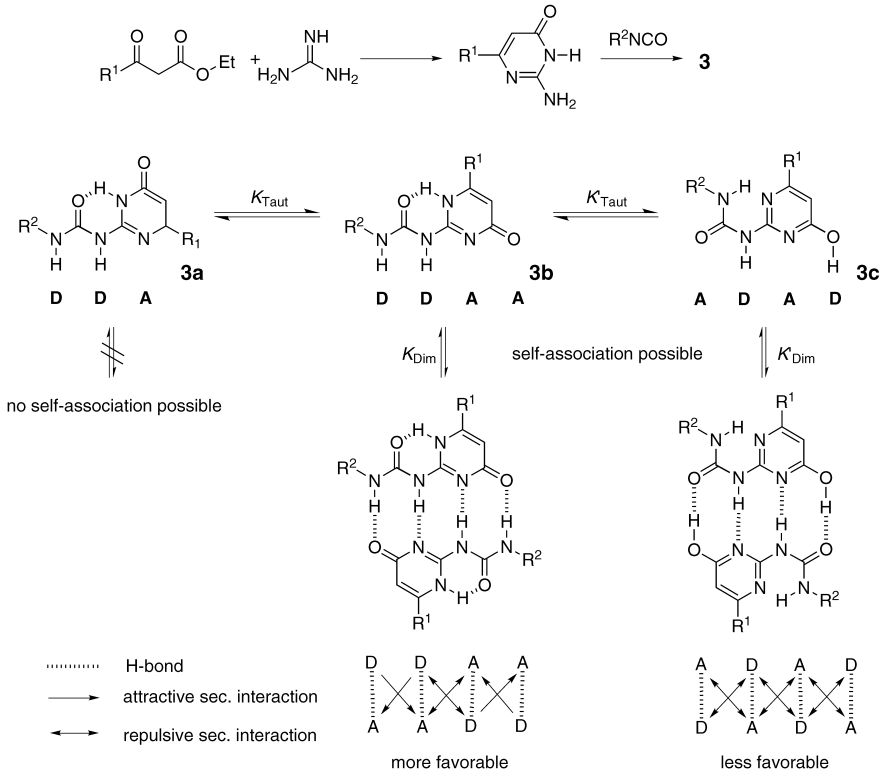


Scheme 1. Diacylpyrimidine **1** and ureidoacylpyrimidine **2** as ADAD bonding motifs according to Meijer and co-workers.

complexation-induced downfield shifts of the NH protons in the ^{1}H NMR spectra, or the shift of the NH stretching frequence to lower wave numbers in the IR spectra.[13] These data showed that the new quadruple hydrogen-bonding motifs have association constants of up to $10^5\,\text{M}^{-1}$ in $CDCl_3$ and are, therefore, indeed more stable than the previously studied DAD–ADA hydrogen-bonding arrays ($K \approx 10^2 - 10^3\,\text{M}^{-1}$).[8] It was also shown that the conformational flexibility of the molecules has a significant impact on the stability of the aggregates; self-association can only occur if all the hydrogen-bonding donor and acceptor sites are arranged in a linear way and point in the same direction, thereby presenting the necessary ADAD "face" (Scheme 1). This requires a *syn* orientation of the amide groups in the heterocyclic systems developed by Meijer and co-workers. Hence, in the case of the monoacylated derivatives **1** the molecules must first undergo an energetically costly conformational change from the more stable *anti* orientation, which can not dimerize, to the less stable *syn* conformation[14] before self-association can take place. The overall binding energy for the dimerization is, therefore, reduced by the energy which has to be paid for this conformational change. The *syn* conformation of the amide bond in the urea derivatives **2** is already stabilized in the individual molecules by an intramolecular hydrogen bond between the outer ureido NH and the heterocyclic nitrogen atom. This preorganization of the molecule means that dimerization can take place without any prior conformational changes. Therefore, the resulting binding energy is substantially higher in **2**.



Scheme 2. Synthesis of 2-ureido-4-pyrimidones **3** (top) and the tautomeric and association equilibria observed in solution (bottom).

3. The AADD Binding Motif

Even more efficient self-assembling quadruple hydrogen-bonding motifs should result from an AADD–DDAA array of donor and acceptor sites according to Jørgensen and co-workers.[15] This proposal can be explained by so-called secondary electrostatic interactions which, in addition to the primary hydrogen bonds, influence the complex stability. Partial negative charges, such as carbonyl oxygen atoms, are electrostatically repulsed by nearby similar negative charges, whereas positive charges, such as amide protons, in proximity have a stabilizing effect. There are thus six repulsive secondary interactions in the ADAD–DADA array besides the four primary hydrogen bonds. However, there are only two such destabilizing interactions in the AADD–DDAA array, but four additional attractive secondary electrostatic interactions. One can thus expect a higher association constant for the AADD–DDAA array relative to the ADAD–DADA one (Scheme 2).

