Supramolecular polymers

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PROEFSCHRIFT

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Supramolecular Polymer Chemistry

1.1 Introduction

Supramolecular chemistry, is a rapidly developing new branch of chemistry which is defined as the chemistry of molecular association and complexes held together by non-covalent interactions.[1,2] This field of chemistry has evolved from *organic chemistry* in which well-defined low molecular weight molecules are synthesised. Inspired by natural systems a large number of synthetic systems showing supramolecular properties has been developed and studied over the last decades.[2-7] Actually, the interest in supramolecular chemistry of polymers is growing. A well-known natural supramolecular system is DNA, whose unique architecture results from cooperative non-covalent interactions, such as multiple hydrogen bonds and hydrophobic interactions. Other prominent examples from nature whose unique properties are due to secondary interactions are collagen and spider silk. Collagen is formed by the association of tropocollagen fibres that consist of three polypeptides coiled into a helical rod. The interactions responsible for the association of the three strands are cooperative hydrogen bonds. The remarkable strength of spider silk originates from the presence of micro-crystalline domains, formed by secondary interactions, and embedded in a flexible matrix. Secondary interactions like hydrogen bonding also hold a prominent role in man-made polymers. The exceptional material properties of nylon, for instance, are owed to the presence of hydrogen bonding between the polymer chains. The major aim of this thesis comprises the use of secondary interactions, especially multiple hydrogen bonding, in supramolecular polymers. In this chapter a concise review on 1) supramolecular polymers and 2) the supramolecular modification of polymers is given. A number of functional units that have been used as building blocks for supramolecular polymers is discussed.

1.2 Building Blocks for Supramolecular Polymers

Supramolecular polymers are defined as polymeric arrays of monomeric units that are brought together by reversible and highly directional secondary interactions, resulting in polymeric properties in dilute and concentrated solution as well as in the bulk. The monomeric units of the supramolecular polymers themselves do not possess a repetition of chemical fragments. The directionality and strength of the supramolecular bonding are important features of systems that can be regarded as polymers and that behave according to well-established theories of polymer physics.[5a,c] Most of these supramolecular polymers have the advantage of being reversible, making them, for instance, easily processable at elevated temperatures. Three main categories of supramolecular polymers can be distinguished: coordination polymers, polymers that are formed via π-π stacking of the monomeric units, and hydrogen bonded polymers. A few examples of supramolecular polymers based on π-π stacking and multiple hydrogen bonds will be discussed in this introduction, because the concepts on which they are based have a direct relevance to the topic of this thesis. Due to their strength, directionality and reversibility, hydrogen bonding interactions are very useful for the construction of supramolecular polymers. The strength of a single hydrogen bond depends on the donor and the acceptor properties of the components, and varies between 5 and 163 $kJ.mol^{-1}$.[8] A way to enhance the interaction between moieties is to implement the cooperativity of multiple hydrogen bonds. It was shown by Jorgenson[9] that the strength of an array of multiple hydrogen bonds not only depends on the number of hydrogen bonds but also on the additional secondary electrostatic interactions between the neighbouring donor and acceptor sites in the array. The first supramolecular polymer that self-assembles using multiple hydrogen bonds was reported by Lehn and co-workers.[10] The complementary groups are uracil and 2,6-diacylaminopyridine derivatives that interact to give a triply hydrogen bonded complex. The flexibility of the tartaric acid based spacer connecting two units ensures that the melting point of the complex is sufficiently low to allow the existence of a liquid crystalline phase. A compound containing a rigid spacer based on 9,10-dialkoxyanthracene is crystalline, on the other hand. However, when the compound is dissolved in 1,1,2,2-tetrachloroethane a birefrigent solution is obtained, which is indicative of lyotropic liquid crystallinity.

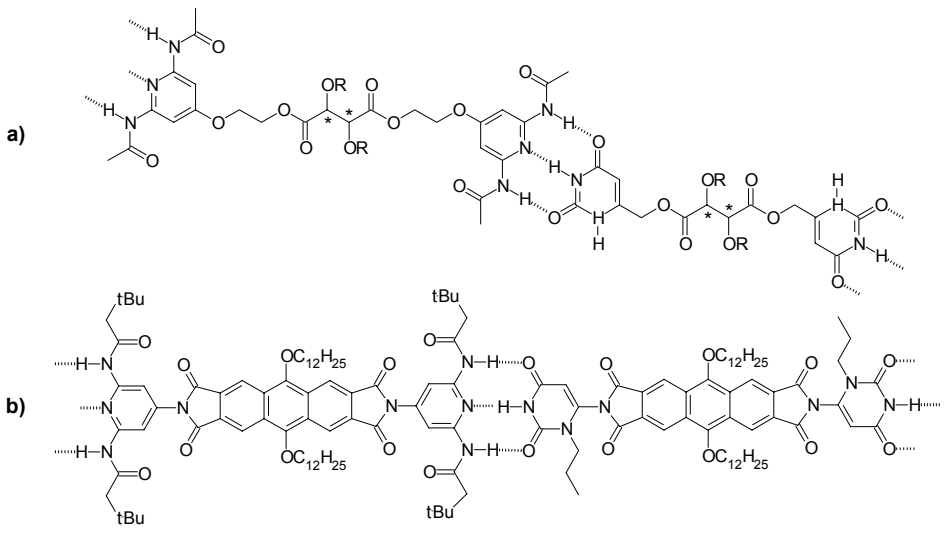


Figure 1.1: *Supramolecular polymers formed by triple hydrogen bonding between uracil and 2,6-diacylaminopyridine. a) with tartaric spacer giving thermotropic mesophases and b) with a rigid 9,10-dialkoxyanthracenic spacer exhibiting lyotropic mesophases.*[10]

Griffin has reported the use of a single hydrogen bond between carboxylic acids and pyridines to form liquid crystalline supramolecular polymers.[11,12] The complex (see Figure 1.2) forms thermoreversible three-dimensional networks that exhibit properties typical of low molecular weight compounds at high temperatures and of polymers at low temperatures. In contrast to the complex with tetrakis(4-pyridyl)pentaerythritol, the complex incorporating 2,2',6,6'-tetrasubstituted biphenyl moiety was found to be liquid crystalline.

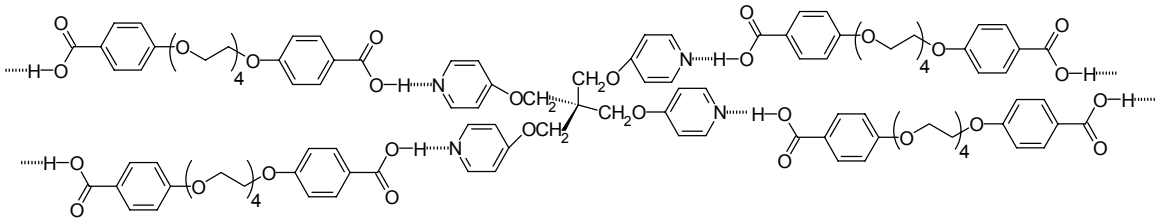


Figure 1.2: *Supramolecular network of Griffin et al. obtained by single hydrogen bonding between tetrakis(4-pyridyl)pentaerythritol and tertaethylene glycol bis(4-benzoic acid).*[11]

Unfortunately, the systems described above are not sufficiently stable to induce conventional polymer-like properties in the bulk and in solution. Theoretically, a K_a of at least 10^3 M^{-1} is needed in order to really have a polymer chain in solution (Figure 1.3).

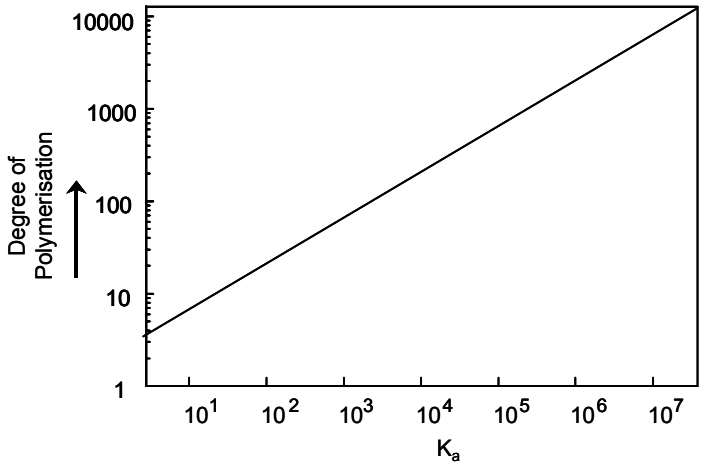


Figure 1.3: *Calculated degree of polymerisation of a supramolecular polymer as a function of the endgroup association constant (K_a) for a 1 M solution of a bifunctional monomer.*

Felix Beijer and Rint Sijbesma of our laboratory have developed units that dimerise via an array of four hydrogen bonds.[13] These include the ureido-*s*-triazine unit that dimerises via a DADA array of hydrogen bonds, and the ureidopyrimidinone unit featuring a DDAA-array of hydrogen bonding sites (Figure 1.4). The association constant of the ureido-*s*-triazine unit in chloroform was determined with IR spectroscopy and was estimated to be 10^4 l.mol^{-1}.[13b-c] With fluorescence spectroscopy the association constant of the ureidopyrimidinone unit in chloroform was calculated to be 6.10^7 M^{-1} chloroform, corresponding to a ΔG of –44 kJ.mol^{-1},[14] approximately 1/8th of the strength of a covalent C-C bond. The preexchange lifetime of the dimers was determined to be 170 ms at 298 K in chloroform. It was found that the ureidopyrimidinone unit is also present in the ureido-pyrimidin-4-ol (enol) tautomeric form, which dimerises in a DADA-array of hydrogen bonding sites.

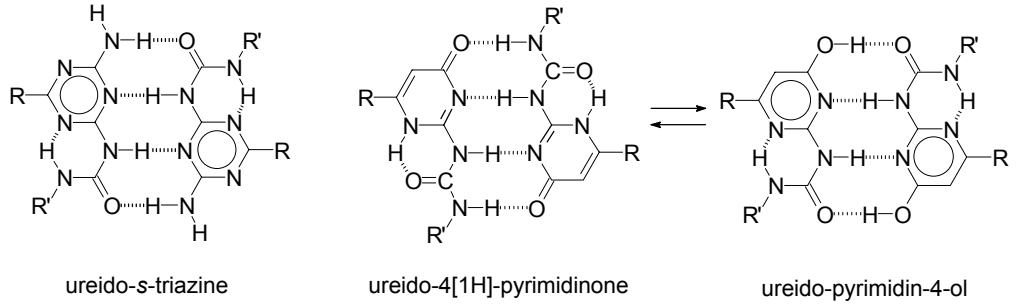


Figure 1.4: *The ureido-s-triazine unit in its dimeric form with a DADA-array of hydrogen bonding sites, and the two tautomeric forms of the ureidopyrimidinone dimers: dimerisation of 4[1H]-pyrimidinone in a DDAA-array and dimerisation of ureido-pyrimidin-4-ol in a DADA-array.*

In particular the ureidopyrimidinone unit has been used successfully for the preparation of supramolecular polymers exhibiting polymer-like properties in bulk and in solution.[13a] Felix Beijer and Luc Brunsveld have synthesised a bifunctional compound that consists of two ureidopyrimidinone units connected via a hexamethylene spacer (see Figure 1.5). Highly viscous solutions were obtained in chloroform, and an elastic solid was obtained when the solvent was removed. However, the compound crystallise after a few days. Brigitte Folmer has synthesised a bifunctional compound with a 2,2,4-trimethylhexamethylene spacer, featuring completely different properties.[13a] The material exhibits viscoelastic properties and does not crystallise.

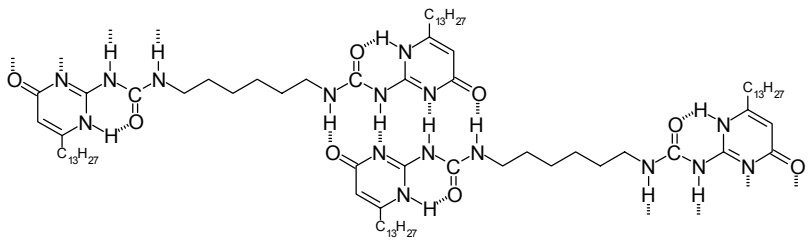
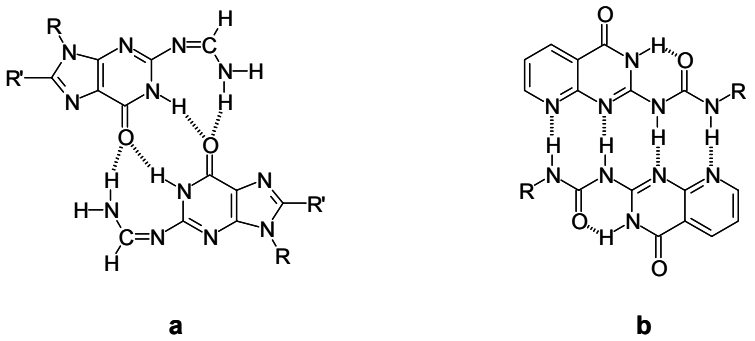


Figure 1.5: *First supramolecular polymer based on quadruple hydrogen bonding units.*[13a]

Molecules, that exhibit a similar, or an even higher strength, were developed by Sessler and Wang, as well as by Zimmerman and Corbin. They have obtained extremely stable dimers formed by quadruple hydrogen bonds. Sessler's dimers are based upon quadruple hydrogen bonded units of a guanidine derivative.[15] Zimmerman and Corbin described a heterocycle designed to contain a self-complementary AADD hydrogen-bonding array.[16]



a **b**

Figure 1.6: *Dimers of quadruple hydrogen bonding units developed by* **a**) *Sessler and Wang*[15] *and* ***b)*** *Zimmerman and Corbin.*[16]

Recently, Gong[17] reported an extremely stable dimer formed via an array of six hydrogen bonds; the association constant was estimated at $1.3x10^9$ $l.mol^{-1}$. Brigitte Folmer has achieved a step towards the formation of an extremely stable dimer that is held together by eight hydrogen bonds.[18] The lifetime of the unit, which is based on two ureidopyrimidinones with a meta-xylylene spacer, is determined to be at least 44 minutes. Ghadiri and his coworkers have obtained nanotubes based on cyclic alternating D,L-peptides that are stacked via eight hydrogen bonds.[19,20] By adjusting the size of the cyclic monomer the internal diameter of the tube was controlled.

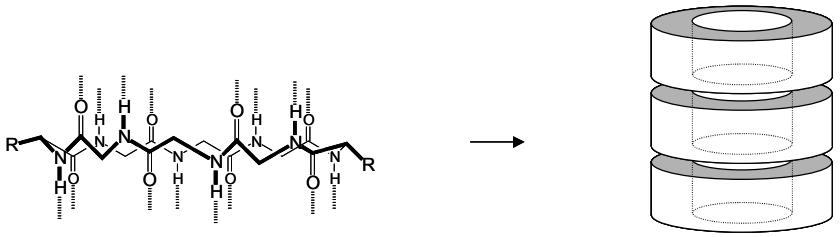


Figure 1.7: *Self-assembled nanotubes based on an eight-membered cyclic peptides.*[20]

Hydrogen bonding in combination with π-stacking interactions have been used to induce a high degree of order in self-assembled systems. For example, tubular polymeric structures were presented by Gottarelli *et al.*[21] They have shown the formation of chiral polymeric columns based on deoxyguanosine in water. These columns consist of stacked discs, which are formed by the association of four guanosine derivatives via hydrogen bonds.

