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Synthesis and Self Assembly of Hydrogen-Bonded Supramolecular Polymers

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Dedicated to Prof. Peter Stanetty on the occasion of his 60th birthday

Summary: New synthetic methodologies towards hydrogen bonded supramolecular polymers are described. Focus is directed on synthetic work towards telechelics with hydrogen bonds either as side chain moieties or as endgroups. Physical ordering effects related to polymers and particles are discussed citing own and related work in ~60 references.

Keywords: hydrogen bond; nanostructuring; supramolecular polymers; synthesis

Introduction

Supramolecular polymers are an increasingly important class of polymers, where designed intermolecular interactions allow a specific tailoring of polymer properties. In contrast to purely covalent bound polymers, new types of structural ordering due the reversible nature of the linkage have been achieved opening way to a biologically inspired structuring of polymers on the nano- and microscale[1] (Figure 1). Important for the directed design of these materials is the introduction of specific functional groups which exert defined intermolecular interactions. Initially demonstrated with the self assembly of small molecules (generated by the pioneering work of Lehn et. al.,[2] Stoddart et. al.[3] and others[4]) the concept was extended to macromolecules by Stadler et. al.,[5] demonstrating the transformation of an elastomer into a thermoplastic elastomers by use of uradiazole moieties as noncovalent crosslinking entities. Therefrom the concept of supramolecular polymer chemistry has been developed by tuning intermolecular forces (such as hydrogen bonds,[6] ionic forces,[7] metal complexes,[8] pi-pi stacking[9] and steric forces[10]) directing molecules into specific 2D- and 3D-order.

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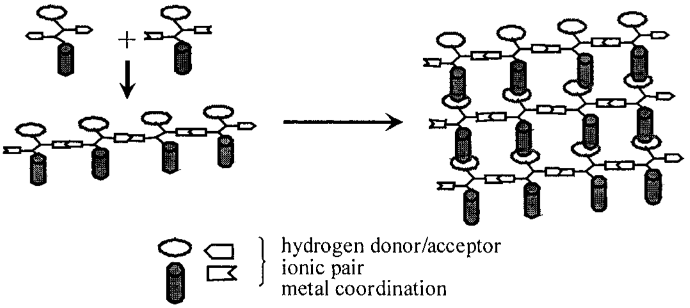

Figure 1 Formation of supramolecular 2D- and 3D-structures via self assembly

Directed hydrogen bonds[6] (Figure 2) have been shown very effective in comparison to other intermolecular forces, in that they allow the tuning of binding constants between several M^{-1} up to 10^7 M^{-1} by use of a specific hydrogen-bond matching pair. Additionally the ability to select specific intermolecular bonding-combinations within several possibilities (i.e.: favoring A-B contact over A-A or B-B binding) is unique to hydrogen bonds. The reversibility of the interaction together with the relative ease of its synthetic approach has speeded up the application of hydrogen bonds as directing forces leading to supramolecular polymers.

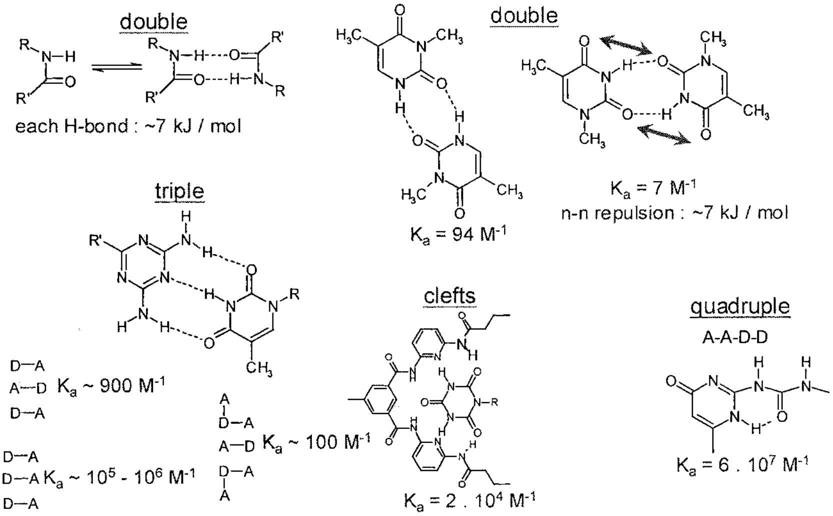

Figure 2 Different hydrogen bonding systems

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A variety of reviews[11] has dealt with the ordering of molecules into supramolecular polymers via directed hydrogen bonding systems. Important for the application of supramolecular polymers however is the synthetic availability of hydrogen bonding motives and their ease of introduction, regarding the broad range of industrial application that have been described. The best hydrogen-bonding system may be useless, would there not exist an easy synthetic methodology for its preparation. Thus the past years have seen applications as rheological modifiers,[12] in photographic processes,[13] as thermoplastic rigidifiers[14] and in the cosmetic industry[15] relying on relatively simple methods to affix hydrogen bonds onto telechelics. The present article therefore focuses on synthetic approaches towards larger molecules and telechelics bearing hydrogen bonding motives. Own contributions as well as literature starting from 2001 are included into this article.