Meijer and co-workers were indeed able to design molecules with such an AADD binding motif based on easily accessible 2-ureido-4-pyrimidones **3** (Scheme 2).[16] Unfortunately, the self-association is complicated by the occurrence of a complex equilibrium of tautomeric forms: the ureidopyrimidones can exist in two different lactam forms (**3a** and **3b**) and one aromatic 4-pyrimidinol form (**3c**), of which the 6[1H]-pyrimidone tautomer **3a** is the most stable one. As a consequence of the different arrangements of donor and acceptor sites in these tautomers only the 4[1H]-pyrimidone **3b** and the pyrimidinol **3c** can form self-assembled dimers: In the case of the 4[1H]-pyrimidones **3b** these dimers possess the desired AADD–DDAA binding motif, whereas the pyrimidinols **3c** exhibit a less stable DADA–ADAD array. It was shown by elaborated NMR studies that a complex mixture of all three possible tautomers exists in solution and that the equilibrium composition is determined by the polarity of the solvent, the concentration of the compound, and any substituent present in the 6-position of the pyrimidine ring. Although the 1:1 stochiometry of the dimers and the quadruple hydrogen-bonding motifs with the DDAA–AADD and ADAD–DADA arrays were established by X-ray crystallography of several compounds in this series, quantitative analysis of the association constants was not possible in $CDCl_3$ because the binding constants were too high for a direct determination by ^1H NMR dilution studies. Meijer and co-workers could only estimate a lower limit for the dimerization of the ADAD–pyrimidinol motif **3c** of $K \approx 10^5\,\text{M}^{-1}$ and for the AADD–pyrimidone motif **3b** of $K \approx 10^6\,\text{M}^{-1}$.[16]

The research group of Meijer chose an indirect method, excimer fluorescence spectroscopy[17] for an experimental determination of the actual association constants. Fluorophoric pyrene groups were attached through an aliphatic linker to the external urea nitrogen atoms of suitable 6-alkyl-substituted pyrimidones which exclusively exist in the tautomeric form **3b**. Dimerization of these ureidopyrimidones results in the formation of excimer homodimers between the two pyrene fluorophors with a significantly red-shifted emission wavelength ($\lambda_{max} = 478$ nm) relative to an isolated pyrene ($\lambda_{max} = 372-399$ nm). The intensity of this new fluorescence emission band at 478 nm can, therefore, be used as an indicator for the extent of dimer formation (Figure 1). As pyrene is strongly fluorescent, this method requires much smaller concentrations than those needed for an NMR dilution experiment. From these data Meijer and co-workers could extract a dimerization constant for the AADD array in **3b** of $K = 6 \times 10^7\,\text{M}^{-1}$, which is significantly higher than the lower limit estimated from the previous NMR studies. A similar value of $K = 10^7\,\text{M}^{-1}$ was determined by Corbin and Zimmermann for their recently developed AADD binding motif **4**.[18] In contrast to the ureidopyrimidones **3** of Meijer and co-workers, dimerization in this case is not hampered by a tautomeric equilibrium, as all the possible tautomers of **4** possess the same AADD array of hydrogen-bonding donor and acceptor sites and are therefore capable of self-association.[19]

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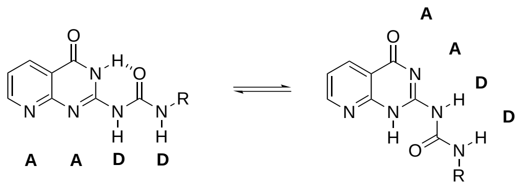


4. Linear Supramolecular Polymers

The extremely efficient self-association of such AADD binding motifs in chloroform now allows for the direct control of the macroscopic physical properties of large supramolecular assemblies.[20] The attachment of more than one such binding motif to oligomer or polymer chains enables new applications in the field of polymer chemistry and material science to emerge. There will again be an extensive self-association of two binding motifs of such “Janus” molecules in chloroform solutions. These binding motifs will not only result in a dimerization but also in a supramolecular linear polymerization, a sort of “supra-polymerization” (Scheme 3).[21] In contrast to conventional polymers, in which the macromolecular chains consist of covalently and hence irreversibly connected monomer units, here supramolecular polymers are obtained which only demonstrate their polymeric properties by the self-association of the corresponding binding motifs.[4, 22, 23] The use of weak and reversible hydrogen bonds to connect different monomer units also provides the first step towards “intelligent”, tailor-made polymers. The strength of the interaction between the various monomer units depends on external parameters and can, therefore, be changed by variation of the solvent, pH value, or temperature.