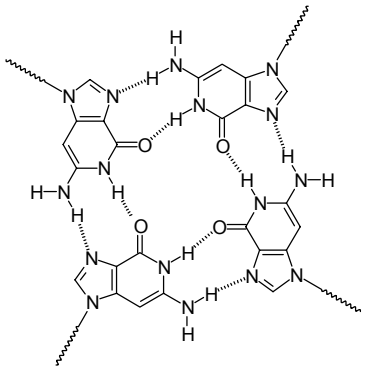


Figure 1.8: *The assembly of a cyclic tetramer based on deoxyguanosine derivatives. The tetramers stack on top of each other in tubular polymeric structures.*[21]

Reinhoudt *et al.* reported on the self-assembly of calix[4]arenes and 5,5-diethylbarbituric acid (DEB) in disc-like nanostructures.[7,22] In addition, the formation of infinite rod-like stacks was observed by self-assembly of calix[4]arene dimelamine **1** with

calix[4]arene dicyanurate **2**.[7,23] In this way the "closed" form is prevented, and only the isomeric "open" form is possible (see Figure 1.9). The noncovalent polymerisation via the complementary top and bottom sites resulted in linear rod-like structures.

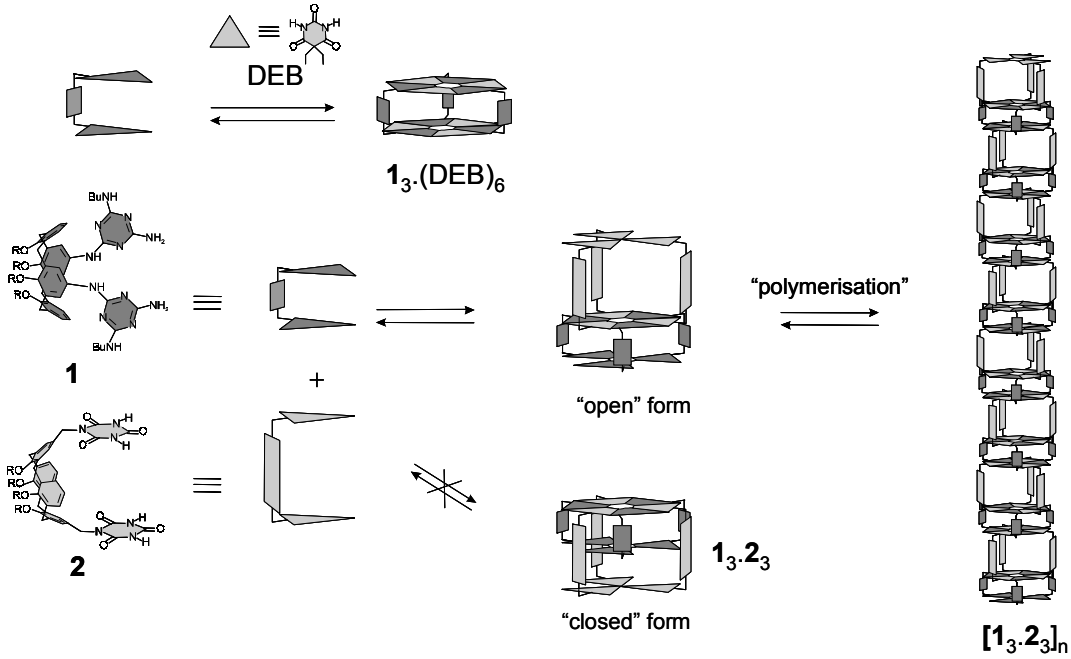


Figure 1.9: *Nanorods based on the cyclic hydrogen bonding motif of cyanuric acid and melamine in bifunctional calix[4]arene derivatives **1** and **2**.*

3,4,5-Trialkoxybenzoic acid derivatives are popular building blocks in self-assembly, because the combination of flexible side chains and a rigid core helps to bring about the formation of columnar structures. The use of this building block was pioneered by Percec and co-workers.[24] They have studied the aggregation behaviour of amphiphiles based on trialkoxybenzoic acid. Due to the combination of the hydrophobic alkoxy chains and the hydrophilic carboxyl group, a wedge-shaped molecule was obtained that forms a hexagonal columnar structure, exhibiting liquid crystalline properties. In these columns the hydrophilic benzoate groups are located in the centre of the disc. Based on these trialkoxyphenyl wedges C_3-symmetric discotic molecules were synthesised by Anja Palmans.[25] The discotic molecules exhibit thermotropic and lyotropic properties. Due to π-stacking in combination with intermolecular hydrogen bonding of the aromatic core columnar structures still persist in dilute solutions. Luc Brunsveld[26] described similar C_3-symmetric discotic molecules, but bearing peripheral ethylene oxide chains. He found that these molecules form columnar

aggregates in polar media. Many more examples exist of columnar aggregates formed by π-stacking of discotic molecules and have been reviewed by Guillon.[27,28]

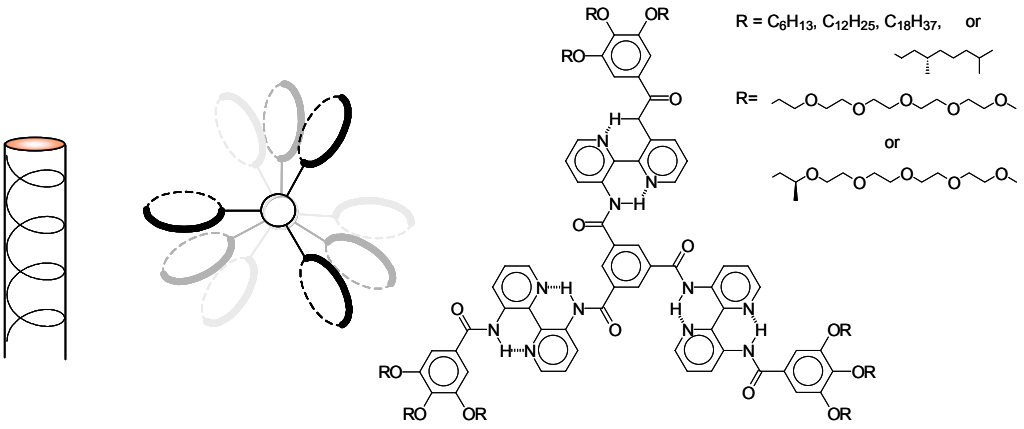


Figure 1.10: *C_3-Symmetric discotic molecules with peripheral alkoxy chains synthesised by Palmans[25], and C_3-symmetric discotic molecules with peripheral ethylene oxide tails studied by Brunsveld.[26]*

1.3 Supramolecular Modification of Polymers

Apart from single molecules also polymers can be provided with supramolecularly associating groups. In principle the properties of low molecular weight polymers can be improved significantly by the introduction of associating end-groups. The advantage of using secondary interactions to increase the "virtual" molecular weight is that these materials would exhibit good mechanical properties at low temperatures but would have a low melt viscosity at high temperatures. Polymers have not only been modified to enhance the material properties, but also to induce liquid crystallinity.

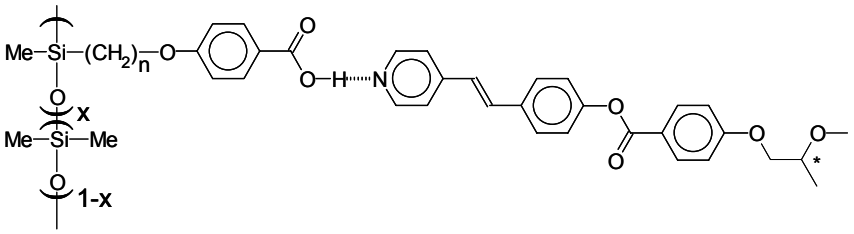


Figure 1.11: *Side chain liquid crystalline polymer obtained from blends of polysiloxane copolymer containing benzoic acid moieties and non-mesogenic optically active stilbazole derivatives.[29]*

Kato and Fréchet have pioneered the modification of polymers with pendant binding sites in order to enhance or induce liquid crystallinity when blended with low molecular weight compounds possessing a complementary binding site.[29] In this way a mesogenic unit is constructed via specific hydrogen bonding. For instance, they have reported on the complexation of benzoic acid functionalised polysiloxanes or polyacrylates with stilbazoles through a single hydrogen bond, which led to the formation of a liquid crystalline material (see Figure 1.11).

Stadler and co-workers[30] have constructed reversible networks of polyisobutene by functionalising the telechelic polymer with 4-urazoylbenzoic acids. Aggregation of the end groups results in double hydrogen bonding, as shown in Figure 1.12; spectacular changes with respect to material properties were found.

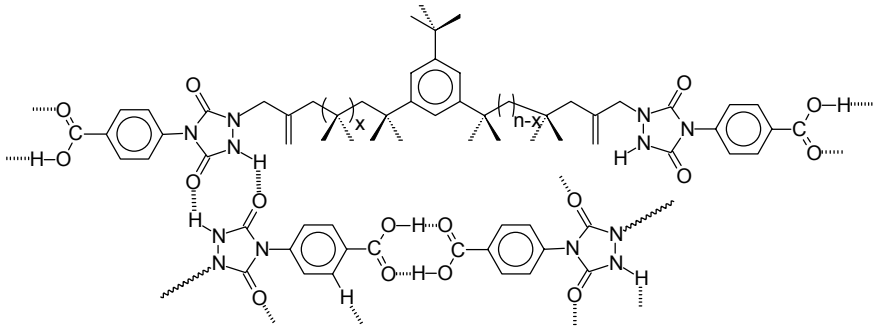


Figure 1.12: *Physically cross-linked telechelic polyisobutylene with 4-urazoylbenzoic acid as a hydrogen donor and acceptor.*[30]

Lillya[31] has shown that small changes in polymer properties result when poly(THF) is capped with carboxylic acid containing functionalities that are capable of dimerising. The changes in properties were ascribed to the formation of large crystalline domains of the end groups. In these polymers, like in the urazole modified polyisobutylene of Stadler,[30] other interactions than hydrogen bonds also play a role, and cause further aggregation to give microcrystalline domains. Lillya and co-workers have also observed a change in polymer properties for end-capped polydimethylsiloxanes containing benzoic acid groups. Lange[32] has described the use of triple hydrogen bonding interactions between the alternating copolymer of styrene and maleimide with melamine (Figure 1.13a), and with the copolymer of styrene and 2,4-diamino-6-vinyl-*s*-triazine (Figure 1.13b). Lange obtained a three-dimensional

polymer network that is formed by the interaction of one melamine molecule with three maleimide units of the copolymer. The introduction of maleimide and 2,4-diamino-*s*-triazine into various polymers results in a homogenous polymer blend. That the role of the triple hydrogen bonds is crucial to guarantee a complete miscibility was demonstrated by the use of *N*-methyl substituted polyimides that prevent the triple hydrogen bonding formation. In this case an inhomogeneous phase-separated polymer blend was obtained.

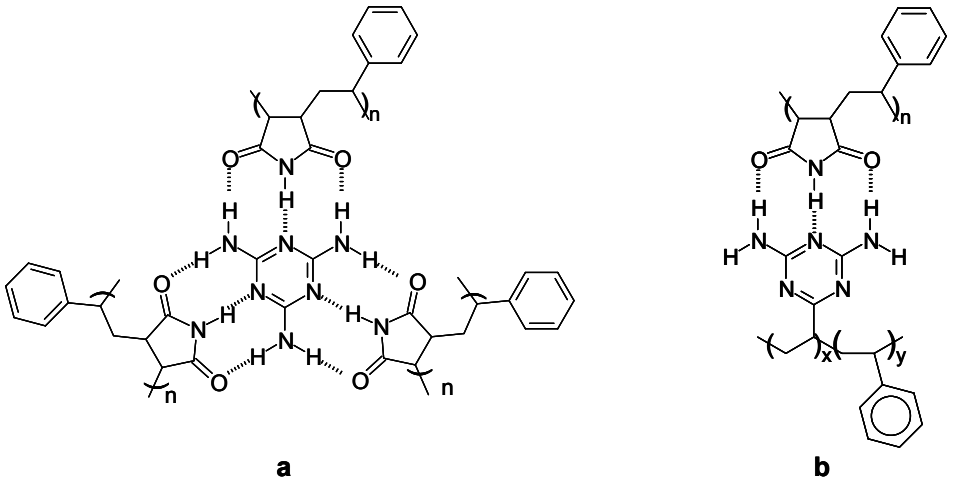


Figure 1.13: *Supramolecular networks of copolymers of styrene and maleimide with **a**) melamine, and with **b**) copolymer of styrene and 2,4-diamino-6-vinyl-s-triazine, formed by triple hydrogen bonds.*

In order to extend the scope of this study, Lange investigated the possibility to obtain reversible polymer networks by functionalising a commercially available polymer with quadruple hydrogen bonding ureidopyrimidinone units.[13,32,33] He showed that a reversible polymer network is obtained which does not require any kind of phase separation in order to have useful material properties. Various commercially available telechelic polymers have been functionalised with ureidopyrimidinone units by Brigitte Folmer.[34,35]

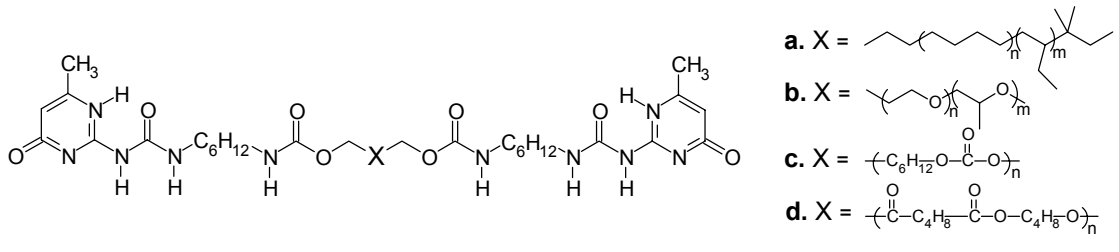


Figure 1.14: *End-group functionalisation of various commercially available polymers.*[34,35]

The chain extension via the array of four hydrogen bonds results in a dramatic change of the material properties. With rheology and DMTA measurements of functionalised poly(ethylene/butylene) (Figure 1.14a), for instance, a rubber plateau at 5.10^6 Pa was found, indicating that the "virtual" molecular weight is extremely high.

Recently, Coates *et al.* have investigated the utility of ureidopyrimidinone as reversible crosslinks in polyolefin elastomers.[36] Random incorporation of small amount of ureidopyrimidinone in amorphous polyolefins resulted in a material with properties completely different from those of the polyolefin homopolymers. Recognition interactions between polystyrene with varying donor-acceptor-donor hydrogen bonding side groups and guest flavin were studied by Rotello.[37] He and his coworkers have shown that the efficiency of recognition between the grafted polystyrene and the guest can be controlled by adjusting the balance between intra- and intermolecular interactions. In addition they have trapped this host-guest complexes in polystyrene films with the goal to create supramolecular devices.

1.4 Aim and Outline of the Thesis

In the previous sections the use of hydrogen bonding and π-stacking in supramolecular polymers was illustrated. The aim of the work described in this thesis is to combine these interactions in supramolecular polymers that fold into a well-defined conformation (see Figure 1.15).

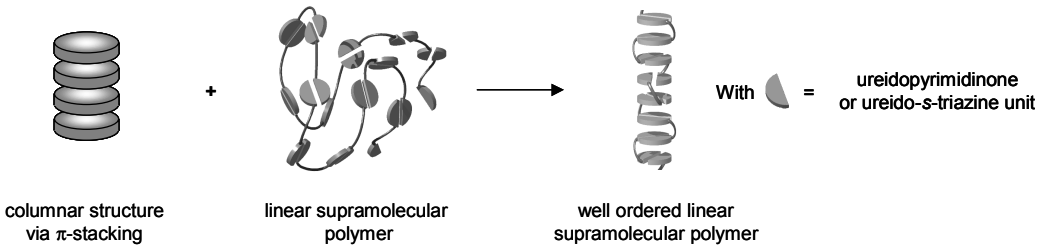


Figure 1.15: *The combination of π-stacking and hydrogen bonding for well-ordered supramolecular polymers.*

These interactions are also used to prepare a completely new class of supramolecular polymers: *supramolecular block copolymers*, in which one block is a conventional macromolecule and the other block is a supramolecular polymer. Issues that are raised concern the dynamics and thermodynamics of such systems: is the new architecture a block

copolymer or a polymer blend? In order to be able to study these novel block copolymers, endgroup functionalised polymers have to be prepared. This principle is schematically depicted in Figure 1.16.