Quadrupolar H-bonding systems

Meijer et. al.[16, 6] have first described the use of very strong, multipolar hydrogen bonding systems, which enable the ordering of small molecules and/or telechelics into supramolecular polymers with high molecular weights. Critical for the ordering process is the presence of a strong ureidopyrimidinone-bond having a binding constant of 6.10^7 M^{-1} in $CHCl_3$.[17] This allows to reach high molecular weights by pure association of small molecular fragments into polymers, helices and gels[18] as well as phase separated structures.[19] Together with its ease of preparation this system represents the technically most promising approach to supramolecular polymeric systems. The synthetic approach [20] (Figure 3) – initially developed for small molecules - starts with hydroxy- or amino-telechelic polymers (**1**), a bivalent isocyanate (such as 2,4-toluene-diisocyanate (TDI), hexamethylenediisocyanat (HDI) or isophoronediisocyanate (IPDI)) and 2-amino-4-hydroxy-6-methylpyrimidine **2** furnishing the ureidopyrimidinone-telechelic polymers **3**. The reaction can be perfomed with a large variety of different telechelics, including poly(ethyleneoxide),[21] poly(ethyleneoxide-co-propyleneoxide),[21] polysiloxanes,[22] polycarbonates,[23] polyesters,[23] poly(vinylchloride),[23] co(polyester-polyamides)[24] and oligo(p-phenylenevinylene).[25] Chiral elements can be included into the midthblock by use of chiral amines or hydroxides.[26] Recently, the method was conducted in a scale-up[20a] reaching 98.8 %

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conversion with poly(ethylenebutylene) (PEB(OH)$_2$) on a kg-scale using dibutyltinlaurate (DBTL) as catalyst and ^{19}F-nmr-spectroscopy to monitor for free hydroxyl-groups from unreacted starting material. Long et. al.[27] have extended the method to the synthesis of telechelic poly(styrene) and poly(isoprene)s.

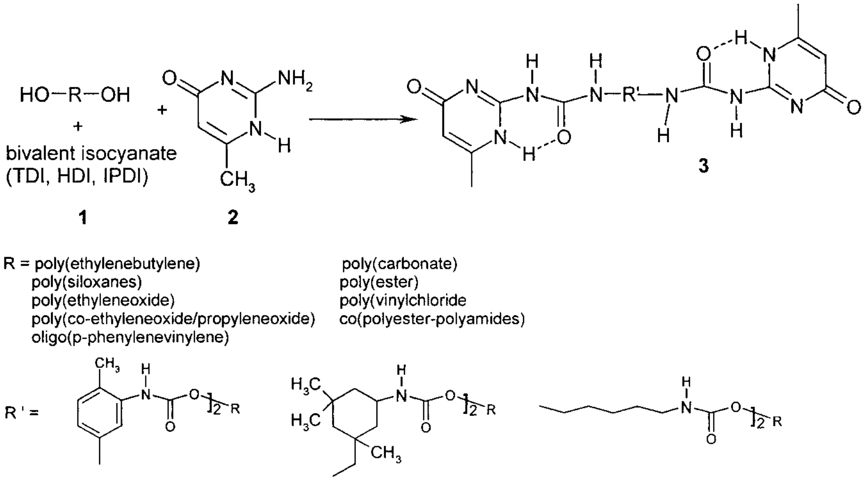

Figure 3 Synthesis of telechelics with quadrupolar hydrogen bonds

Loontjens et. al.[28] have extended the method to more industrial relevant products by using melamine in place of 2-amino-4-hydroxy-6-methylpyrimidine (Figure 4). They reacted hydroxy-telechelic poly(tetrahydrofurane) **4** (2000 g mol^{-1}) with IPDI and melamine to generate the endcapped polymer **5**.

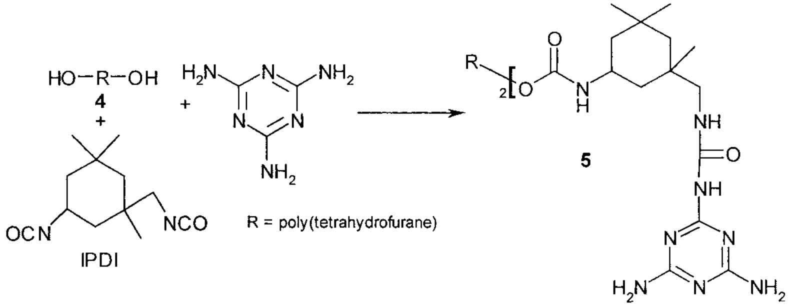

Figure 4 Quadrupolar hydrogen bonds via melamine / isocyanate adddition

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The nature of this hydrogen bond leads to self aggregation as indicated by its high viscosity comparable to high molecular weight polymers and also visible due to its semi-crystalline properties. Ureidodeazapterin, a new quadrupolar receptor developed by Zimmermann et. al.[29] follows a similar protocol via bivalent isocyanates making it applicable to affixation onto dendrimeric systems.

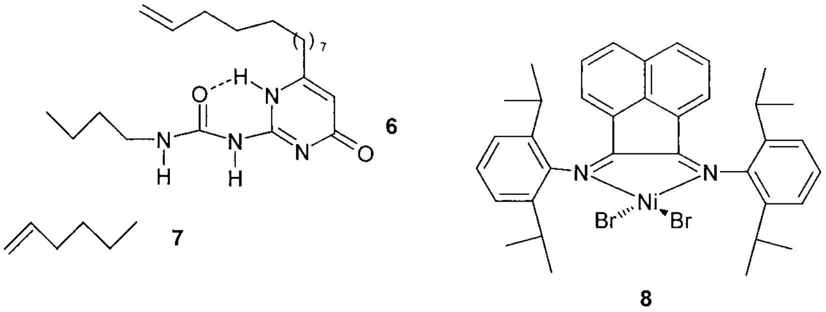

Figure 5 Synthesis of poly(olefins) with quadrupolar hydrogen bonds

An important contribution towards polyolefins modified with quadrupolar hydrogen bonds was developed by Coates et. al. (Figure 5).[30] They succeded in the incorporation of up to 2 mol% of 2-ureido-4[1H]-pyrimidinone (UP-) functionalized monomers **6** during Ziegler-Natta polymerization of 1-hexene **7**. Diethylaluminium (together with the Ni-catalyst **8**) is critical in activating the nickel catalyst precursor as well as reacting with the UP-monomer thus removing acidic hydrogens and protecting Lewis basic sites from reaction with the nickel catalyst. The final polymer can form crosslinks under formation of a thermoreversible network displaying an elastomeric behavior.