The first reversible polymer based on this principle was obtained by Meijer et al. through the self-association of a bifunctional molecule **5**, in which two ureidopyrimidone binding motifs were covalently linked through an alkyl chain (Scheme 4).[24] Compound **5** shows an association number of more than 500 in chloroform.[25, 26]

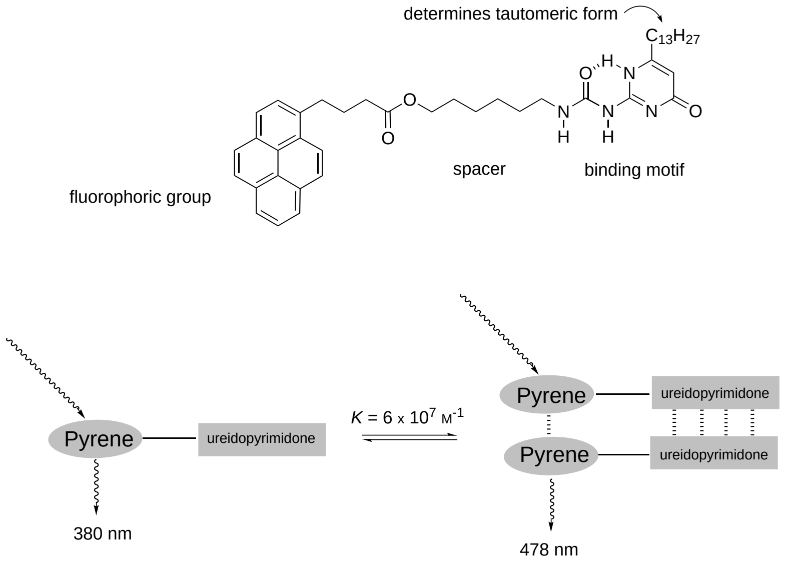
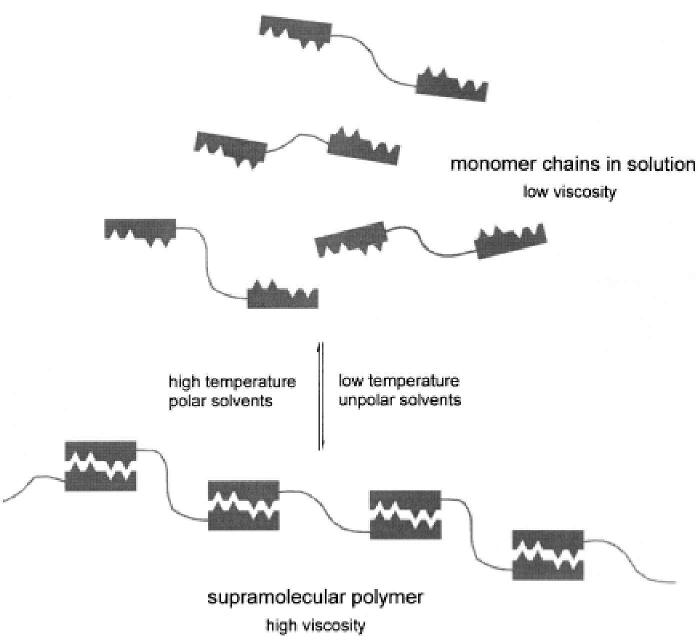
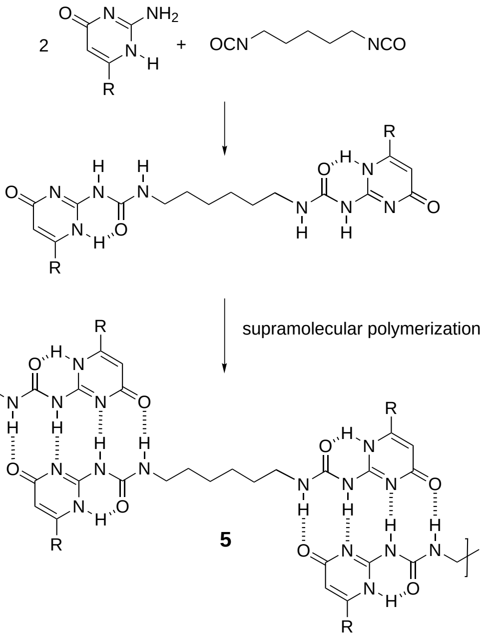


Figure 1. Determination of the dimerization constant for compounds of type **3** by using excimer fluorescence spectroscopy of a pyrene derivative.



Scheme 3. Supra-polymerization of bifunctional “Janus” molecules.