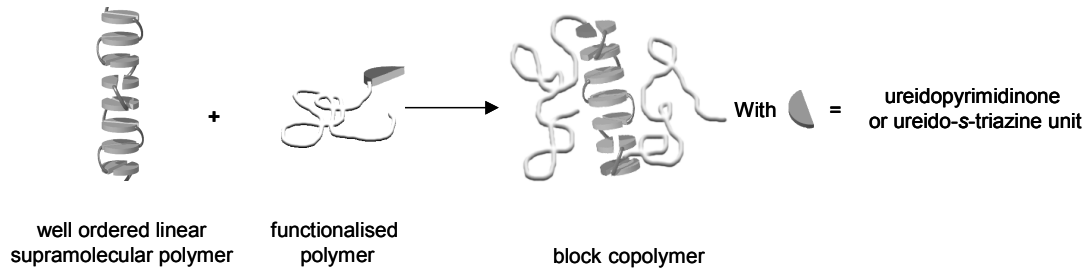


Figure 1.16: *Schematic representation of supramolecular systems formed via quadruple hydrogen bonds of ureidopyrimidinone or ureido-s-triazine units.*

In chapter 2 are described the full details of the synthesis and properties of functionalised hexamethyltrisiloxane and telechelic poly(dimethylsiloxanes), in which the assembly of ureidopyrimidinone end groups leads to strong modification of their properties. Throughout this chapter, the properties of the bifunctional materials are compared with those of analogues in which quadruple hydrogen bonding of the functionalities is prevented by an O-benzyl-protecting group. In chapters 3 and 4 the possibility is investigated to obtain highly ordered structures by combining the concept of linear supramolecular polymers formed by bifunctional molecules as described in chapter 2, with the columnar organisation of trialkyloxyphenylureido-*s*-triazine. The design is based on the expectation that covalent linkage of two trialkyloxyphenylureido-*s*-triazine moieties through an alkyl spacer would induce the formation of linear self-assembled polymers that would adopt a well-defined secondary structure. In chapter 3 the synthesis and the thermal behaviour of monofunctional and bifunctional compounds bearing the trialkyloxyphenylureido-*s*-triazine moieties is presented. The effects of the linker in bifunctional compounds, and the effect of extending the rigid core of the dimeric unit with a phenyl or a pentafluorphenyl substituent, on the stability of the mesophase are studied. Chapter 4 deals with the aggregation of mono- and bifunctional ureido-*s*-triazine compounds described in chapter 3. Hydrogen bonding together with π–stacking and solvophobic interactions are employed in order to obtain superstructures that persist in solution. For the study of the aggregation of the synthesised molecules, different techniques like rheology, UV and CD spectroscopy, and SANS were used. Compounds based on the 2-ureido-4-pyrimidinone unit were expected to give more stable columns in apolar

solutions due to the higher association constant of this unit. The synthesis and the aggregation behaviour of monofunctional and bifunctional ureidopyrimidinones are studied in chapter 5. The effects of length and preorganisation of the spacer on the aggregation behaviour is investigated. In addition we have investigated the possibility to synthesise a bifunctional molecule that contains a chiral (–)-cystine spacer, and obtain a column with a preferred handedness by transfer of chirality from the chiral spacer into the phenyl-pyrimidinone core. Finally, in chapter 6 the synthesis and characterisation of monofunctional poly(ethylene/butylene) and polystyrene, and bifunctional poly(ethylene/butylene) are described. This chapter focuses on the assembly of triblock and multiblock copolymers from functionalised polystyrene or functionalised hydrogenated polybutadiene copolymer and a supramolecular polymer introduced in chapter 3.

1.5 References and Notes

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2

Supramolecular Polymers from Linear Telechelic Siloxanes*

Abstract

*Telechelic oligo- and poly(dimethylsiloxanes) provided with two ureidopyrimidinone (Upy) functional groups, have been prepared via a hydrosilylation reaction. The compounds have been characterised in solution by ^{1}H-NMR spectroscopy and viscometry, and in the solid state by ^{1}H-NMR and ^{13}C-NMR, FTIR spectroscopy, and rheology measurements. The measurements show that the Upy groups in **1** and **2** are associated via quadruple hydrogen bonds in a DDAA array, whereas the O-benzyl-protected analogues **1-Bn** and **2-Bn** do not associate, and therefore, behave like low molecular weight compounds. The amorphous bifunctional molecules **1** and **2** behave like entangled polymers, whose mechanical behaviour is characterised by a rubber plateau with a modulus of approximately 10^{5} Pa, and a relatively high activation enthalpy for stress relaxation (ΔH = 127 kJ.mol^{-1} and 54 kJ.mol^{-1} for **1** and **2**, respectively). The degree of polymerisation of **1** and **2**, was estimated to be above 100 for **1** and approximately 20 for **2**, and is strongly dependent on the amount of monofunctional impurities that can act as chain stopper.*

* Part of this work has been published: a) Hirschberg, J.H.K.K., Beijer, F.H., van Aert, H.A., Magusin, P.C.M.M., Sijbesma, R.P., Meijer, E.W. *Macromolecules* **1999**, *32*, 2696. b) Sijbesma, R.P., Beijer, F.H., Brunsveld, L., Folmer, B.J.B., Hirschberg, J.H.K.K., Lange, R.F.M., Lowe, J.K.L., Meijer, E.W. *Science* **1997**, *278*, 1601.

2.1 Introduction

The physical properties of linear polymers and organic molecules are strongly modified when they are provided with associating end groups.[1-31] When the end groups associate through non-directional interactions, like e.g. coulomb forces in telechelic ionomers[1], and hydrophobic interactions in hydrophobically endcapped urethanes (HEUR),[2] clusters of end groups are formed, and a reversible network results. These materials exhibit interesting and useful rheological properties. Polymers with partly directional hydrogen bonding end groups have also been studied. Stadler studied in detail the effect of hydrogen bonding of the functional groups in urazole-modified polyolefins.[3] In these materials, the hydrogen bonding groups aggregate in a cooperative fashion to form ordered clusters, leading to thermoplastic elastomers. Lillya has shown that modest changes in rheological properties result when poly(THF) is capped with carboxylic acid containing functionalities, capable of dimerisation.[4] The changes in properties were ascribed to the formation of large crystalline domains of end groups. In these polymers, like in the urazole-modified polyisobutylene, other interactions next to hydrogen bonds play a role as well, and cause further aggregation to give microcrystalline domains.

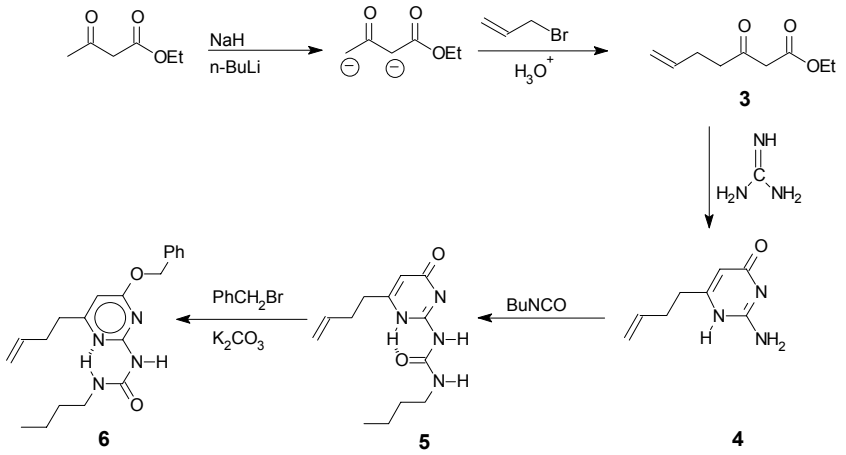
Polymers in which the end groups exclusively form dimers, but do not aggregate further, are of great interest. Telechelic polymers with such end groups would form long chains by concatenation of molecules. When the aggregation of end groups is sufficiently strong and directional, even low molecular weight telechelic building blocks ($M_w < 10^3$) would give materials in which chain entanglements give rise to polymer-like properties, such as rubber elasticity. Although the directionality required for specific dimerisation is inherently present in hydrogen bonds, the strength of this type of interaction is limited (an average value of –7.9 kJ/mol for a single hydrogen bond in chloroform is reported[5]), and high degrees of polymerisation are not readily achieved, unless anisotropy of the medium in liquid crystalline material imposes end-to-end association.[6] Examples of linear self-assembly in liquid crystalline phase are reported by Lehn, who used triple hydrogen bonding between diaminopyridine and uracil end groups,[7] and by Griffin, who studied complexes of diacids with bis- and tetrapyridyls.[8] Kato and Fréchet have described liquid crystalline polymers derived from pyridine-carboxylic acid couples.[9,10] Flexible spacer units, and stronger hydrogen bonding interactions than the ones used by Kato, Griffin and Lehn are required to

obtain isotropic polymer melts and solutions with high degrees of polymerisation (DP). It was shown[11] that a self-complementary hydrogen bonding unit based on ureido-pyrimidinone (UPy) features dimerisation constants exceeding 10^6 M^{-1} in chloroform,[12] and it was found[13,14] that low molecular weight bifunctional molecules containing this functional group in many ways behave like polymers.

The present chapter describes the full details of the synthesis and properties of telechelic poly(dimethylsiloxanes) **1** and **2**, in which the assembly of UPy end groups leads to strong modification of their properties. Even in compound **1**, with only 13 atoms in the main chain of the spacer, many properties that are typical for polymers are observed. Throughout this chapter, the properties of the bifunctional materials are compared with those of analogues **1-Bn** and **2-Bn**, in which quadruple hydrogen bonding of the functionalities is prevented by an O-benzyl protecting group.

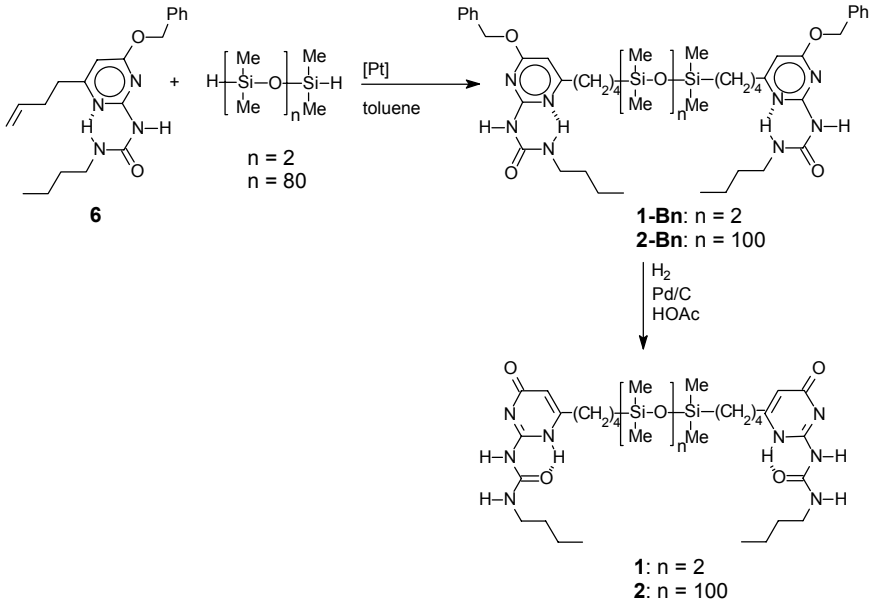
2.2 Synthesis

Because telechelic hydride-terminated dimethylsiloxanes of various lengths are commercially available compounds, that can be functionalised in high yields by a hydrosilylation reaction with alkenes,[15] telechelic siloxanes with two different lengths were prepared by using the 6-(3-butenyl)-substituted UPy **5** and its O-benzyl protected derivative **6**. These compounds were synthesised according to Scheme 2.1.



Scheme 2.1: *Synthesis of 6-(3-butenyl)-2-butylureido-4[1H]-pyrimidinone **5** and 4-benzyloxy-6-(3-butenyl)-2-butylureidopyrimidine **6**.*

First, the dianion of ethyl acetoacetate was alkylated with allyl bromide,[16] followed by condensation of the resulting β-keto ester with guanidinium carbonate. The product of this reaction, isocytosine **4**, was reacted with *n*-butylisocyanate to yield UPy **5**, which in turn was O-benzylated in moderate yield with benzyl bromide in DMF to give **6**. Attempts to couple compound **5** with hydride terminated dimethylsiloxanes were not very successful. The ^{1}H-NMR spectrum of the crude reaction mixture showed that a side product was formed in which the siloxane was attached to the oxygen atom of the enol tautomer of **5**. This side product could not be separated from the product and, therefore, O-benzyl derivative **6** was used in the hydrosilylation reaction.



Scheme 2.2: *Synthesis of telechelic UPy functionalised siloxanes **1** and **2**.*

Hydrosilylation reactions of **6** with α,ω-bishydride terminated hexamethyltrisiloxane or polydimethylsiloxane (M_n = 6000 g/mol) were carried out in toluene under a dry nitrogen atmosphere, using platinum-divinyltetramethyldisiloxane complex as a catalyst (Scheme 2.2). A small excess of **6** was employed to ensure complete conversion of the silane end groups. During the reaction, the disappearance of Si-H signals at 4.7 ppm was monitored by ^{1}H-NMR spectroscopy. Reactions were complete after 48 h. Compound **1-Bn** was purified by column chromatography followed by recrystallisation from hexane, while compound **2-Bn** was triturated several times with methanol in order to remove highly soluble **6**. End group analysis of **2-Bn** by ^{1}H-NMR showed that due to fractionation in the trituration procedure n

had increased from 80 to 100 repeat units. Hydrogenolysis of **1-Bn** and **2-Bn** was performed in THF/ethanol using activated palladium on carbon as a catalyst. Compound **1** was purified by column chromatography followed by recrystallisation from ethyl acetate, yielding analytically pure white needles in 85% yield with a melting point of 112 °C. Purification of compound **2** using trituration was not successful. Therefore, the crude product was dissolved in a mixture of chloroform and ethanol, from which the chloroform was selectively evaporated at low vacuum, resulting in a precipitation of the product as a viscous oil. Although NMR and IR showed only resonances of pure product, it seems reasonable to assume that **1** is more pure than **2**. The reaction scheme used here proves to represent a general route in which reasonable amounts of telechelic polysiloxanes can be made, from which the precursors can be used as non-sticky model compounds.

2.3 Hydrogen Bonding of the Functional End Groups

Previous studies[9] established that the UPy functional group dimerises with high dimerisation constants in solvents like $CDCl_3$ or toluene. In the solid state, the molecules are also present as dimers. However, the exact mode of association was shown to be dependent on the solvent and substituents. Specifically, the functional group may direct the dimers of being either a keto tautomer or of an enol tautomer.