Nucleobase-derived H-bonding systems

Nucleobase-modified molecules were among the first structures investigated within supramolecular ordering phenomena, mainly due to their similarity to DNA-bonding structures. Lehn et. al.[2] and others [31] have used this interaction to assemble small molecules and nanoparticles as well as to control particle-surface interaction. The binding forces within this type of interaction are weak (usually below 1000 M^{-1}), thus representing a more dynamic force in

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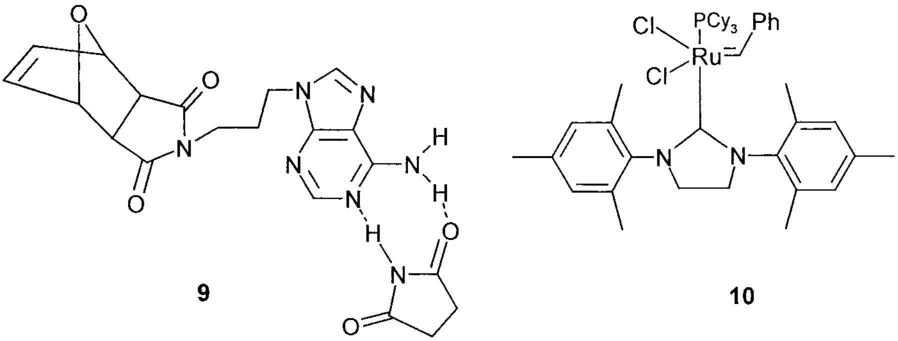
comparison to the aforementioned quadrupolar hydrogen bonding systems. Thus the endgroup-specific as well as the multiple affixation of adenine-, thymine-, uracile- and guanine nucleobases are an important factors for the design of supramolecular polymers.



9

10

Figure 6 Synthesis of nucleobase-modified polymers via ROMP

Ring opening metathesis polymerization (ROMP) has recently found its way into the polymerization of monomers with hydrogen bonds due to the development of 1st and 2nd generation Grubbs-catalysts.[32] Sleiman et. al.[33] have developed a method masking the sometimes destructive effect exerted by hydrogen bonding systems leading to larger polydispersities (Figure 6). They employed an adenine containing monomer **9**, to which succinimide was added as a noncovalent "protecting-group". This strategy significantly improves the possibility to prepare block copolymers with polydispersities ranging between 1.20 – 1.60 together with monomodal distributions by use of Grubbs-catalyst **10**. In contrast (Figure 7, next page) Rotello et. al.[34a] used a succinimidyl-substituted poly(norbornene) (**11**) to react with an aminoalkyl-thymine (**12**) to prepare the thymine-substituted polymer (**13**) in high yields. Another method relying on a postmodification strategy furnished the poly(styrene) polymer **14**.[34b] Similar systems have been described recently by Puskas et. al. [34c] generating crosslinked polymer spheres with a thymine-functionalized surface.

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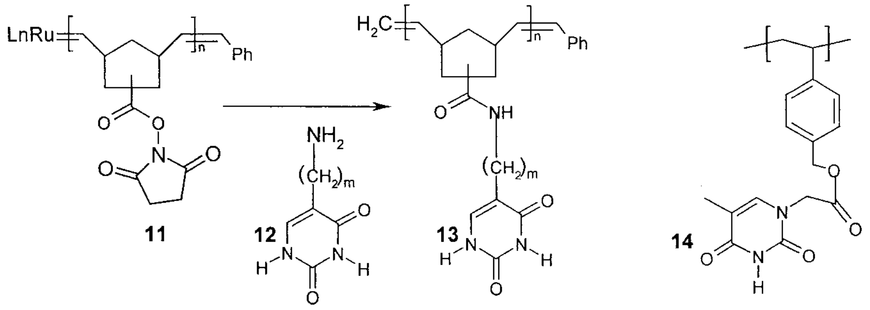

Figure 7 Synthesis of polymers **13** and **14** via postmodification methods

The synthesis of endgroup-modified polyisobutylenes has been demonstrated in our group by use of highly reactive intermediates.[35] (Figure 8). Polyisobutylene, prepared by living polymerization methods[36] can be transformed into PIB-OH (**15**) in quantitative yields. Reaction with formaldehyde under acidic conditions furnishes the chloromethyl-methylether (**16**), which is highly activated towards nucleophilic substitution reactions by silylated nucleobases (**18**) such as thymine, uracil and cytosine. This method yields the corresponding nucleobase-endgroup-modified PIB with narrow polydispersities (1.20) in quantitative yields as proven by MALDI-analysis and represents a general activation method for the nucleophilic substitution on telechlics.