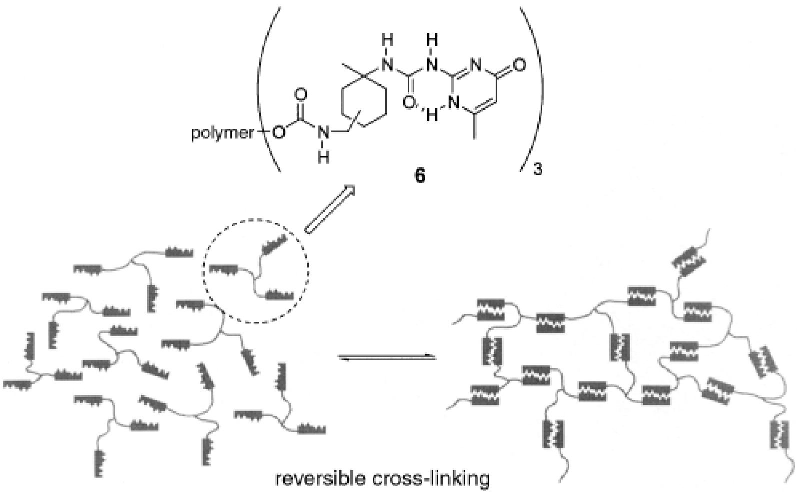
Scheme 4. Synthesis of the first supramolecular homopolymer **5**.

Such solutions are highly viscous and display all the properties of a classical polymer. Noteworthy, however, as this is not found in a conventional polymer, is the strong concentration and temperature dependance of the viscosity. This observation can be explained by the effect of temperature on the strength of the hydrogen bonds between two ureidopyrimidone binding motifs connecting two different chains. The hydrogen bonds are first weakened by increased thermal motion and are finally broken, hence at higher temperatures the material eventually displays only those properties related to the individual monomer units and the solution becomes more fluid and less viscous. The polymeric properties are again restored on decreasing the temperature. Similar effects are observed by the addition of a polar, protic solvent, which also disrupts the hydrogen bonds; the addition of small amounts of trifluoroacetic acid causes a dramatic decrease in the viscosity of the solution.

5. Noncovalently Cross-Linked Polymers

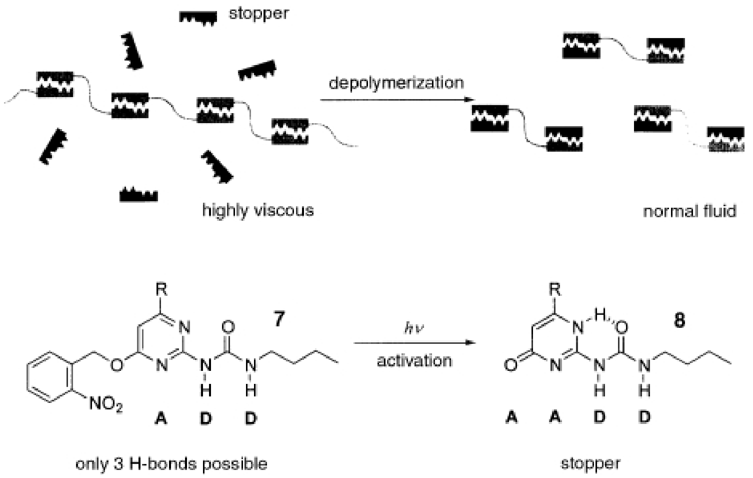
Of course, more than two self-complementary ureidopyrimidone units can also be incorporated into a single molecule. This gives rise to supramolecular 3D networks of type **6** (Scheme 5), which can exhibit completely new properties compared to conventional cross-linked polymers. These materials change with an increasing number of cross-links from a viscous liquid to an elastic solid. The structural composition of covalently cross-linked polymers is normally not precisely defined. The number of cross-links—which is an important parameter for the materials properties—can only be approximately controlled by variation of the polymerization conditions (for example, catalyst concentration, additives).[27] Once formed, the cross-links are irreversible. This situation leads to the trapping of a kinetic polymerization state. The material often contains structural defects such as unreacted functional groups which have an undesired influence on the material properties. This problem does not exist with noncovalently cross-linked polymers. As hydrogen bonds continously dissociate and reform, such a polymer is always close to its thermodynamically favored state. Hence, the density of cross-links in the network is higher and the material becomes stiffer. The application of external pressure, which results in structural defects caused by disruption of hydrogen-bonded cross-links, results in spontaneous reorganization: the material self-heals.

The reversibility of the supramolecular polymerization process can be nicely demonstrated by the addition of a monofunctional ureidopyrimidone stopper **8** to a highly viscous solution of the bifunctional Janus molecule **5**.[25] The stopper **8** interferes with the polymerization through a competitive association with the ureidopyrimidone head



Scheme 5. Reversibly cross-linked supramolecular 3D polymers.