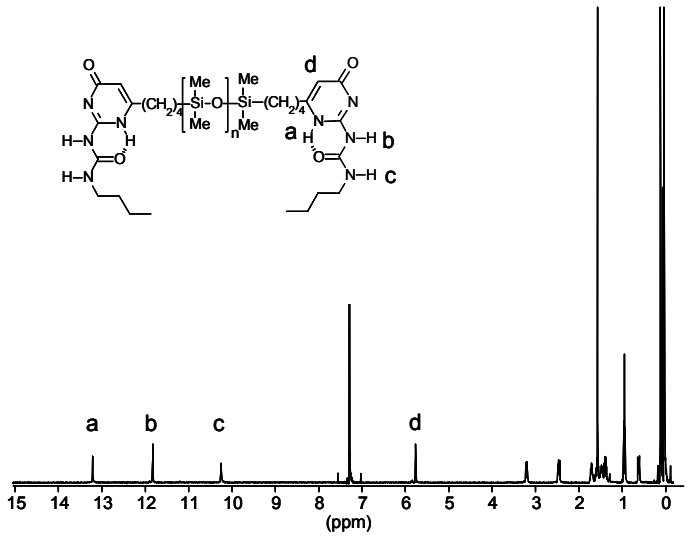


Figure 2.1: *^{1}H-NMR spectrum of compound **1** in $CDCl_3$. The positions of the NH signals at low field indicate that the functional groups are dimerised in the keto-tautomeric form.*

Each of these tautomers is easily identified by characteristic features in the ^{1}H-NMR and FTIR spectra. Consequently, it is relatively straightforward to establish the extent and mode of association of the UPy groups in **1** and **2** in solution and in bulk. The ^{1}H-NMR spectrum of compound **1** in $CDCl_3$ is shown in Figure 2.1. The positions of the NH signals at 13.2, 11.8, and 10.2 ppm, along with a pyrimidinyl resonance at 5.8 ppm indicate that the functional groups are dimerised, and that the molecules are exclusively present in the keto tautomeric form.

IR spectroscopy is very sensitive for detecting changes in hydrogen bonding of the UPy group. The FTIR spectrum of the keto form of the ureido-pyrimidinone shows a characteristic band at 1696 cm^{-1} attributed to the pyrimidinone carbonyl stretch vibration, which is absent in the enol tautomer. The spectra in Figure 2.2, of **1** in $CDCl_3$ solution, of crystalline and amorphous **1** and of amorphous **2**, display a band at this characteristic position, showing that the UPy functionalities remain dimerised in the keto tautomer in all these phases.

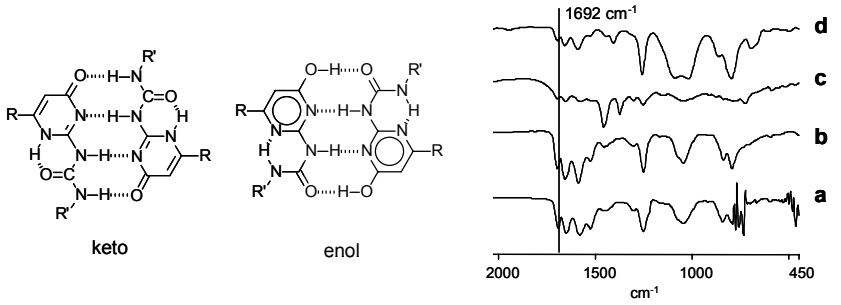


Figure 2.2: *Left: Modes of dimerisation of the UPy functional group via quadruple hydrogen bonding: Keto tautomer and enol tautomer. Right: FTIR spectra of compound **1** in $CDCl_3$ solution (a); amorphous **1** (b); crystalline **1** (c); amorphous **2** (d). The characteristic band at 1696 cm^{-1} of the pyrimidinone carbonyl stretch vibrations is indicative for the presence of the keto tautomer.*

2.4 Thermal Properties

Several properties distinguish polymers from low molecular weight compounds. Among these are the propensity to form glasses and pronounced differences in the rheological behaviour. Phase behaviour of compounds **1** and **2** was investigated with DSC. The thermal behaviour of compound **1** shows pronounced effects of hydrogen bonding (Figure 2.3). When obtained by precipitation from solvent, compound **1** is crystalline, with a

melting point of 112 °C, as shown by a first heating scan. A subsequent cooling and heating scans reveal a glass transition at 25 °C. Crystallisation of **1** from the bulk is remarkably difficult, since even annealing at 100°C for 3 hours does not result in reappearance of the melting isotherm.

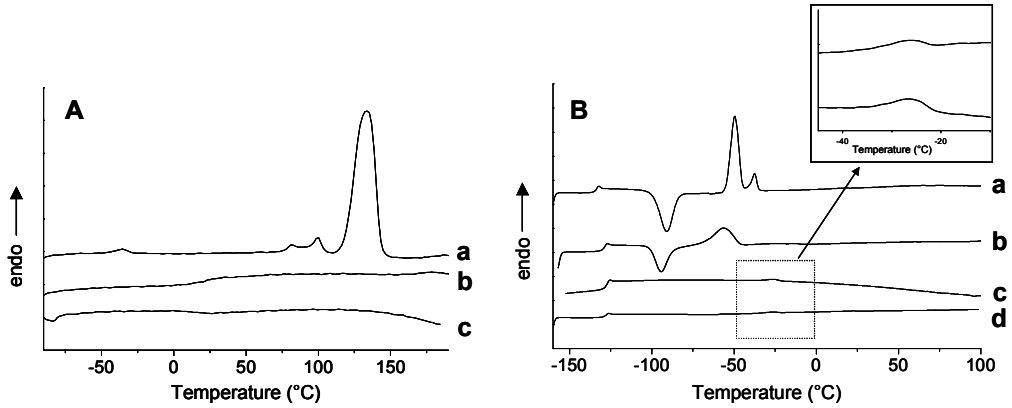


Figure 2.3: *A) DSC traces of compound **1** at a heating rate of 20 °C/min.; 1st heating run (a), 2nd heating run (b), 1st cooling run (c). B) DSC traces of PDMS (a) and telechelic PDMS derivatives at a heating rate of 20 °C/min.; Compound **2-Bn** (b); Compound **2**, second heating run (c); Compound **2** after annealing for 2 h at –60 °C (d).*

In the compounds with the polymeric spacers, it is instructive to compare the differences between the protected and unprotected material. Compound **2-Bn**, which cannot associate via quadruple hydrogen bonds, shows a DSC thermogram (Figure 2.3B, trace b) similar to that of unfunctionalised PDMS, with a T_g at –129 °C, crystallisation at –75 °C and subsequent melting at –50 °C. Hydrogen bonded product **2**, on the other hand displays different behaviour. A glass transition is present at the same temperature as in **2-Bn**, but the strong crystallisation exotherm of the siloxane spacers is absent (Figure 2.3B, trace c). Crystallisation does not occur when **2** is annealed at –60 °C for 2 h (Figure 2.3B, trace d). A small but significant endotherm is observed at –25 °C, which has a much lower ΔH (0.8 J/g) than the melting endotherm of **2-Bn** (13.5 J/g).

2.5 Solid-state NMR Spectroscopy

The crystalline and amorphous phases of **1** were characterized further by solid-state ^{13}C and ^{1}H-NMR spectroscopy. The ^{13}C-NMR spectrum of the amorphous phase shows a

broadening of the lines relative to the crystalline phase. The width of the line at 105 ppm remarkably increases from 90 to 300 Hz. Based on its chemical shift and fast cross-polarisation behaviour (T_{CH} = 30 μs) this resonance is assigned to the protonated hetero-aromatic carbon at position **d** in the molecule structure (Figure 2.1). Its measured transverse relaxation time T_2 in the amorphous phase is 3.7 ms, which corresponds to only a minor homogeneous contribution of 86 Hz to the total line width. Apparently, the resonance at 105 ppm is mainly affected by strong inhomogeneous broadening. This probably reflects heterogeneous packing effects in the amorphous material, indicating that the regular stacking of hydrogen bonding units in the crystal is hardly present in the amorphous phase. This picture is confirmed by broadening of the other resonances in the spectrum.

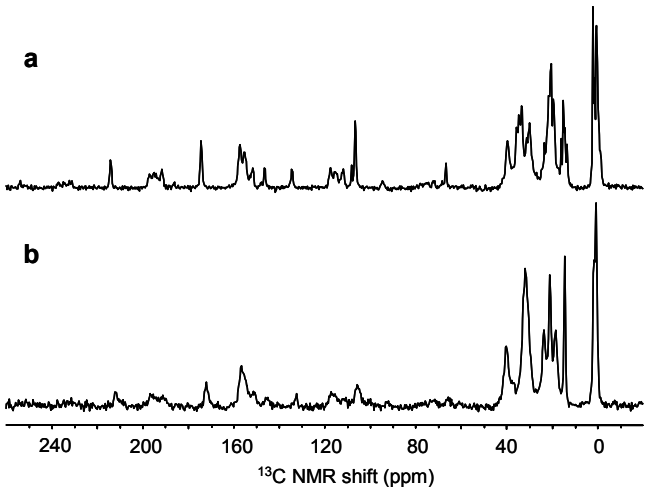


Figure 2.4: *CPMAS ^{13}C-NMR spectrum of crystalline **1** (**a**) and amorphous **1** (**b**). The sharper signals of the crystalline material as compared to those of the amorphous material reflect the perfect regular packing in the crystalline phase.*

To compare the molecular mobility of **1** in the crystalline and in the amorphous phase, WISE experiments were carried out. This NMR technique links the capacity of ^{13}C-NMR to resolve chemically inequivalent ^{13}C nuclei with the power of ^{1}H-NMR to yield mobility information by combining the two in a two-dimensional correlation experiment[17]. A horizontal trace in the WISE spectrum in Figure 2.5 at the vertical position of a specific ^{13}C resonance shows the NMR line shape of the protons within 5 Å distance of the selected carbon. Residual molecular motions in organic materials at a time scale ≤ 10^{-5} s cause narrowing of the proton line. The wider the proton line shape, the more rigid the corresponding part of the molecule.

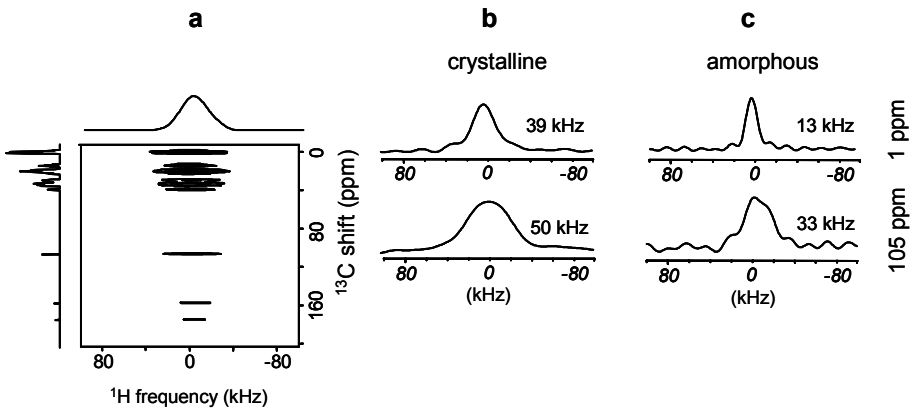


Figure 2.5: *Two-dimensional WISE spectrum of crystalline **1** correlating ^{1}H-NMR lineshapes to ^{13}C resonance positions in the MAS spectrum (a); horizontal traces at 1 and 105 ppm for the crystalline modification of **1** representing the proton lineshape of the methyl groups in the siloxane spacer, and the C-H proton in the UPy hydrogen bonding unit, respectively (b); Same two traces for the amorphous material (c); Linewidths at half height as determined from gaussian lineshape fitting are indicated.*

The four traces shown in Figure 2.5 illustrate the line shapes of the proton of the heterocycle in the hydrogen bonding units and the methyl groups of the siloxane spacers in the crystalline and amorphous phase. The line shapes show that the methyl groups are more mobile than the UPy groups both in the crystalline and amorphous phase, and that the amorphous material is characterised by a higher mobility of both the flexible and the more rigid parts of the molecule, as expected from the increased free volume. Other types of ^{13}C and ^{1}H-NMR relaxation confirm the increased molecular mobility in amorphous relative to the crystalline material. For instance, proton $T_{1\rho}$ values were measured via the ^{13}C resonances after cross-polarisation. Due to spin diffusion, no distinction between spacers and hydrogen bonding units can be made. The proton $T_{1\rho}$ of amorphous **1**, being 5.5 ms, is much smaller than that of the crystalline material, ca. 150 ms, indicating a strongly increased mobility in the 10^{-4} s range. Averaged by the spin diffusion, these proton $T_{1\rho}$ values predominantly reflect the mobility of the proton rich siloxane spacers and alkyl side groups. To specifically study the mobility of separate hydrogen bonding units, ^{13}C transverse relaxation (T_2) of the two modifications of **1** was compared. In contrast to various sorts of proton relaxation, ^{13}C relaxation times reflect more localised features of molecular fragments. The values for the sp_2 resonances in amorphous **1** are about half as large as for its crystalline modification. E.g., the ^{13}C T_2 value of the carbonyl resonance in the hydrogen bonding unit is 3.6 ms in the amorphous, and 9.4 ms in the crystalline material. A major cause for T_2 relaxation of the sp_2

resonances with their large chemical shift anisotropy is probably rotational mobility in the range ≤ 10^{-3} s. This indicates that in the amorphous material the hydrogen bonding units have a high mobility as well.

2.6 Solution Viscosity

The viscosity behaviour of telechelic siloxane **1** differs strongly from its protected precursor **1-Bn** in $CHCl_3$ solution. The differences become clear in a double logarithmic plot of the specific viscosity $\eta_{sp} = (\eta / \eta_{solvent})-1$ against the concentration (Figure 2.6).

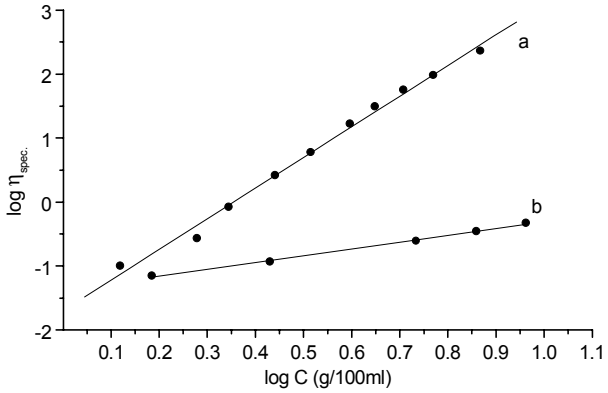


Figure 2.6: *Specific viscosities of compounds **1** (a) and **1-Bn** (b) in $CHCl_3$ versus concentration. The measurements were performed at 20 °C.*

The viscosity of **1** is significantly higher at all concentrations, and has a much higher concentration dependence than the viscosity of **1-Bn**. Straight lines can be fitted reasonably well to the viscosity data of both compounds, indicating that a simple power law relates the viscosity and the concentration. The lines have slopes of 3.9 and 1.06, respectively. The latter value agrees well with the Stokes-Einstein law for the viscosity of solutions of hard spheres, indicating there is no concentration dependent association of molecules of **1-Bn**. The concentration dependence for compound **1** is much stronger, and the slope is in reasonable agreement with the predicted value[18] of 3.55-3.75 for the solution viscosity of reversible polymers.

2.7 Rheology Measurements

Dynamic oscillatory shear measurements were performed on compounds **1**, **1-Bn**, **2** and **2-Bn**. The contrast between O-protected and hydrogen bonding compounds is large in the analogues **1** and **1-Bn** with short spacers: whereas the mechanical properties of compound **1-Bn** could not be determined due to its low viscosity above, and to its fast crystallisation below the melting point, viscoelastic properties of the amorphous modification of compound **1** above T_g are distinctly polymer-like (Figure 2.7).