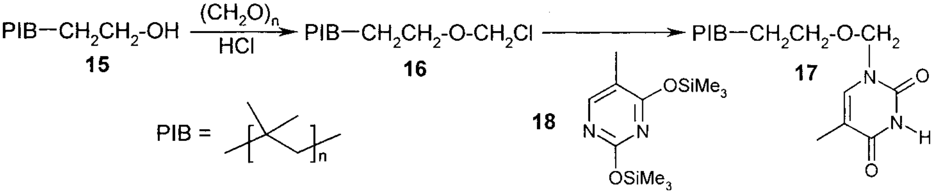

Figure 8 Synthesis of nucleobase telechelic poly(isobutylenes)

Rowan et. al.[37] have used an anhydride-approach to attach modified nucleobases **20**, **21**, and **22** onto poly(tetrahydrofurane) (pTHF) (Figure 9, next page). Hydroxy-telechelic pTHF was substituted with 3-bromo-propanol and subsequently with the anhydrides (**23**) of the corresponding N-carboxymethyl-nucleobases **20** – **22**. This method represents an easy access to various nucleobase-terminal polymers (**19**) due to the easy preparation of amino-telechelic polymers. A modification of this method[38] uses nucleophilic substitution reactions of alkylbromides with silylated nucleobases.

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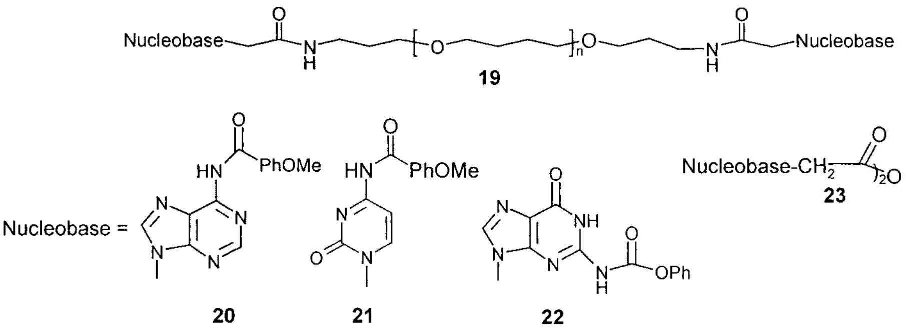

Figure 9 Preparation of poly(THF) with nucleobase endgroups

Michael addition of nucleobases onto acryloyl-endgroup modified poly(cis-isoprene) **25** has been exploited by Long et. al.[39] in their synthesis of thymine- and adenine modified polymer **26** (Figure 10). The reaction proceeds simply by adding the sodium-salt of thymine or adenine to a solution of **25**, which can be prepared by reaction of the corresponding hydroxy-telechelic polymer **24** with methacryloyl chloride.

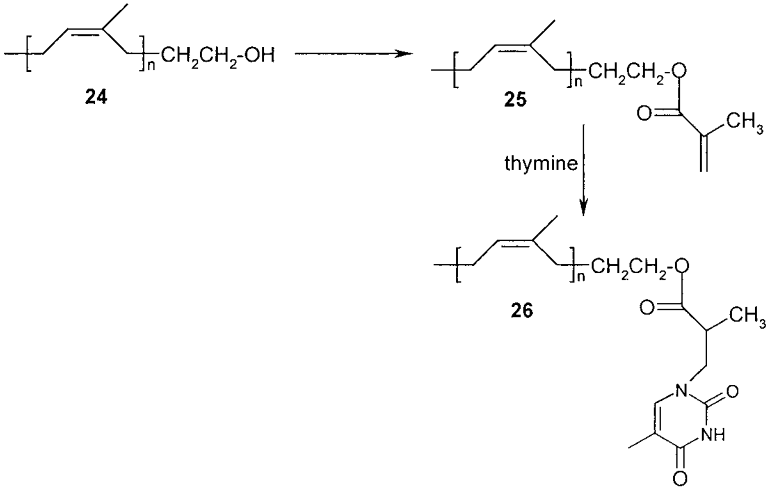

Figure 10 Modification of poly(isoprene) by Michael-addition

Other authors[40] have used atom transfer radical polymerization (ATRP) to introduce thymine and adenine residues at the initiating end (Figure 11, next page). 5-O-(2-Bromo-2-methyl-propanoyl)-modified nucleosides **27** and **28** were employed as initiators or monomers,

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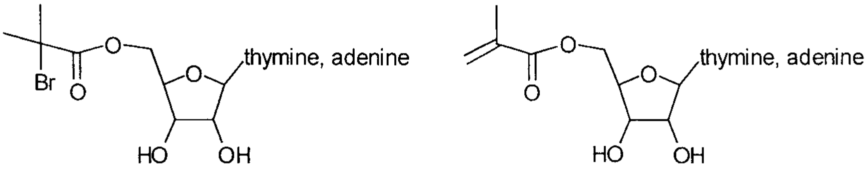
respectively for ATRP. The method can be extended to side chain modified poly(methylmethacrylates) as described by Haddleton et. al.[41]