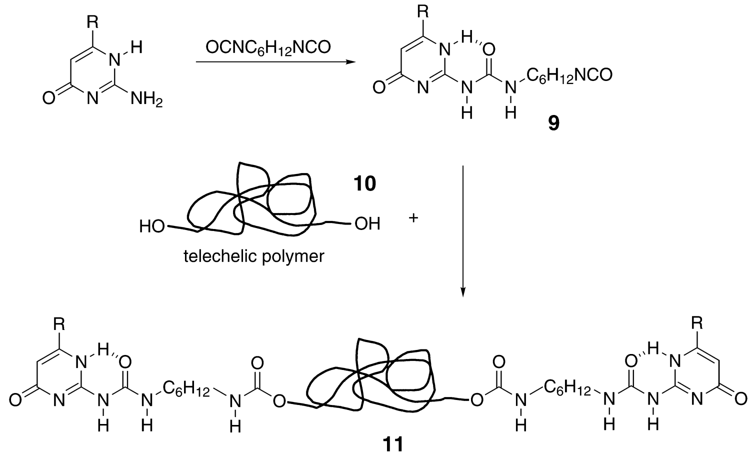
groups of **5** and thus induces rapid depolymerization (Scheme 6). The viscosity of the solution decreases dramatically with increasing concentration of stopper **8**. When the stopper is masked in the form of a photolabile nitrobenzyl ether such as in **7**, the depolymerization can be initiated by external photolysis.[28] The masked stopper with its triple hydrogen-bonding motif does not form dimers with the quadruple hydrogen-bonding motifs in **5** which are stable enough to effectively compete with the polymerization. Photolysis causes the cleavage of the nitrobenzyl ether protecting group and liberates the fourth hydrogen-bonding site, the carbonyl group of the pyrimidone ring. The stopper is now activated and can cause depolymerization. Unfortunately, the process is so far not reversible, and so a complete photochemical switching is not yet possible.



Scheme 6. Depolymerization of a supramolecular polymer induced by addition of a monofunctional stopper **8** (top), which can be liberated photochemically from an inactive precursor **7** (bottom).

6. End Group Modified Telechelic Polymers

New materials with interesting macroscopic properties can be obtained by attaching the ureidopyrimidone binding motif to polysiloxane oligomers or telechelic[29] polymers based on polyethylenes/polybutylenes, polyethers, polycarbonates, or polyesters.[30] For this purpose Meijer et al. developed a general, large-scale synthesis based on *N*-ureidoalkylisocyanates **9** (Scheme 7). Reaction of the isocyanate group with appropriate nucleophiles such as hydroxy or amino groups, which form the end groups of classical telechelic polymers **10**, leads to the corresponding supramolecular polymer units **11** in good yields. Alternatively, alkenyl-substituted ureidopyrimidones can be used directly as monomers for copolymerization with simple alkenes using Ziegler–Natta conditions as was shown recently by Coates and co-workers.[31]



Scheme 7. General synthetic scheme for the end-group modification of telechelic polymers with self-associating hydrogen-bonding motifs.

In contrast to unmodified telechelic polymers, such hybrid materials exhibit improved properties as a result of the self-association which increases their virtual molecular weight.[32] For example, the functionalization of a poly(ethylene/butylene) copolymer with hydroxy end-groups resulted in a macroscopically visible change in the material properties:[30] Whereas the dihydroxy telechelic copolymer is a viscous liquid, the ureidopyrimidone end-group-modified polymer is an elastic solid as a result of the additional supramolecular linking of the individual polymer chains (Figure 2).

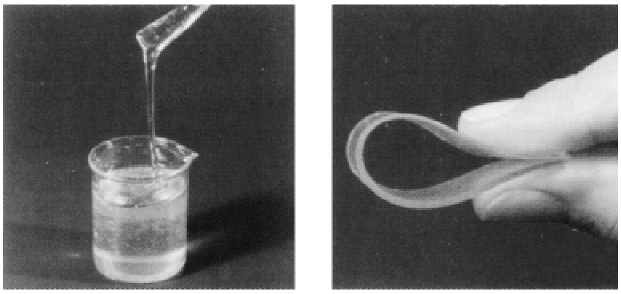
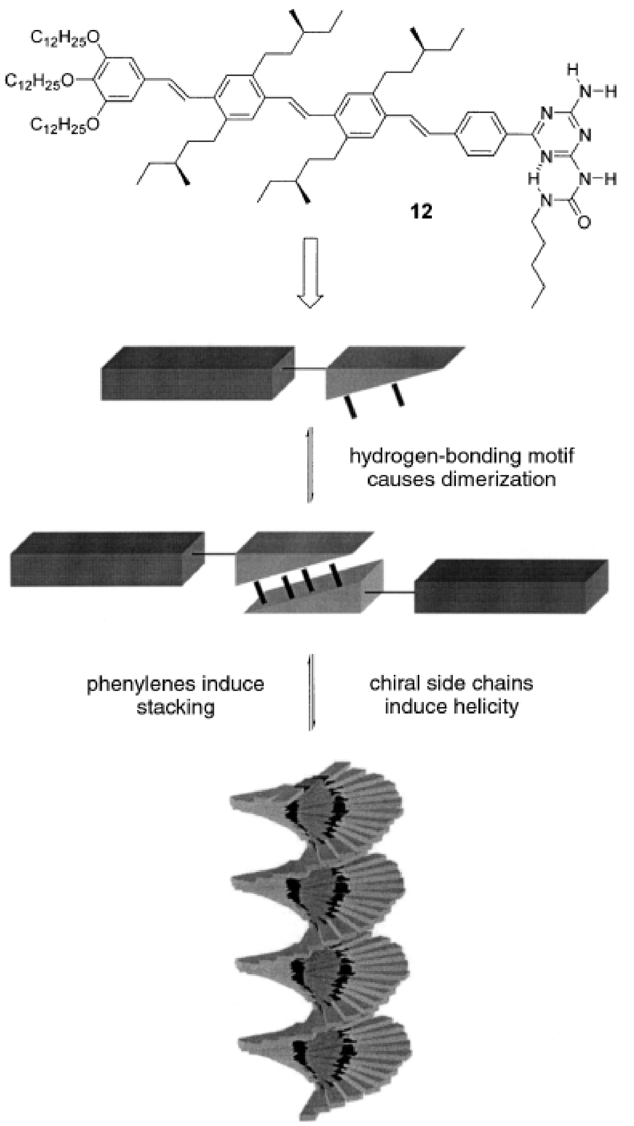