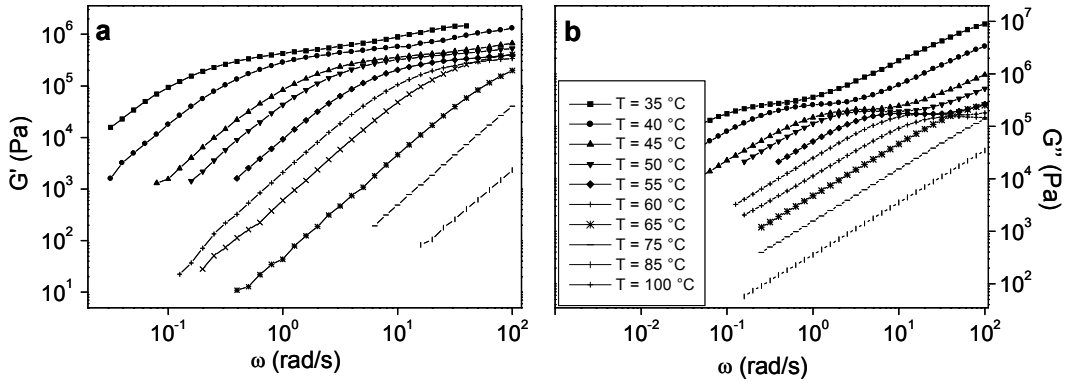


Figure 2.7: *Storage moduli (**a**) and loss moduli (**b**) of **1** between 35 and 100 °C.*

At temperatures below 70 °C, a narrow rubber plateau is observed with a storage modulus of approximately 2×10^5 Pa. The plateau modulus is only slightly dependent on temperature. At 35 °C and 45 °C, an upturn of the storage modulus to the glassy state is observed at high frequencies. In the absence of physical crosslinks, the rubber plateau implies the presence of elastically active polymeric chains of **1** between entanglements. The degree of polymerisation of **1** must be substantially higher than the critical entanglement molecular weight (which is in the order of 3×10^4 g/mol for polydimethylsiloxane) to give rise to a plateau of the width observed in Figure 2.7. The observed mechanical properties of **1** are, therefore, caused by polymeric chains with a DP exceeding 100.

Storage moduli of compound **2** in a range of temperatures are shown in Figure 2.8. It is evident that in this case mechanical measurements are sensitive to phase transitions. At the lowest temperature (–39 °C), below the weak endotherm observed in DSC (see Figure 2.3),

G' is nearly independent of frequency. At temperatures above this transition, the compound shows a transition from viscous flow at low frequencies to rubbery behaviour at higher frequencies.

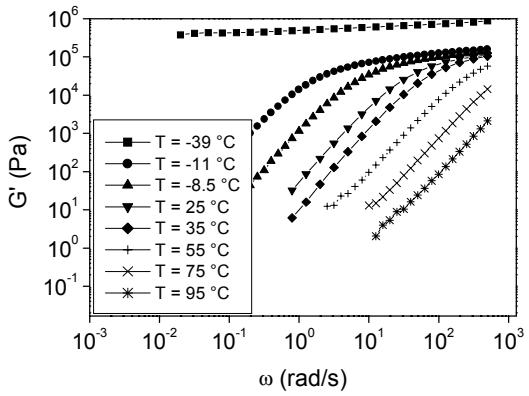


Figure 2.8: *Storage modulus isotherms of **2**.*

In contrast to this, O-benzyl-protected compound **2-Bn** exhibits only fluid-like behaviour in the whole temperature range. The differences between the two compounds at a single temperature are discernible in a plot of G' and G'' (Figure 2.9). Compound **2-Bn** is fluid like, (G'<G'') at all frequencies, whereas in compound **2** the lines of G' and G'' cross each other at a frequency of 50 rad/s.

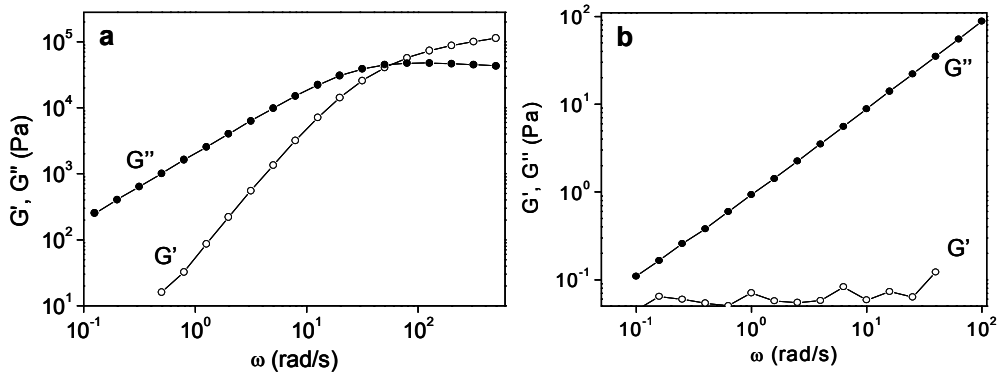


Figure 2.9: *Storage (o) and loss (•) moduli of compounds **2** (**a**) and **2-Bn** (**b**) at 298 °K.*

Frequency-independent complex viscosities are observed for compound **2-Bn** at all temperatures measured (Figure 2.10b), which is typical for low molecular weight polymers below their entanglement molecular weight, whereas the complex viscosity of **2** decreases strongly at higher frequencies. At low frequencies, the complex viscosity of compound **2** at 30 °C is 2×10^3 times the viscosity of **2-Bn**. Using this ratio, and assuming that the viscosity

of linear aggregates of **2** depends on the molecular weight in the same way as in PDMS,[19] a rough estimate of the degree of polymerisation of **2** can be made. Such a calculation indicates that on average 20 molecules of **2** ($M_n = 7.5 \times 10^3$) associate to form a chain with an M_n of 1.5×10^5.

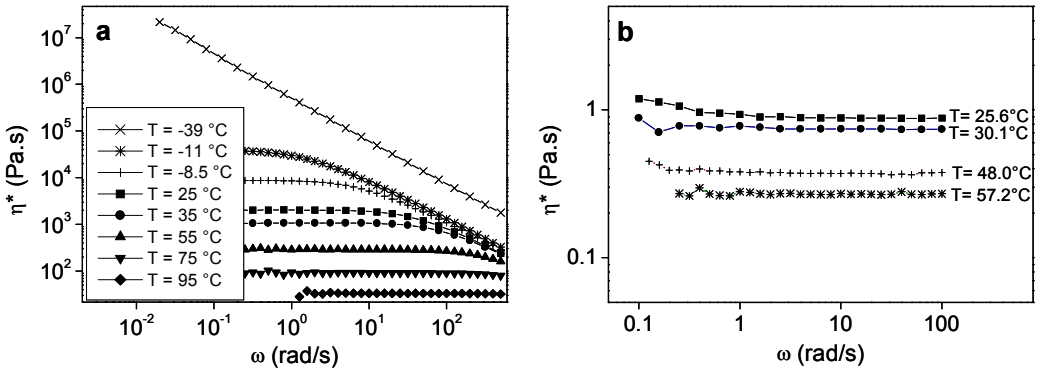


Figure 2.10: *Complex viscosities of compounds **2** (**a**) and **2-Bn** (**b**).*

Activation parameters for stress relaxation of compounds **1** and **2** were determined from the temperature dependence of the zero shear viscosity.[20] At low frequencies, the complex viscosity is equivalent to the zero shear viscosity η_0. From the slope of a semi logarithmic plot of η_0 vs. 1/T (Figure 2.11), activation parameters for stress relaxation were calculated.*

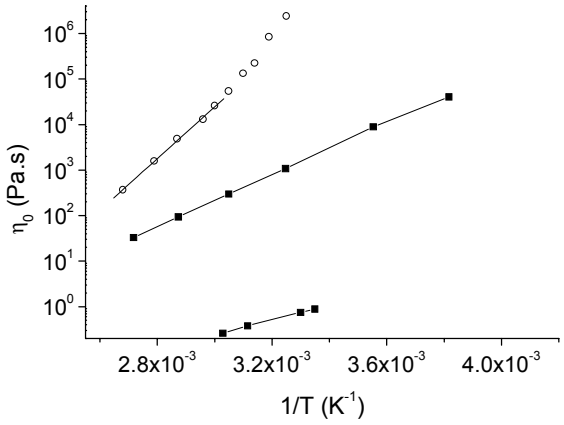


Figure 2.11: *Semi-logarithmic plot of the zero shear viscosity (η_o) of **1** (o), **2** (•) and **2-Bn** (■) against the reciprocal of the absolute temperature.*

* The following relationship was used: $\eta = c \times \exp(\Delta H/RT)$.

For compound **1**, the glass transition at 25 °C results in a curved plot and only the data above 60 °C were used. These results in activation parameters of 127 kJ/mol for **1,** 54 kJ/mol for **2** and 37 kJ/mol for **2-Bn**. Clearly, association results in a higher barrier, by inhibiting local relaxation.

2.8 Conclusions

The dramatic differences between protected compounds **1-Bn** and **2-Bn** and the active compounds **1** and **2** give strong evidence for the polymeric character of **1** and **2**, which is due to non-covalent interactions. In solution, there is good agreement between the concentration dependence of the viscosity of solutions of **1** and the behaviour of entangled solutions of reversible polymers predicted by Cates,[21] who calculated that the zero shear viscosity would scale with the concentration to the power 3.5-3.7. The results suggest that the solutions of **1** are semi-dilute, i.e. the supramolecular chains of **1** overlap at the concentrations studied. In bulk, the strength and high directionality of the interactions is directly reflected by the properties of **2**. The small endotherm in DSC at –25 °C is ascribed to melting of crystalline domains of dimerised UPy end groups, similar to what was reported by Stadler for urazole end groups in telechelic polybutadienes, in which, however, the melting of the domains occurs at a much higher temperature (396 K). In contrast to this, the functional groups in compound **1** do not form crystalline domains. The compound can be obtained as either a completely crystalline material, or as an amorphous material with a T_g at 25 °C, which does not show any sign of crystallization or formation of microcrystalline domains. The reluctance with which this modification of **1** crystallises is a result of the high viscosity of the supramolecular polymer, and reflects the high degree to which the short spacers restrict the functional groups to organise in ordered domains. The absence of microcrystalline domains in **1** above room temperature is confirmed by solid state NMR measurements, which show that there is no significant difference in mobility between the UPy functional groups and the spacers in this molecule. The strong temperature dependence of the behaviour of **2** as compared to that of the protected derivative **2-Bn** is perhaps one of the most convincing arguments for the polymeric nature of **2**. The presence of a broad rubber plateau in the modulus of **1** is either due to entanglements, or to physical crosslinks in microcrystalline domains. With rheological measurements, it is difficult to discriminate between these

possibilities in **1**, but the DSC results suggest that below –25 °C, the physical crosslinks are indeed present, while at higher temperatures a viscoelastic polymer-like material is obtained. In compound **1**, DSC and NMR suggest that crystalline domains are not formed. The height of the plateau in **2** shows that it is a rubber plateau; at the lowest temperature, an upturn to the glassy state is visible. In conclusion, this study has shown that it is possible to make random coil, completely amorphous polymers in which some of the covalent bonds in the main chain have been replaced by hydrogen bonds. This was achieved by utilising the unique properties of the UPy functional group that dimerises with an extremely high association constant, but has little tendency to associate further in microcrystalline domains.

2.9 Experimental Section

General Methods.

All experiments were performed under a nitrogen atmosphere. Dry tetrahydrofuran (THF) was obtained by distillation over sodium/potassium/benzophenone. Dry toluene was obtained by distillation and degassed by repeated freeze-thaw cycles. Pyridine, ethanol and dimethylformamide (DMF) were dried over 4Å molecular sieves. All solvents were of p.a. quality unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 or a Brucker AC 400 with TMS as internal reference. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m). Infrared (IR)-spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. All samples were heated from 20°C to 700°C at a heating rate of 10°C/min. Differential scanning calorimetry (DSC) measurements were obtained with a Perkin-Elmer Pyris-1 at a heating rate of 20°C/min. Melting points were determined with a Jenaval polarizing microscope equipped with a Unkam THMS 600 heating device. Elemental analyses were obtained using a Perkin-Elmer 240 and a Perkin-Elmer 2400. Electrospray ionisation mass spectrometry (ESI-MS) was carried out on a Perkin-Elmer API 300 MS/MS mass spectrometer. Viscosities were determined with Ubbelohde micro-viscometers with a suspended level bulb of different capillary tube diameters. Before measurements, low viscosity samples were passed through a filter of 5 μm. Dynamic mechanical measurements were performed on a Rheometrics fluid spectroscopy RFSII, a Rheometrics RDS and a Rheometrics RMS800 in a cone-plate geometry.

Ethyl 3-oxo-6-heptenoate (3). Compound **3** was prepared according to a literature method[22] (bp 106-108°C at 15 mmHg, lit:106-108 °C). IR (KBr): ν = 3040, 2981, 1744, 1641, 1236 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 5.82 (m, 1H, *H*C=CH_2), 5.01 (m, 2H, H_2C=C), 4.20 (q, 2H, OCH_2), 3.45 (s, 2H, CH_2), 2.66 (t, 2H, CH_2), 2.34 (m, 2H, CH_2), 1.30 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 202.4, 167.6, 137.1, 116.04, 61.9, 49.9, 42.5, 27.92, 14.6.

6-(3-Butenyl)-isocytosine (4). A dry two-neck flask, containing guanidine carbonate (18.02 g, 0.10 mol) was flushed with nitrogen and stoppered with a septum cap. Then dry ethanol (200 mL) was added. While stirring, crude ethyl 3-oxo-6-heptenoate (from 26 g, 0.2 mol of ethylacetoacetate), was slowly added. The reaction mixture was stirred vigorously and heated under reflux for 24 h. Part of the solvent was distilled off, and the product was precipitated by addition of water. The precipitate was filtered, washed with water, cold ethanol and cold acetone, and dried under vacuum (13.73 g, 42%). T_m = 200 °C. IR (KBr): ν = 3377, 3134, 2692, 1677, 1640, 1618, 1552, 1398 cm^{-1}. ^1H NMR (DMSO d_6): δ 10.74 (s, 1H, NH), 6.54 (s, 2H, NH_2), 5.80 (m, 1H, *H*C=CH_2), 5.40 (s, 1H, pyrimidyl), 5.01 (m, 2H, H_2C=C), 2.3 (m, 2×2H, 2 CH_2). ^{13}C NMR (DMSO d_6): δ 166.0, 164.5, 155.8, 137.7, 115.2, 100.0, 35.6, 31.5. Anal. Calcd. for $C_8H_{11}N_3O$ (165.19): C 58.17, H 6.71, N 25.44. Found: C 58.14, H 6.68, N 25.53.

6-(3-Butenyl)-2-butylureido-4[1]-pyrimidinone (5). Butyl isocyanate (2.86 mL, 25.4 mmol) was added slowly to a solution of 6-(3-butenyl)-isocytosine (3.0 g, 18.2 mmole) in dry pyridine (36 mL). The reaction mixture heated under reflux for 3 h. The pyridine was removed by evaporation. The crude product was recrystallised from ethanol to give 4.2 g (87%) of **5**. T_m = 118 °C. IR (KBr): ν = 3424, 2957, 1700, 1662, 1586, 1527, 1257 cm^{-1}. ^1H NMR ($CDCl_3$): δ 13.24 (s, 1H, NH), 11.87 (s, 1H, NH) 10.14 (s, 1H, NH), 5.84 (s, 1H, pyrimidyl), 5.79 (m, 1H, *H*C=CH_2), 5.09 (m, 2H, CH_2=CH), 3.25 (m, 2H, N-CH_2), 2.58 (t, 2H, Ar-CH_2CH_2), 2.43 (m, 2H, Ar-CH_2CH_2), 1.59 (m, 2H, N-CH_2CH_2), 1.39 (m, 2H, N-CH_2CH_2CH_2), 0.96 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 173.1, 156.6, 154.7, 151.4, 135.1, 116.9, 106.1, 39.8, 31.9, 31.5, 30.8, 20.2, 13.8. Anal. Calcd. for $C_{13}H_{20}N_4O_2$ (264.33): C 59.07, H 7.63, N 21.20. Found: C 59.26, H 7.91, N 21.50.