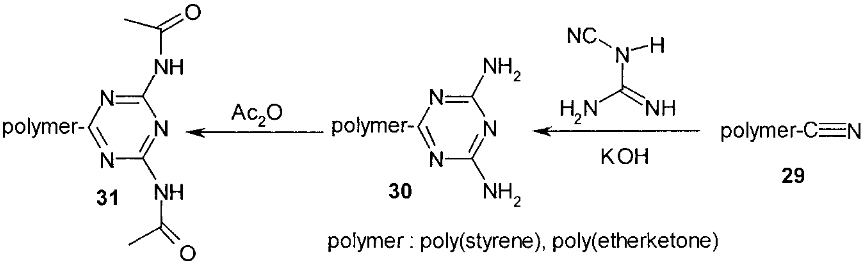


27 **28**

Figure 11 Nucleobase-functional initiators and monomers for ATRP

Aminotriazine and 2,6-diaminopyridine ligands

2,4-Diaminotriazines as well as derivatives therefrom form, together with 2,6-diaminopyridine ligands, a highly versatile class of H-bonding moieties.[42] Their binding strength ranges between 10^2 M^{-1} to approx. 10^3 M^{-1} with the corresponding matching thymine-, flavine and phtalimide guests. Recent work done by Rotello et. al. has demonstrated the high structuring ability of these receptors via multivalent binding sites under formation of nanoparticle-polymer[43] as well as polymer-surface nanostructures.[44]



31 **30** **29**

Figure 12 Synthesis of triazine-modified polymers

Other effects reported by our group[45] relate to the intimate mixing of immiscible polymers (such as poly(isobutylenes) and poly(etherketones)) mediated by matching hydrogen bonds under formation of nanophaseseparated (instead of macrophaseseparated) pseudo-block copolymers.

The attachment of 2,4-diaminotriazines to polymers is achieved by reaction of dicyandiamide with nitriles under alkaline reaction conditions[46] (Figure 12). Critical for the

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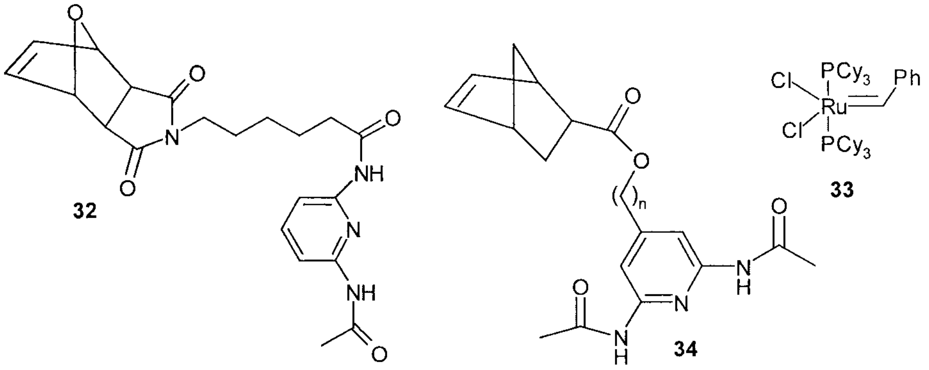
completion of this reaction is the use of an alcoholic solvent (or dispersant). Thus the nitrile-functionalized polymer **29** (either endgroup- or sidechain functionalized) can be reacted with dicyandiamide yielding the corresponding 2,4-diamino-1,3,5-triazine modified polymer **30**. Subsequent acylation is usually performed with anydrides furnishing the acyl-modified receptors **31**. The reaction has recently been reported by Rotello et. al.[47] on various poly(styrene)s and in our group[48] on endgroup modified poly(etherketones).



32 **33** **34**

Figure 13 2,6-Diaminopyridine polymers via ROMP

Similar to previous examples ROMP is able to polymerize 2,6-diaminoacyl-pyridine containing monomers **32** and **34** under formation of the homo- and block-copolymers (Figure 13). Sleiman et. al.[49] as well as Weck et al.[50] used the Grubbs catalyst **33** for this reaction obtaining homo-, di- and triblock copolymers with polydispersities ranging between 1.06 – 1.20. The *exo*-isomer of **34** was found to yield products with lower polydispersity than the *endo*-isomers.

Quite surprisingly ATRP is able to polymerize substrates with 2,6-diamino-pyridine ligands (Figure 14).[51] A functional initiator **35** bearing 2-bromo-propanoyl-moieties was used to initiate the polymerization of butyl- and methyl methycrylate as well as styrene furnishing the polymers **36** with molecular weights of 2600 – 6000 and polydispersities ranging from 1.10 – 1.37. Critical was the use of pentamethyl diethyelentriamine (PMDETA) instead of conventional 2,2-bipyridine ligands in the case of styrene as monomer. The same ligand could be introduced in the "middle-block" of a poly(lactide) polymer **38** by anionic ring opening polymerization of lactide (polydispersities 1.34; M_n = 10 000) using the functionalized intiator **37**.

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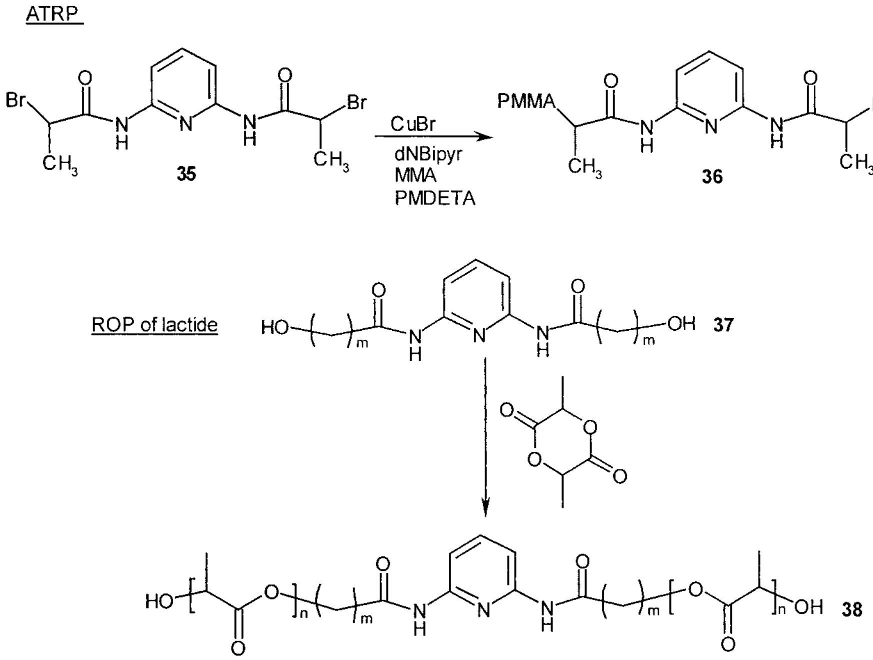