Figure 2. Changing the macroscopic properties of a telechelic poly(ethylene/butylene) copolymer **10** (left) by end-group modification with self-associating hydrogen-bonding motifs **11** (right).[30b]

7. Hierarchical Order in Supramolecular Polymers

Besides linking of the ureidopyrimidone head groups through hydrogen bonds, the mechanical properties of such end group modified supramolecular polymers are also determined by interactions between the polymer chains themselves. This situation opens the way to obtain supramolecular polymers with a higher degree of structural order by incorporation of specific structure-determining groups into the periphery of such systems. For example, the bifunctional ureidopyrimidone **5** forms a supramolecular polymer with a random-coil structure in chloroform. If one modifies the binding motifs by attaching oligo(*p*-phenylenevinylene) groups with chiral side chains, such as in **12**, the resulting supramolecular polymers display a helical superstructure (Scheme 8).[33] In addition to the hydrogen-bonding-based self-association, π–π interactions between the aromatic rings of the oligo(*p*-phenylenevinylene) groups cause a columnar



Scheme 8. Formation of a helix through π–π stacking of hydrogen-bonded dimers. Reprinted with permission from the American Chemical Society from ref. [33b].

stacking of the planar head-group dimers. The chiral side chains then induce a helical twist, as could be shown by CD spectroscopy. Again, the extent of the stacking and the helical twist can be controlled by the solvent and the temperature: neither in DMSO nor above 80 °C could any Cotton effect typical of helical structures be observed.

8. Outlook

The first steps toward the supramolecular synthesis of "intelligent" materials with tailor-made properties have been made. However, the exclusive use of hydrogen bonds thus far also limits any potential future application of these systems. The quadruple hydrogen-bonding motifs presented here display their unique and efficient self-association properties only in solvents of low polarity such as chloroform; more polar solvents or even water destroy the hydrogen bonds and, therefore, also their positive effects on the materials properties. Hence, the long-term goal must be to develop new systems, in addition to the binding motifs accessible so far, that also display stable association in aqueous solvents. One possibility in this context is to incorporate additional electrostatic or hydrophobic interactions[34] into self-complementary hydrogen-bonding motifs. Some first and promising examples already do exist and one can look forward to future developments in this field.

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[1] a) G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, 1st ed., Oxford University Press, New York, **1997**; b) J. Israelachvili, *Intermolecular & Surface Forces*, 2nd ed., Academic Press, London, **1992**.

[2] a) D. Philp, J. F. Stoddart, *Angew. Chem.* **1996**, *108*, 1242–1286; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1154–1196; b) D. S. Lawrence, T. Jiang, M. Levitt, *Chem. Rev.* **1995**, *95*, 2229–2260.

[3] a) G. M. Whitesides, J. P. Mathias, C. T. Seto, *Science* **1991**, *254*, 1312–1319; b) N. B. Bowden, M. Weck, I. S. Choi, G. M. Whitesides, *Acc. Chem. Res.* **2001**, *34*, 231–238; c) C. V. K. Sharma, *J. Chem. Educ.* **2001**, *78*, 617–622; d) D. Rouvray, *Chem. Br.* **2000**, *36*(7), 26–29.