4-Benzyloxy-6-(3-butenyl)-2-butylureidopyrimidine (6). Using a syringe, benzyl bromide (1.58 mL, 13.24 mmol) was added to a suspension of compound **5** (1.0 g, 3.8 mmole) and potassium carbonate (1.83 g, 13.24 mmol) in dry DMF (25 mL). The suspension was stirred vigorously at 80 °C for 24 hours. Acetone was poured into the reaction mixture, the resulting suspension was filtrated, and the residue was washed with DMF and acetone. Water was then added to the filtrate. The white precipitate was filtered and washed with water. Recrystallisation from ethanol/water (3:1 v/v), followed by recrystallisation from hexane yielded 1.04 g (78 %) of pure **6**. T_m = 85°C. IR (KBr): ν = 3217, 3075, 3002, 2956, 1687, 1601, 1548, 1326, 1275 cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.21 (s, 1H, NH), 7.39 (m, 5H, Ph-H) 7.13 (s, 1H, NH), 6.22 (s, 1H, pyrimidinyl), 5.84 (m, 1H, *H*C=CH_2), 5.33 (s, 2H, CH_2-Ph), 5.10 (m, 2H, CH_2=CH), 3.37 (m, 2H, CH_2 butyl), 2.70 (t, 2H, CH_2), 2.46 (m, 2H, CH_2), 1.59 (m, 2H, CH_2 butyl), 1.45 (m, 2H, CH_2 butyl), 0.96 (t, 3H, CH_3 butyl). ^{13}C NMR ($CDCl_3$): δ 170.1, 170.0, 157.4, 154.3, 136.8, 136.0, 128.6, 128.2, 115.7, 100.1, 68.2, 39.6, 36.5, 32.0, 31.8, 20.2, 13.7. Anal. Calcd. for $C_{20}H_{26}N_4O_2$ (354.45): C 67.77, H 7.39, N 15.81. Found: C 67.81, H 7.36, N 15.88.

1,5-Bis[4-benzyloxy-(2-butylureido-pyrimidinyl-6)-butyl]-1,1,3,3,5,5-hexamethyl-1,3,5-trisiloxane (1-Bn). In a glove box, a solution of 1,3,5-hexamethyltrisiloxane (6.99 g, 33.56 mmole), compound **6** (23.92 g, 67.49 mmole) and platinum catalyst PC072 (136 µL of a 2.1%-2.4% solution in xylene, ± 0.0136 mmole) in toluene (135 mL) was prepared. Outside the glove box, the solution was heated to 80 °C and stirred for 24 h

under a nitrogen atmosphere. After evaporation of the solvent, the crude product was purified by column chromatography. The product was finally recrystallised from hexane to give 18.5 g (60%) of pure **1-Bn**. T_m = 78°C. IR (KBr): ν = 3216, 3070, 3000, 2957, 1677, 1603, 1550, 1344, 1256, 1042, 796 cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.27 (s, 2H, NH), 7.35 (m, 10H, Ph-H), 7.19 (s, 2H, NH), 6.19 (s, 2H, pyrimidyl), 5.30 (s, 4H, CH_2-Ph), 3.36 (q, 4H, N-CH_2), 2.58 (t, 4H, Si-$CH_2CH_2CH_2CH_2$), 1.70 (m, 4H, Si-$CH_2CH_2CH_2$), 1.57 (m, 4H, N-CH_2CH_2), 1.41 (m, 8H, N-$CH_2CH_2CH_2$ and Si-CH_2CH_2), 0.95 (t, 6H, CH_3 butyl), 0.56 (t, 2H, Si-CH_2), 0.06 (s, 12H, Si-CH_3), 0.01 (s, 6H, Si-CH_3) ^{13}C NMR ($CDCl_3$): δ 170.1, 170.0, 157.4, 154.5 , 135.9, 128.5, 128.2, 99.8, 68.0, 39.5, 37.0, 31.9, 31.8, 22.9, 20.2, 18.1, 13.7, 1.2, 0.14. Anal. Calcd. for $C_{46}H_{72}N_8O_6Si_3$ (917.39): C 60.22, H 7.91, N 12.21. Found: C 60.74, H 7.98, N 12.22.

1,5-Bis[(2-butylureido-4-oxo-1,4-dihydropyrimidyl-6)-butyl]-1,1,3,3,5,5-hexamethyl-1,3,5-tri-siloxane(1). Compound **1-Bn** (1.8 g, 1.96 mmole), Pd/C (10 wt%; 0.3 g, 0.282 mmole), THF (60 mL), EtOH (30 mL) and acetic acid (0.1 g, 1.66 mmol) were mixed together in a Parr reactor. The reaction mixture was flushed several times with nitrogen, then with hydrogen. Then the reactor was shaken under a hydrogen atmosphere of approximately 4 atm for 24 h. After removal of the catalyst by filtration, the solvent was evaporated. The crude product was purified by column chromatography and finally recrystallised from EtOAc to yield 1.23 g (85%) of **1**. T_m = 112°C. IR (KBr): ν = 3211, 2958, 1699, 1660, 1585, 1526, 1304, 1255, 1041, 795 cm^{-1}. ^1H NMR ($CDCl_3$)**:** δ 13.19 (s, 2H, NH intramolecular), 11.87 (s, 2H, NH intermolecular) 10.15 (s, 2H, NH), 5.81 (s, 2H, pyrimidyl), 3.23 (q, 4H, N-CH_2 butyl), 2.46 (t, 4H, $SiCH_2CH_2CH_2CH_2$), 1.65 (m, 4H, $SiCH_2CH_2CH_2$), 1.58 (m, 4H, CH_2 butyl), 1.38 (m, 8H, CH_2 butyl and $SiCH_2CH_2$), 0.94 (t, 6H, CH_3 butyl), 0.56 (t, 4H, $SiCH_2$), 0.07 (s, 12H, outer $SiCH_3$), 0.01 (s, 6H, inner $SiCH_3$). ^{13}C NMR ($CDCl_3$): δ 173.0, 156.6, 154.7, 152.3, 105.7, 39.8, 32.4, 31.5, 30.5, 22.7, 20.2, 17.9, 13.8, 1.3, 0.15. Anal. Calcd. for $C_{32}H_{60}N_8O_6Si_3$ (737.14): C 52.14, H 8.20, N 15.20. Found: C 52.25, H 8.22, N 15.17.

α,ω-Bis[(4-benzyloxy-2-butylureidopyrimidinyl-6)-butyl]polydimethylsiloxane (2-Bn). Compound **2-Bn** was prepared in a similar way as compound **1-Bn**. Starting with polydimethylsiloxane bishydride (27 g, 4.5 mmol; $M_n = 6 \times 10^3$ $g.mol^{-1}$), a product was obtained which was triturated three times with 30 mL of methanol, yielding 24.42 g (90%) of a low viscous oil which showed no impurities in ^1H-NMR. T_g = –55°C. IR (KBr): ν = 3224, 3070, 3000, 2963, 1688, 1598, 1344, 1261, 1092, 803 cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.37 (s, 2H, NH), 7.99 (s, 2H, NH), 7.34 (m, 10H, Ph-H), 6.20 (s, 2H, pyrimidyl), 5.37 (s, 4H, CH_2-Ph), 3.41 (q, 4H, N-CH_2), 2.60 (t, 4H, Si-$CH_2CH_2CH_2CH_2$), 1.72 (m, 4H, Si-$CH_2CH_2CH_2$), 1.61 (m, 4H, N-CH_2CH_2), 1.41 (m, 8H, N-$CH_2CH_2CH_2$ and Si-CH_2CH_2), 0.97 (t, 6H, CH_3 butyl), 0.60 (t, 2H, Si-CH_2), 0.1 (s, m×6H, ($C\underline{H}_3$)$_2$Si)

α,ω-Bis[(2-butylureido-4-oxo-1,4-dihydropyrimidinyl-6)-butyl]polydimethylsiloxane (2). Compound **2-Bn** (10 g, 1.17 mmole), Pd/C (10 wt%; 0.11 g, 0.1 mmole), THF (100 mL), ethanol (50 mL) and acetic acid (0.03 g, 0.5 mmole) were mixed together and transferred into a Parr reactor. The reaction mixture was flushed several times with nitrogen, then with hydrogen. The reactor was shaken under a hydrogen atmosphere of approximately 4 atm for 24 h. After filtration of the catalyst, the solvent was evaporated. The

crude product was dissolved in dichloromethane/ethanol (3:1), and then dichloromethane was evaporated. The title product precipitated at the bottom of the flask, and the upper ethanol-layer was removed. After being dried under vacuum, the yield was approximately 9 g of a highly viscous oil. IR (KBr): ν = 2962, 1700, 1652, 1593, 1550, 1260, 1018, 800 cm^{-1}. ^1H NMR ($CDCl_3$): δ 13.21 (s, 2H, NH), 11.89 (s, 2H, NH) 10.17 (s, 2H, NH), 5.84 (s, 2H, pyrimidinyl), 3.25 (q, 4H, N-CH_2), 2.47 (t, 4H, Si-$CH_2CH_2CH_2CH_2$), 1.68 (m, 4H, Si-$CH_2CH_2CH_2$), 1.59 (m, 4H, N-CH_2CH_2), 1.41 (m, 4H, N-$CH_2CH_2CH_2$), 1.41 (m, 4H, Si-CH_2CH_2), 0.94 (t, 6H, CH_3 butyl), 0.56 (t, 4H, Si-CH_2), 0.06 (s, m×6H, Si-CH_3)

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19. Below 3.3×10^4 g/mol, the viscosity of PDMS is proportional to the molecular weight, while at higher molecular weights, it is proportional to $M^{3.9}$.
20. The zero viscosity $\eta_o = \eta_{\text{frequency} \to 0}$. These values were obtained by the eye.
21. This model has been applied to aqueous solutions of wormlike micelles (Cates, M.E., Candau, S.J. *J. Phys.: Condens. Matter*, **1990**, *2*, 6869) and to complexes of copper with carboxylic acids in decalin (Dammer, C., Maldivi, P., Terech, P., Guenet, J.-M. *Langmuir*, **1995**, *11*, 1500).
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3

Thermotropic Liquid Crystalline Behaviour of Disc-Shaped Ureidotriazine Derivatives*

Abstract

Monofunctional and bifunctional compounds based on trialkoxyphenyl-s-triazine were synthesised and characterised. The molecules associate via four hydrogen bonds resulting in a large planar discotic core that is surrounded by six flexible alkoxy side chains. This architecture is conducive to the formation of stable columnar mesophases. Indeed, all compounds were found to be thermotropic liquid crystalline over a temperature range of up to 220 degrees. Optical polarisation microscopy showed focal conic textures typically observed for hexagonal mesophases. It was found with X-ray diffraction that the mesophases of compound ***2a*** *have a pseudo-hexagonal structure. Intercolumnar distances of respectively 32 Å for* ***1b*** *and 35 Å for* ***2a*** *were found. An attempt to enhance the stability of the columnar mesophases was made by introducing an additional phenyl group in the molecule, either as N-phenylamino substituted or as phenylureido substituted derivatives* ***3-6****. Extending the planar core does not influence the stability of the liquid crystalline mesophases. The liquid crystalline mesophase of equimolar mixtures of non-fluorinated compounds* ***5*** *and pentafluorphenyl compounds* ***6*** *is different from that of the individual compounds. The temperature range of the mixture in which the mesophase is stable does not change significantly.*

* Part of this work has been published: Hirschberg, J.H.K.K., Brunsveld, L., Vekemans, J.A.J.M., Sijbesma, R.P., Meijer, E.W. *Nature* **2000**, *407*, 167, and Hirschberg, J.H.K.K., Sijbesma, R.P., Beijer, F.H., Meijer, E.W., in preparation.

3.1 Introduction

In thermotropic and lyotropic mesophases, the formation of columns may result from different types of interactions between molecular or macromolecular species. In general, each column consists of a central rigid core that is surrounded either by a flexible part of the molecule, for instance aliphatic chains, or by solvent molecules. Hydrogen bonds have shown to be a useful way to form large cores. A typical example found in nature of a complex that forms columnar structures is that of DNA. DNA is build up from two helical strands held together by hydrogen bonding between complementary nucleotides. DNA features lyotropic properties due to its rigid rod-like superstructure that is maintained by a combination of solvophobic interaction and multiple hydrogen bonds. Numerous examples[1-11] exist of the stabilisation of columnar mesophases by the enlargement of a rigid core. Lehn[1] has obtained liquid crystalline materials by bringing together two different complementary units. For instance, a disc-shaped dimer was obtained by mixing bis(acylamino)pyridine with uracil, and thus a building block resulted that exhibits columnar liquid crystallinity.[1a] Kato[2] has reported on a bis(acylamino)pyridine-alkoxybenzoic acid complex that exhibits thermotropic liquid crystalline properties. Kato and Fréchet[3] have described liquid crystalline materials that are obtained with the use of single hydrogen bonds in pyridine-carboxylic acid heterocouples. In our group, Felix Beijer[4] has prepared hetero-complexes of diaminotriazines and uracil,[5] in which both components are substituted with a 3,4,5-tris(dodecyl)phenyl group (Figure 3.1). These complexes are held together by triple hydrogen bonds, and they were found to exhibit thermotropic liquid crystalline properties.

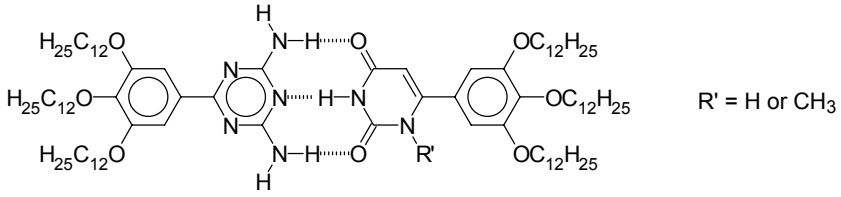
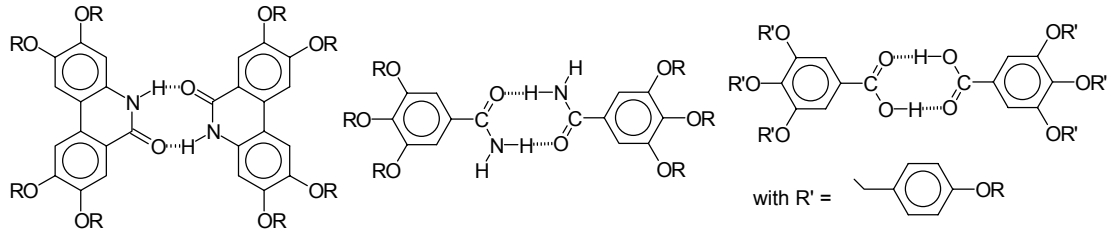


Figure 3.1: *Diamino-s-triazine-uracil heterocouples exhibiting thermotropic liquid crystalline properties.*[5]

In addition to columnar structures consisting of complementary molecules, homodimeric,[6-9] homotrimeric[10] and homotetrameric[11] complexes have been prepared that organise in columns. Lillya[6] reported on self-complementary 6(5*H*)-phenanthridinones that

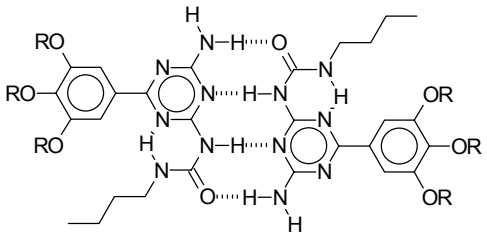
can dimerise via double hydrogen bonds to form columnar mesophases. Lattermann[7] also employed amide bonds for the construction of large planar cores. These dimers also form discotic mesophases.



a **b** **c**

Figure 3.2: *Self-complementary amides described by Lillya[6] (**a**) and Lattermann[7] (**b**), and carboxylic acids described by Malthête[9] (**c**). R represents an alkyl chain.*

Felix Beijer has studied in detail the association of a self-complementary molecule based on *s*-triazine that dimerises via four hydrogen bonds (K_{dim} = 20000 M^{-1}).[4] He has shown that these compounds are planarised by intramolecular hydrogen bonding. The formation of the dimer leads to a disc with a large coplanar core surrounded by six flexible alkyl side chains (Figure 3.3). This architecture is conducive to the formation of a columnar mesophase. He found that the compound is liquid crystalline and that the textures grown from the isotropic state are typically for D_h (discotic hexagonal) phases. X-ray diffraction studies clearly indicate that the mesophase of **1a** is discotic.