Figure 14 Use of functional 2,6-diaminopyridines as initiators

The attachment of 2,6-diaminopyridine ligands to POSS (polyhedral silsesquioxane) was described by Rotello et. al.[52] (Figure 15, next page). POSS-derivatives serve as important surface modification agents due to their small size (approx. 1.5 nm diameter) making them ideal as modifiers for polymers and ceramic systems.[53] Critical for the modification is a nucleophilic displacement reaction between a halobenzyl-modified POSS **40** and 4-hydroxy-2,4-diaminoacyl-pyridine. The transformation yields a monosubstituted POSS-derivative **41**, which can crosslink supramolecular polymers with pendant thymine functionalities as well as assemble on surfaces selectively.

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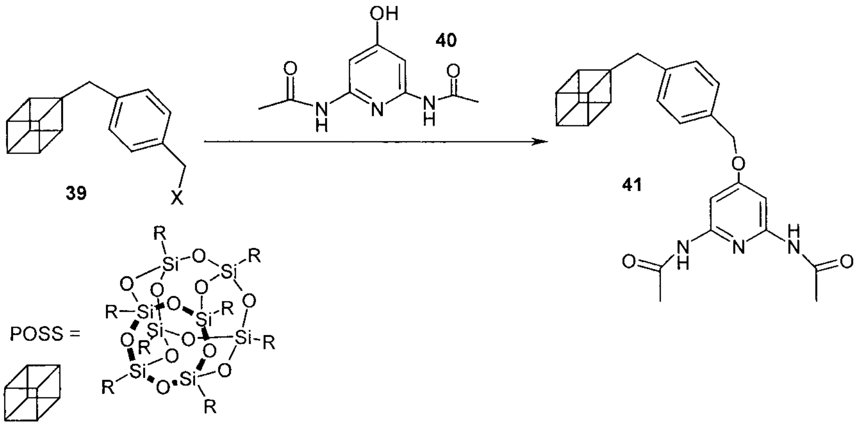
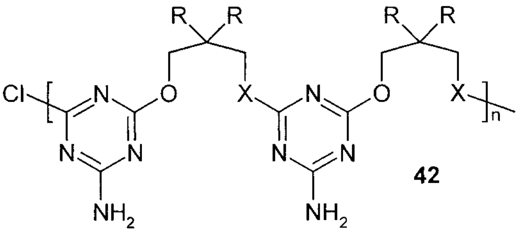


R =cyclopentyl
X = Cl, Br

Figure 15 Attachment of 2,6-diaminopyridine-fragments to POSS

A highly creative approach towards polymers with 2,6-diaminotriazine ligands has been reported by Krische et. al (Figure 16).[54]



42

X = NH, O
R = CH_3, benzyl

Figure 16 5-Amino-2,4,6-triazine-polymer **42**

They generated polymer **42** with an extremely high density of trazine moieties by simple nucleophilic substitution reaction between 2,2-substituted aminopropanols and 2,4-dichloro-6-amino-1,3,5-triazines. The polymers reach molecular weights up to 45 000 and can assemble into dublex-strands by self association (K_{ass} = 100 M^{-1}) after solvent casting. Additionally this system gives rise to a variety of structural features via self assembly with other complementing hydrogen bonding systems. A similar system with self assembling dendrimers by triazines has been described by Simanek et. al.[54b]

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Mixed systems with differing H-bonds

The following section comments on the preparation of various types of H-bonding systems with different structures. Zimmermann et al.[55] (Figure 17) have prepared dendrimers with self complementing triple hydrogen bonds. The procedure followed a stepwise pathway starting with a nucleophilic substitution reaction between a benzylbromo-terminal dendrimer **43** and the naphtyridine **44** furnishing the adduct **45**. This can be transformed in a sequence of steps into the final product **46**, bearing the self complementing receptor. The most important structural feature of this hydrogen bonding structure is the side-edge-on complementarity, which can be used to assemble small dendrimeric fragments into larger dendrimers via assembly of the inner core.