[4] a) F. Vögtle, *Supramolecular Chemistry*, Wiley, Chichester, **1991**; b) J.-M. Lehn, *Supramolecular Chemistry*; *Concepts and Perspectives*, VCH, Weinheim, **1995**; c) J. W. Steed, J. L. Atwood, *Supramolecular Chemistry*, Wiley, Chichester, **2000**.

[5] D. H. Williams, M. S. Westwell, *Chem. Soc. Rev.* **1998**, *27*, 57–64.

[6] For a recent review, see D. C. Sherrington, K. A. Taskinen, *Chem. Soc. Rev.* **2001**, *30*, 83–93.

[7] a) G. M. Whitesides, E. E. Simanek, J. P. Mathias, C. T. Seto, D. N. Chin, M. Mammen, D. M. Gordon, *Acc. Chem. Res.* **1995**, *28*, 37–44; b) C. MacDonald, G. M. Whitesides, *Chem. Rev.* **1994**, *94*, 2383–2420.

[8] S. C. Zimmermann, P. S. Corbin, *Struct. Bonding (Berlin)* **2000**, 63–94.

[9] F. H. Beijer, R. P. Sijbesma, J. A. J. M. Vekemans, E. W. Meijer, H. Kooijman, A. L. Spek, *J. Org. Chem.* **1996**, *61*, 6371–6380.

[10] For a detailed discussion of all the possible geometric arrays of quadruple hydrogen-bonding motifs, see U. Lüning, C. Kühl, *Tetrahedron Lett.* **1998**, 5735–5738.

[11] For a first example of hydrogen-bonding motifs with five or six linear hydrogen bonds, see a) H. Zeng, H. Ickes, R. A. Flowes, B. Gong, *J. Org. Chem.* **2001**, *66*, 3574–3583; b) P. S. Corbin, S. C. Zimmerman, *J. Am. Chem. Soc.* **2000**, *122*, 3779–3780.

[12] F. H. Beijer, H. Kooijman, A. L. Spek, R. P. Sijbesma, E. W. Meijer, *Angew. Chem.* **1998**, *110*, 79–82; *Angew. Chem. Int. Ed.* **1998**, *37*, 75–78.

[13] a) C. S. Wilcox in *Frontiers in Supramolecular Chemistry and Photochemistry* (Eds.: H.-J. Schneider, H. Dürr), VCH, Weinheim, **1990**, pp. 123–144; b) K. A. Connors, *Binding Constants*, Wiley, New York, **1987**, chap. 2 and 5.

[14] A. R. Katritzky, I. Ghiviraga, *J. Chem. Soc. Perkin Trans. 2* **1995**, 1651–1653.

[15] a) W. L. Jørgensen, J. Pranata, *J. Am. Chem. Soc.* **1990**, *112*, 2008–2010; b) J. Pranata, S. G. Wierschke, W. L. Jørgensen, *J. Am. Chem. Soc.* **1991**, *113*, 2810–2819.

[16] F. H. Beijer, R. P. Sijbesma, H. Kooijman, A. L. Spek, E. W. Meijer, *J. Am. Chem. Soc.* **1998**, *120*, 6761–6769.

[17] S. H. M. Söntjens, R. P. Sijbesma, M. H. P. van Genderen, E. W. Meijer, *J. Am. Chem. Soc.* **2000**, *122*, 7487–7493.

[18] P. S. Corbin, S. C. Zimmerman, *J. Am. Chem. Soc.* **1998**, *120*, 9710–9711.

[19] Self-complementary ADAD and AADD binding motifs which are not influenced by a tautomeric equilibrium but which show much weaker binding ($K \approx 10^4\,\mathrm{M}^{-1}$) as a consequence of the absence of stabilizing secondary interactions have been synthesized recently: B. Gong, Y. Yan, H. Zeng, E. Skrzypczak-Jankuum, Y. Wah Kim, J. Zhu, H. Ickes, *J. Am. Chem. Soc.* **1999**, *121*, 5607–5608.

[20] In the meantime, the ureidopyrimidone motif has also been used for the noncovalent linking of two fullerenes: a) M. T. Rispens, L. Sanchez, J. Knol, J. C. Hummelen, *Chem. Commun.* **2001**, 161–162;

b) J. J. Gonzalez, S. Gonzalez, E. M. Priego, C. Luo, D. M. Guldi, J. de Mendoza, N. Martin, *Chem. Commun.* **2001**, 163–164.

[21] Self-assembled molecular capsules are formed in a 1:1 dimerization when rigid, concave spacers are used: B. J. B. Folmer, R. P. Sijbesma, H. Kooijman, A. L. Spek, E. W. Meijer, *J. Am. Chem. Soc.* **1999**, *121*, 9001–9007.

[22] a) N. Zimmerman, J. S. Moore, S. C. Zimmerman, *Chem. Ind.* **1998**, 604–610; b) A. Cifferi, *Supramolecular Polymers*, Marcel Dekker, New York, **2000**.