1a: R = $C_{12}H_{25}$

Figure 3.3: *Dimeric form of tridodecyloxyphenylureido-*s*-triazine.*[4]

In the previous chapter the use of four hydrogen bonds for the construction of linear supramolecular polymers has been discussed. For this purpose quadruple hydrogen bonding ureidopyrimidinone units were employed. Viscosity and rheology measurements have shown that these low molecular weight bifunctional compounds exhibit polymer-like properties,

which can be explained by the presence of entangled random coils of long polymer chains. The purpose of the present work is to investigate the possibility to obtain highly ordered structures by combining the concept introduced in chapter 2 with the columnar organisation of trialkyloxyphenylureido-*s*-triazine. It was envisioned that the linkage of two trialkyloxyphenylureido-*s*-triazine moieties through an alkyl spacer would lead to linear self-assembled polymers displaying columnar architecture, as depicted schematically in Figure 3.4.

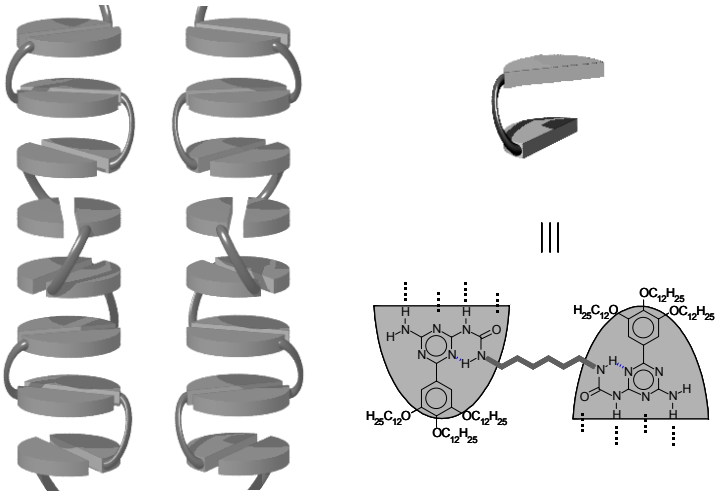


Figure 3.4: *Schematic representation of a proposed arrangement of bifunctional molecules in the columnar aggregates.*

The size of the planar cores can be made even larger by introducing an additional phenyl group that enhances π-stacking. The packing of the columnar structures can also be stabilised by mixing pentafluorphenyl with non-fluorinated phenyl derivatives.[12] Consequently, columnar stacks consisting of alternating aromatic/pentafluoraromatic compounds might be formed. The stacking of the two different discotic molecules may result in columns of higher stability.

In this chapter the synthesis and thermotropic properties of monofunctional ureido-*s*-triazines (UTr) **1**, **3**, **5** and **6** and bifunctional ureido-*s*-triazines **2** and **4** are described. Optical polarisation microscopy and DSC were used to study the thermal behaviour of the compounds. X-ray diffraction was used to investigate the structure of the mesophases. The phase behaviour of monofunctional compounds is studied. Also the effect of the linkage in bifunctional compounds or the effect of the phenyl substitution in compounds **3**-**6** in

mesophase stabilisation is studied. Pentafluorphenylureido-*s*-triazines **6** were synthesised with the aim to obtain alternating stacks of dimers of **5** and **6** in 1:1 mixtures of these compounds.

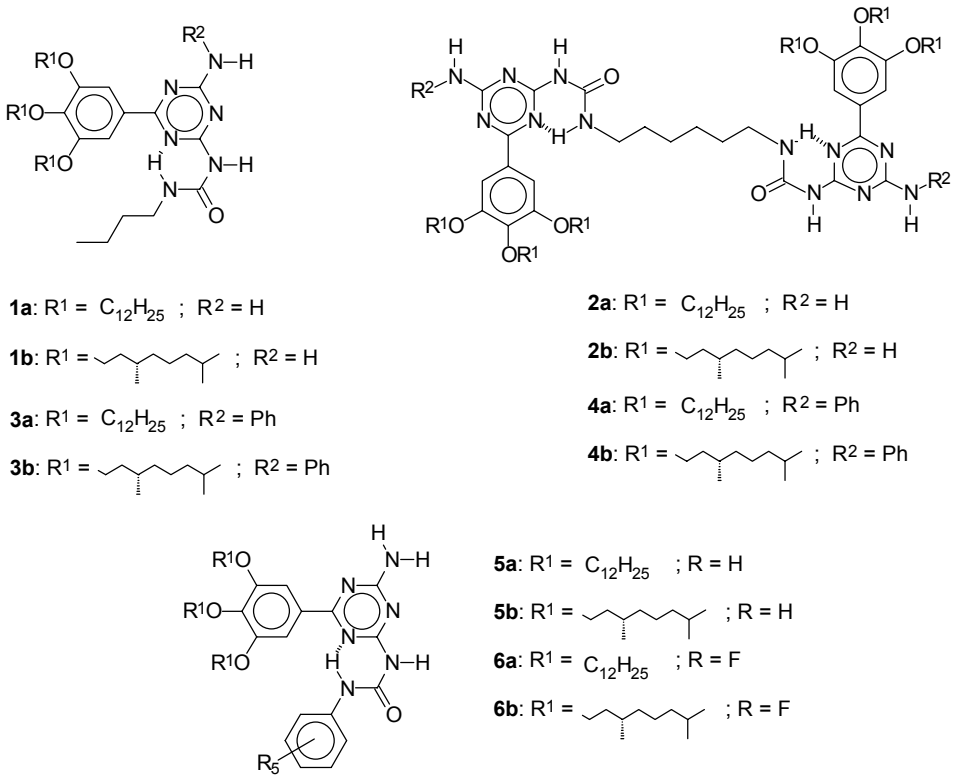


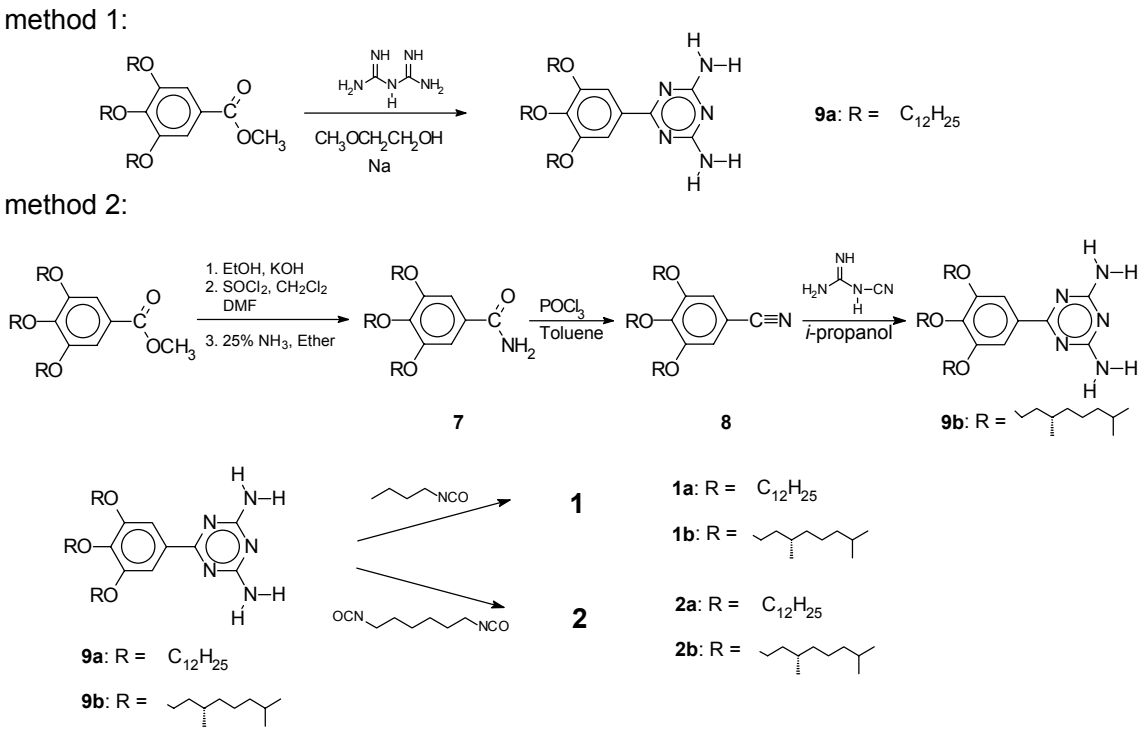
Figure 3.5: *Mesogenic trialkoxyphenylureido-s-triazine derivatives studied in this chapter.*

3.2 Synthesis and Characterisation

3.2.1 Aminobutylureido 1 and Hexamethylene-bis(aminoureidotriazine) 2

2,4-Diamino-*s*-triazines **9a** and **9b** were synthesised either by a cyclocondensation of methyl trialkoxybenzoate with biguanide sulphate[13] (method 1 in Scheme 3.1) or by condensation of trialkoxybenzonitrile with dicyandiamide (method 2 in Scheme 3.1). In general, the reaction of the methyl benzoate proceeded in much lower yields, probably due to the hydrolysis of the ester groups by water that is formed during the condensation. Hydrolysis of the ester to the acid was confirmed by IR and NMR analysis of the reaction mixture. As a result of this side reaction, yields were below 50%. An important drawback of method 2, however, is that the nitrile derivative is not readily available, and has to be prepared via a

four-step synthesis. Nevertheless, the chiral 2,4-diamino-*s*-triazine **9b** was prepared via this route because the condensation of the methyl benzoate gave a yield of 10% only. For the synthesis of chiral **9b** (see Scheme 3.1), chiral methyl benzoate was hydrolysed to the corresponding acid with potassium hydroxide in ethanol. The acid chloride was then synthesised via a reaction with thionyl chloride in dichloromethane in the presence of a trace of dimethylformamide as catalyst. A solution of the acid chloride in diethyl ether was shaken with 25% NH_3 to yield the carboxamide **7**. Dehydration of **7** with $POCl_3$ in toluene gave the corresponding benzonitrile **8**. Finally, condensation of the nitrile with dicyandiamide[14] afforded **9b** in an overall yield of 51%.



Scheme 3.1: *Two different synthetic methods for the preparation of s-triazine, and synthetic route toward monofunctional **1** and bifunctional **2**.*

Compounds **1** and **2** were prepared by acylation with *n*-butylisocyanate and 1,6-diisocyanatohexane, respectively, in pyridine. In order to prevent the formation of diacylated amino-*s*-triazine, the reaction for the synthesis of **1** was terminated after 2 hours, before a significant amount of diacylated product had been formed. The synthesis of bifunctional compound **2** was performed with a large excess (3.5 to 4 equivalents) of **9** in order to prevent the formation of mono-acylated triazine, *i.e.* triazine that is acylated by one 1,6-

diisocyanatohexane, and the formation of diacylated **9** —in this case both amino groups in **9** are acylated by two 1,6-diisocyanatohexane. The excess of diamino-*s*-triazine was recovered by precipitation in ethyl acetate followed by column chromatography. Compounds **1** and **2** were characterised with IR, NMR, elemental analysis and MALDI-TOF MS or ES-MS. The formation of hydrogen bonded dimers of the ureido-*s*-triazine functional groups of these compounds in chloroform solution is demonstrated by the large downfield shifts of the NH proton signals in ^{1}H NMR as depicted for compound **1b** in Figure 3.6. This was also found by Felix Beijer for the achiral anologue **1a**.[4]

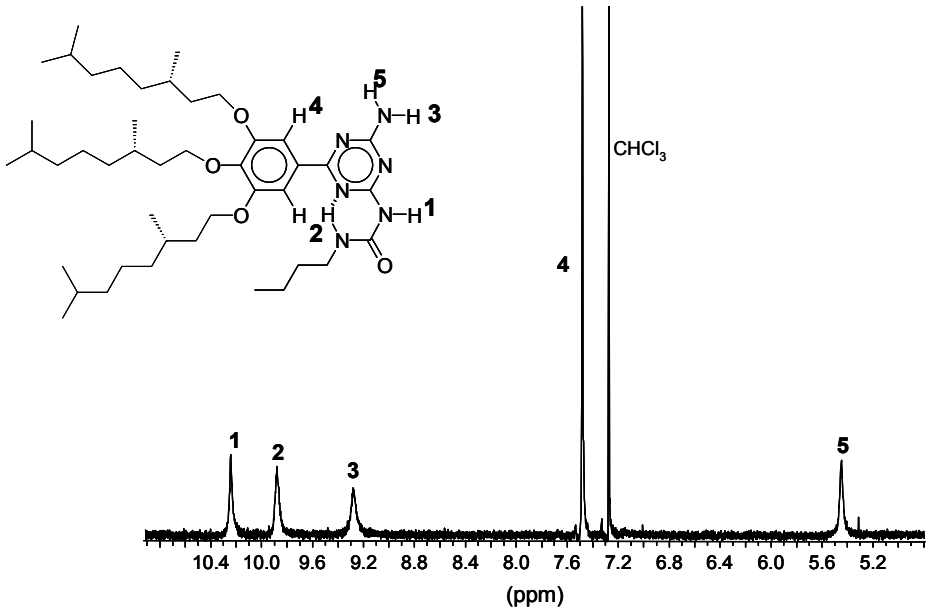
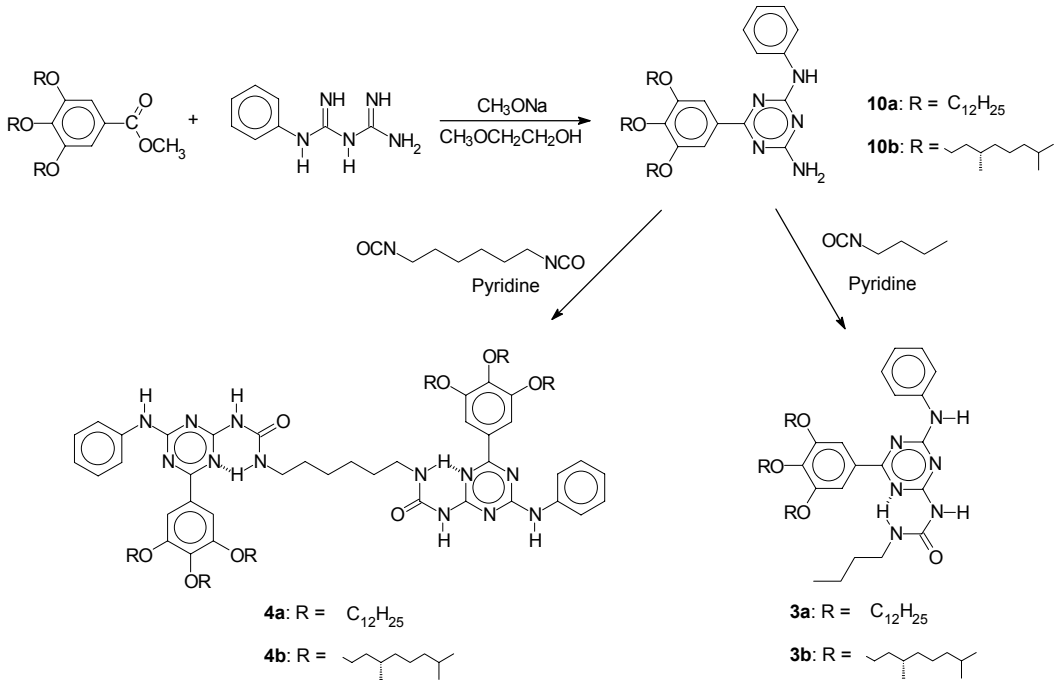


Figure 3.6: *^{1}H NMR spectrum of compound **1b** recorded in $CDCl_3$. The signals assigned to the NH protons are observed at low field, which is an indication for the formation of hydrogen bonds. In this particular case (**1b**) a dimer is formed.*

3.2.2 Phenyl-aminobutylureido 6 and Hexamethylene-bis(phenylamino-ureido-triazine) 2

Compounds with an extended aromatic core were synthesised by cyclocondensation of the methylester with phenylbiguanide.[15,16] Koshelev *et al.* and Mamalis *et al.* have described this type of condensation in ethanol and have used sodium ethoxide as the base. Reactions under these conditions with methyl 3,4,5-trialkoxybenzoate gave low yields. In our hands the highest yields were obtained in methoxyethanol with sodium methoxide as a base.