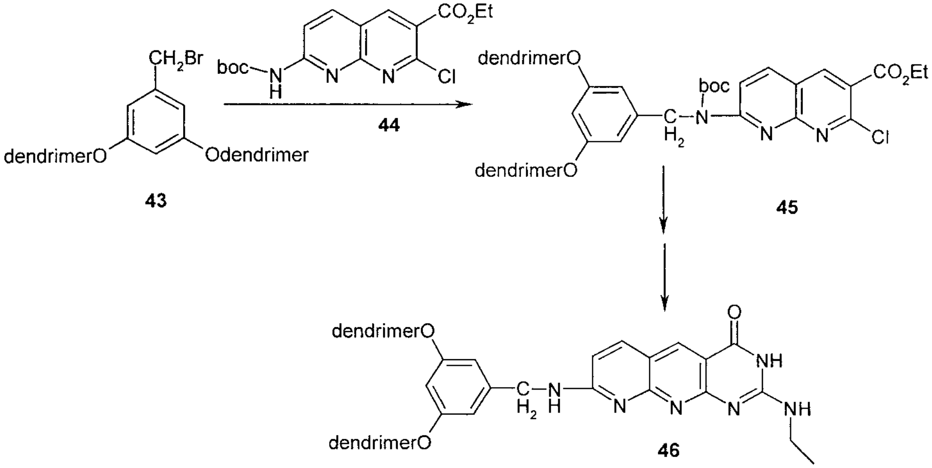

Figure 17 Functionalization of dendrimers with self-associating shells

Some simple, but efficient hydrogen bonding systems are composed in Figure 18. The synthesis of symmetrical urea derivatives was reported by Bouteiller et. al.[56] by reaction of amines with triphosgene. A variety of symmetrically substituted ureas **47** bearing alkyl and aryl moieties can thus be achieved opening a possible mode for an efficient industrial preparation of self complementing polymers. Linear chain assembling systems[57] such as **48** have been described by a variety of authors, where simple diacid-pyridinium-ion interaction leads to liquid-

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crystalline behavior. Ladder-type poly(siloxanes) **49**[58] with multiple amide-bonding have been described by Zhang et. al. generating sheet-type structures via template-type synthesis.

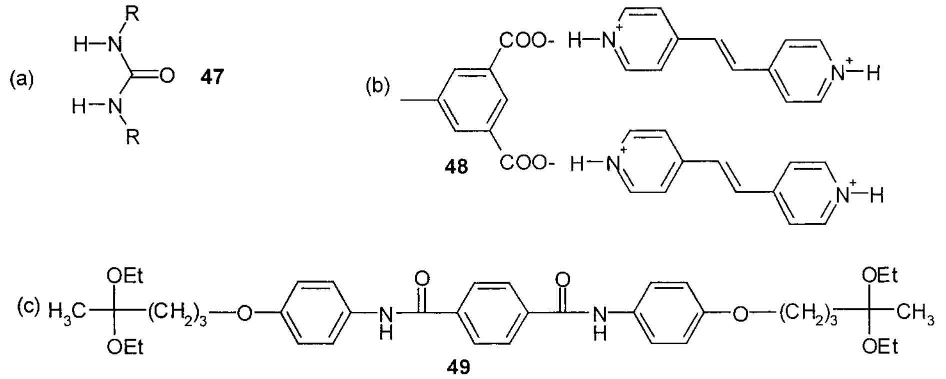

Figure 18 Various types of H-bonding systems

An important and quite new approach to amino-acid modified polymers was recently reported by Bai et. al.[59] attaching D-valine residues onto poly(phenylacetylene) backbones in high density (Figure 19). Phenylacetylene monomer **50** could be polymerized using $[Rh(nbd)Cl]_2$ furnishing polymer **51** with molecular weights of 371 000 and polydispersities of 7.90.

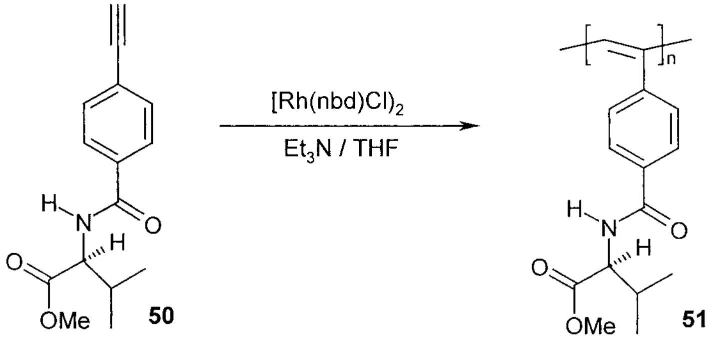

Figure 19 Incorporation of amino-acid derivatives

The polymer forms helices by intrastrand association between the D-valine amide bonds in dependence of their ionization state. Single as well as double helical strands were formed induced by the pendant chirality of the D-valine moieties.

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H-bonding systems with Cyanuric / Barbituric acid

The cyanuric acid-melamine interaction has proven an efficient tool for self recognition and self assembly processes in the past, mainly developed by Whitesides and coworkers.[60] This system features the organization into rosette-type aggregates with high structural diversity representing supramolecular organic synthesis and can be easily extended for the organization of high molecular weight compounds such as calixarenes and dendrimers as well as regio- and stereoselection of host-guest interaction.