[23] Rebek and co-workers have designed supramolecular "polycaps", in which the association results from a chloroarene-induced dimerization of calixarene units in unpolar solvents: R. K. Castello, R. Clark, S. L. Craig, C. Nuckolls, J. Rebek, Jr., *Proc. Natl. Acad. Sci. USA* **2000**, *97*, 12418–12421.

[24] In contrast to this first surpamolecular homopolymer, the polymers designed by the research groups of Lehn, Griffin, as well as Kato and Fréchet at the beginning of the 1990s were based on the heteropolymerization of two different molecules with complementary binding properties: a) C. Fouquey, J.-M. Lehn, A.-M. Levelut, *Adv. Mater.* **1990**, *2*, 254–257; b) J.-M. Lehn, *Makromol. Chem. Macromol. Symp.* **1993**, *69*, 1–17; c) C. Alexander, C. P. Jariwala, C. M. Lee, A. C. Griffin, *Makromol. Chem. Macromol. Symp.* **1994**, *77*, 283–294; d) C. M. Lee, A. C. Griffin, *Makromol. Chem. Macromol. Symp.* **1997**, *117*, 281–290; e) T. Kato, J.-M. Fréchet, *Makromol. Chem. Macromol. Symp.* **1995**, *98*, 311–326.

[25] R. P. Sijbesma, F. H. Beijer, L. Brunsveld, B. J. B. Folmer, J. H. Ky Hirschberg, R. F. M. Lange, J. K. L. Lowe, E. W. Meijer, *Science* **1997**, *278*, 1601–1604.

[26] Heterodimerization of different ureidopyrimidone motifs can be used for the construction of cyclic aggregates: S. H. M. Söntjes, R. P. Sijbesma, M. H. P. van Genderen, E. W. Meijer, *Macromolecules* **2001**, *34*, 3815–3818.

[27] B. Tieke, *Makromolekulare Chemie*, VCH, Weinheim, **1997**.

[28] B. J. B. Folmer, E. Cavini, R. P. Sijbesma, E. W. Meijer, *Chem. Commun.* **1998**, 1847–1848.

[29] A telechelic polymer is a low molecular weight polymer or an oligomer with reactive end groups such as hydroxy, amino, carboxy, isocyanate, epoxide, or vinyl.

[30] a) J. H. Ky Hirschberg, F. H. Beijer, H. A. van Aert, P. C. M. M. Magusin, R. P. Sijbesma, E. W. Meijer, *Macromolecules* **1999**, *32*, 2696–2705; b) B. J. B. Folmer, R. P. Sijbesma, R. M. Versteegen, J. A. J. van der Rijt, E. W. Meijer, *Adv. Mater.* **2000**, *12*, 874–878.

[31] L. R. Rieth, R. F. Eaton, G. W. Coates, *Angew. Chem.* **2001**, *113*, 2211–2214; *Angew. Chem. Int. Ed.* **2001**, *40*, 2153–2156.

[32] For example, Stadler and co-workers have shown how even weak hydrogen bonds between polymer chains can improve material properties: a) M. Müller, A. Dardin, U. Seidel, V. Balsamo, B. Ivàn, H. W. Spiess, R. Stadler, *Macromolecules* **1996**, *29*, 2577–2583; b) M. Müller, U. Seidel, R. Stadler, *Polymer* **1995**, *36*, 3143–3150, and references therein.

[33] a) A. El-ghayoury, E. Peeters, A. P. H. J. Schenning, E. W. Meijer, *Chem. Commun.* **2000**, 1969–1970; b) J. H. Ky Hirschberg, L. Brunswald, A. Ramzi, J. A. J. M. Vekemans, R. P. Sijbesma, E. W. Meijer, *Nature* **2000**, *407*, 167–170; c) A. P. H. J. Schenning, P. Jonkheijm, E. Peeters, E. W. Meijer, *J. Am. Chem. Soc.* **2001**, *123*, 409–416.

[34] For some recent examples on the importance of ionic and hydrophobic interactions for supramolecular aggregation in aqueous solution, see a) S. Lahiri, J. L. Thompson, J. S. Moore, *J. Am. Chem. Soc.* **2000**, *122*, 11315–11319; b) M. Sirish, H. J. Schneider, *J. Am. Chem. Soc.* **2000**, *122*, 5881–5882; c) T. Grawe, T. Schrader, M. Gurrath, A. Kraft, F. Osterod, *Org. Lett.* **2000**, *2*, 29–32; d) C. Schmuck, *Chem. Eur. J.* **2000**, *6*, 409–417; e) C. Schmuck, *Eur. J. Org. Chem.* **1999**, 2397–2403; f) L. Isaacs, D. Witt, J. C. Fettinger, *Chem. Commun.* **1999**, 2549–2550.

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