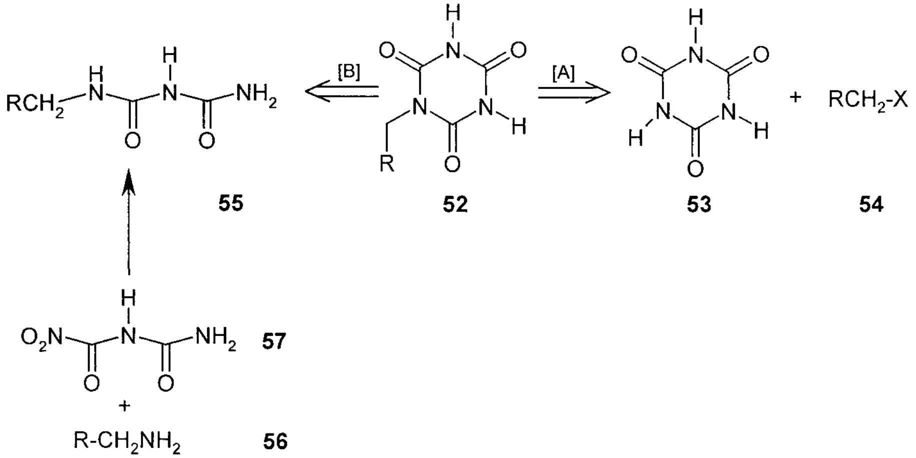

Figure 20 Synthetic methodology towards cyanuric acid derivatives

The fixation of cyanuric acid moieties can be accomplished by two synthetic pathways (Figure 20): Either direct fixation of cyanuric acid **53** by nucleophilic substitution onto alkyl halogenides **54** (pathway A)[61] or stepwise, sequential reaction via N-alkyl biurets **55** (pathway B).[62] The direct pathway suffers from a drawback in that multiple substitution can hardly be prevented, leading to the attachment of more than one residue R onto the cyanuric acid ring (maximum three residues on each nitrogen). The N-Alkyl-biurets in contrast can be prepared by reaction of alkyl- and arylamines **53** with nitrobiuret **57** in good yields.

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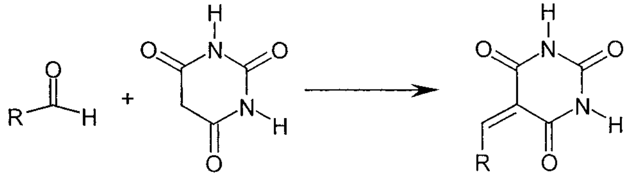

58 **59** **60**

R = poly(etherketone)

Figure 21 Synthesis of barbituric acid telechelic poly(etherketones)

Alternatively, barbituric acid derivatives can be used as equivalent hydrogen bonding structures (Scheme 21). An easy access to barbituric acid modified oligo- and poly(etherketone)s is developed[63] in our group linking aldehyde terminal polymers **58** and barbituric acid **59** by a Knoevenagel type condensation reaction. This method leads to an efficient conversion to the telechelic polymer **60**, whose double bond can be further stabilized by hydrogenation.

An important effect of cyanuric acid / 2,4,6-triaminopyrimidine on the crystallization behavior of poly(propylene) was reported by Mühlhaupt et. al..[64] Long chain substituted cyanuric acid / 2,4,6-triaminopyrimidine derivatives ("tectons") were extruded into poly(propylene). The tectons form nanoscale superstructures in the polymer matrix forming a superstructure in the melted polymer. This leads to a plastizising effect and a strong impact on the rheological properties of the polymer.

Cleft-type hydrogen bonding systems

Lehn et. al.[65] have developed the first multivalent receptor displaying a cleft-type arrangement of hydrogen bonds together with a A-B type interaction with barbituric acid (Figure 2, second page). This interaction has a binding strength of 2.10^4 M^{-1} and leads to the formation of fibers and chiral aggregates in solution. An important issue in this respect is the attachment of this receptor type onto telechelic structures with high efficiency. We recently have succeeded in transforming the synthetic methodology developed by Lehn et. al.[65a] to poly(isobutylenes) PIB (Figure 22).[35] The living nature of this cationic polymerization reactions allows the generation of PIB **61** bearing terminal, primary hydroxyl groups.[66] Polymer **61** can be transformed into the

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corresponding bromide **62** in quantitative yield thus offering an anchor point for the multivalent receptor. Important in this respect is the transformation of functional groups in a 100 % efficiency, which is limited due to the specific solubility of PIB in only few solvents. The optimization of each step is therefore necessary, leading to products of uniform chemical identity. The final product **63** can thus be obtained in quantitative yields as proven by MALDI-analysis.

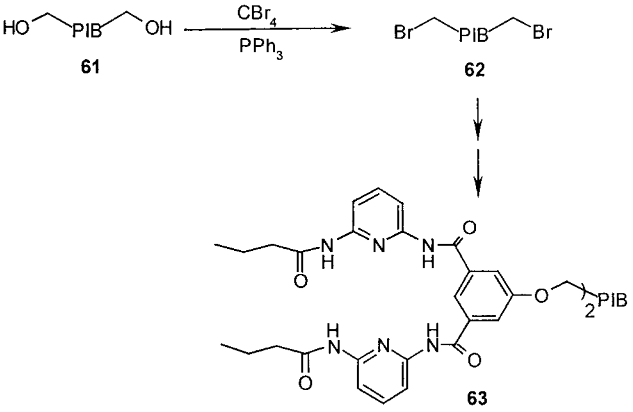

Figure 22 Synthesis of poly(isobutylene) (PIB) - telechelic hydrogen-bond acceptors

Conclusion

The preparation of telechelics functionalized with defined hydrogen bonding systems is already far advanced and allows the buildup of a large variety of polymer-architectures together with defined endgroups. Both approaches – the direct introduction of functional monomers, as well as the modification of polymers after the polymerization – can be successfully applied. Critical in any case are interferences between the living type of polymerization with the polar nature of the (hydrogen-bond type) monomers as well as the efficiency of many postmodification-methods, which seldom reach 100 % conversion even with large excesses of reagents. Therefore a combination of both methods is usually applied and leads to the victory of hydrogen-bonded supramolecular polymers.

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