In the reaction, a trace of the benzoic acid was formed, which was removed by column chromatography on alumina.



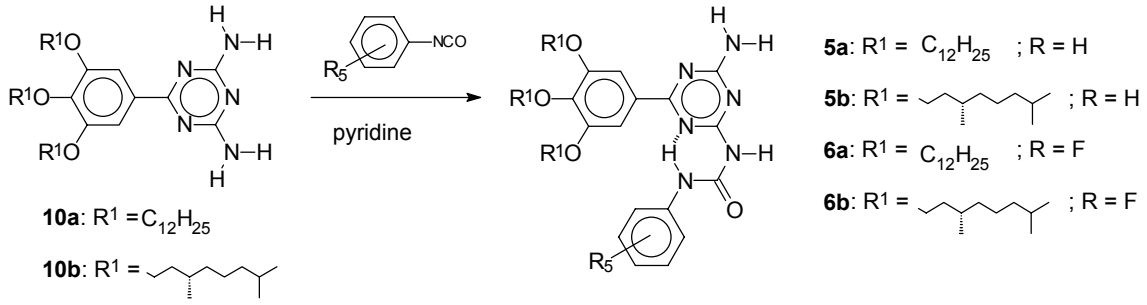
Scheme 3.2: *Synthetic route for N-phenylated monofunctional **3** and bifunctional **4**.*

Acylation of **10** with *n*-butylisocyanate or 1,6-diisocyanatohexane gave **3** and **4** in reasonable (59 % for **4a**) to good yields (88 % for **3a**). Unlike the diaminotriazines, the mono-protected amino compounds **10** are not susceptible to diacylation. As a consequence, a large excess of the triazine is not needed for the synthesis of the bifunctional compounds **4**. Precipitation from a concentrated chloroform solution into ethyl acetate, to remove unreacted triazine followed by column chromatography afforded the pure compounds. All compounds were characterised with NMR, IR and elemental analysis (Scheme 3.2).

3.2.3 Phenyl- and Pentafluorphenylureido Triazines

Phenyl- and pentafluorphenylureido triazines **5** and **6** were synthesised from diaminotriazine **9** with phenylisocyanate and pentafluorphenylisocyanate, respectively (Scheme 3.3). The reaction with the aromatic isocyanates in refluxing pyridine proceeded more smoothly than with alkylisocyanates. Mono-acylated product had already been formed after 20 minutes, concurrent with extensive diacylation. Even if 1 equivalent of the

isocyanate was used, diacylated adduct was formed. Therefore, and because column chromatography was difficult, yields of **5** and **6** (between 32 and 66%) are much lower than in the reactions with alkylisocyanates.



Scheme 3.3: *Synthesis of phenyl- and pentafluorphenylureidotriazines **5** and **6**, respectively.*

The products were purified by precipitation from a concentrated chloroform solution into ethanol followed by chromatography. The off-white precipitate was isolated via filtration or centrifugation. Compounds **5** and **6** were characterised with ^{1}H-, ^{13}C NMR and ^{19}F NMR for the fluorinated derivatives.

3.3 Optical Polarisation Microscopy and DSC Analyses

3.3.1 Optical Polarisation Microscopy

The thermotropic behaviour of **1b**,[17] **2**, **3**, **4**, **5** and **6** was studied using optical polarisation microscopy (OPM). For all compounds clear birefringent textures were observed. The mesophases are present over a broad temperature range. For all compounds, focal conic (fan-like) textures were grown by slowly cooling at a rate of 5 °C/min from the isotropic state. These focal conic textures are typical for D_h (discotic hexagonal) phases.[18] Figure 3.7 illustrates the textures grown for compounds **1b**, **2b**, **4b**, **3a** and **6b** by annealing from the isotropic phase.

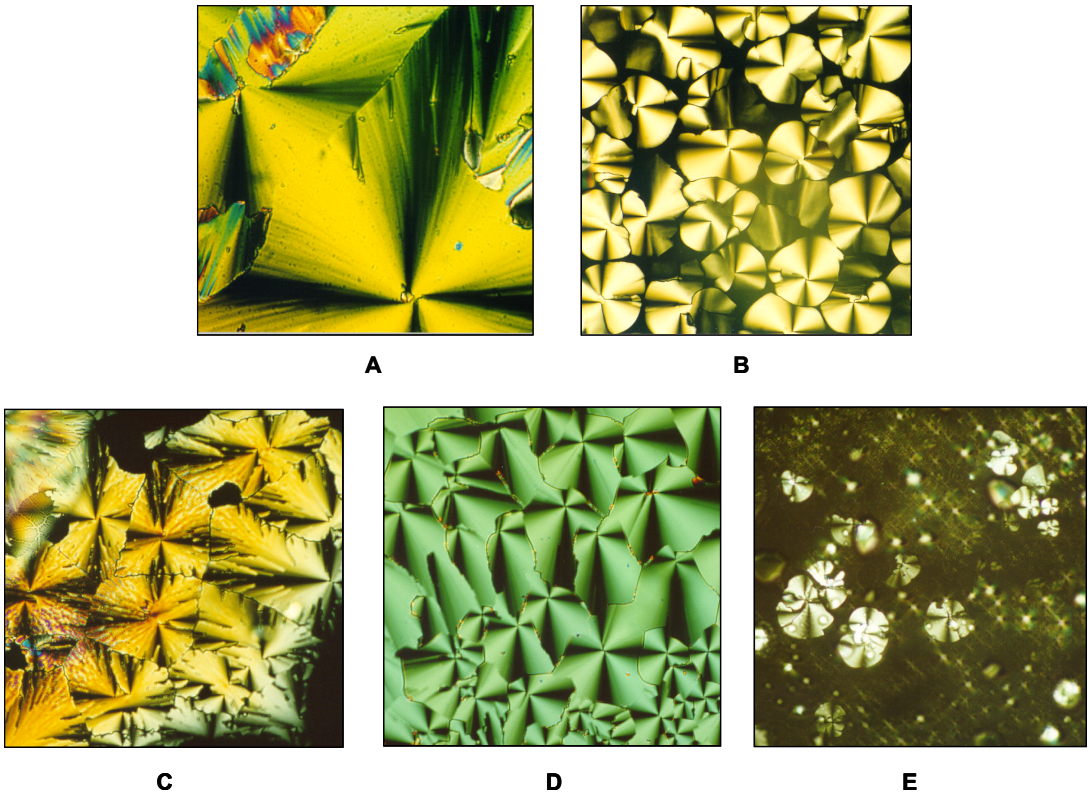


Figure 3.7: *Textures as observed under a polarisation microscope for compound **1b** at 20 °C (A), bifunctional compound **2b** at 20 °C (B), compound **4b** at 20 °C (C), compound **3a** at 145 °C (D) and compound **6b** at 20 °C (E).*

3.3.2 Differential Scanning Calorimetry

In order to study the mesophases in more detail, DSC measurements were performed. The phase transition temperatures and the corresponding enthalpies are summarised in Table 3.1 and Table 3.2. The second heating DSC traces* in Figure 3.8 show the phase transitions upon heating and cooling of monofunctional compound **1b**, and bifunctional compounds **2a** and **2b**. The traces were recorded from –100 to 220 °C, well below their decomposition temperature (T_{dec} = 280 °C). Upon heating of **1b**, **2a** or **2b** a large and broad endotherm, starting at approximately –50 °C is observed. This endotherm can be ascribed to the melting of the alkoxy side chains;[19] in other words, the transition from the crystalline phase to the liquid crystalline mesophase. For monofunctional **1b** the clearing temperature is observed at 189 °C.

* First heating runs are not shown in the figures. Only second heating runs or first cooling runs are displayed.

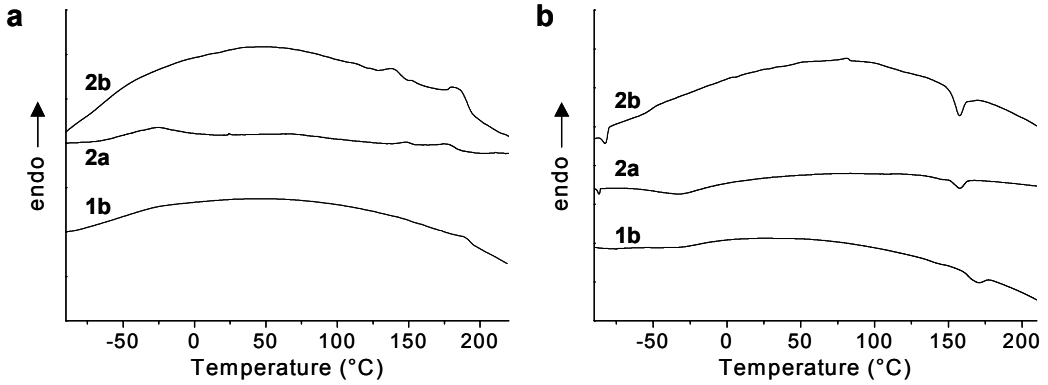


Figure 3.8: *DSC traces of compounds **1b**, **2a** and **2b**: **a)** 2nd heating curves measured at a rate of 20 °C/min, and **b)** 1st cooling curves measured at a rate of 20°C/min.*

An additional transition is observed as a small exotherm only in the cooling DSC trace. The DSC traces of both bifunctional compounds **2** feature an additional endotherm besides the transition to the isotropic phase. They are found at 148 °C for **2a** and at 139 °C for **2b**, and must probably be ascribed to a transition from an ordered to a less ordered mesophase. None of the compounds show significant changes under the polarisation microscope around these temperatures.

Table 3.1: *Thermotropic properties of compounds **1a**,[a] **1b**, **2a**, and **2b** obtained from DSC.*

Compound	K	T[b,c]	M_1	T (*ΔH*)	M_2	T (*ΔH*)	I
		°C		°C (k*J/mol*)		°C (k*J/mol*)	
1a	•	85	•	162	•	183	•
1b	•	–28	-[d]	-[d]	-[d]	189 (*4*)	•
2a	•	–26	•	148 (*1.2*)	•	178 (*2.1*)	•
2b	•	–30	•	142 (*1.9*)	•	187 (*5.6*)	•

• Phase is observed; K = crystalline phase; M_1 and M_2 = mesophases 1 and 2, respectively; I = isotropic phase; [a] The values were obtained from Felix Beijer[4]; [b] The maximum was taken as the temperature; [c] The enthalpy could not be determined accurately due to the broadness of transition; [d] A weak M_1 to M_2 transition was observed only in the cooling curve at approximately 150 °C.

For the compounds with an extended aromatic core (**3-6**), DSC traces were also recorded. As displayed in Figure 3.9, these compounds behave strongly different. Compound **3a** is crystalline at room temperature (confirmed with OPM), and features a crystal to crystal transition with melting at 40 °C and subsequent recrystallisation at 50 °C, directly followed

by an endothermic melting transition at 74 °C. This transition is ascribed to a crystalline to liquid crystalline transition. The compound becomes isotropic at 152 °C. The chiral analogue **3b** is liquid crystalline at room temperature. A melting point was not observed. Around 114 °C, a transition to a second mesophase takes place and a clearing temperature of 137 °C is observed. Both bifunctional compounds **4a** and **4b** exhibit thermotropic properties over a broad temperature range. For **4a** a clear, but broad, melting transition is observed at –21 °C. A second mesophase appears at 111 °C, and the material becomes isotropic at 195 °C. Compound **4b** is liquid crystalline at room temperature as shown with OPM. The DSC trace of **4b** features two transitions. An exotherm of approximately 30 $kJ.mol^{-1}$ emerges before the transition into the isotropic phase. OPM clearly shows that above and below this transition the material is liquid crystalline, which means that the exotherm cannot be ascribed to a recrystallisation of the material. We assume that a new mesophase is formed exhibiting a better packing of the mesogens. Furthermore, neither a T_g, nor a melting point are clearly visible in the thermogram of **4b**. No additional mesophases could be distinguished either with DSC. The transitions and calculated enthalpy values of compounds **3**-**6** are listed in Table 3.2.

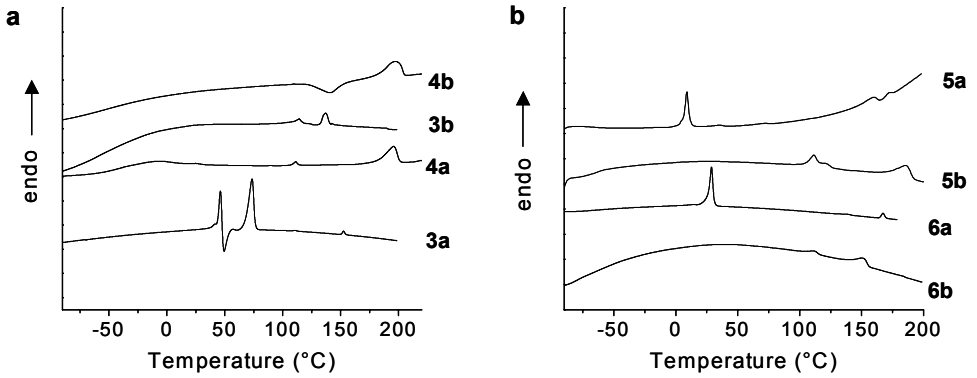


Figure 3.9: *DSC thermograms of s-triazines with an extended rigid core. A) 2nd heating curves of monofunctional **3** and bifunctional **4** measured at a rate of 20 °C/min, and B) 2nd heating curves of phenylureidotriazine **5** and pentafluorphenylureidotriazine **6** measured at a rate of 20°C/min.*

The thermal properties of chiral **5b** and **6b** differ strongly from their achiral analogues **5a** and **6a**. The achiral compounds are crystalline at room temperature, whereas the chiral compounds show mesomorphic behaviour over a broad temperature range. The DSC trace of compound **5a** features two mesophases (see Figure 3.9), while compound **6a** displays a single mesophase from 29 °C to 167 °C. As shown by DSC, compound **5b** exhibits a T_g at –

63 °C with a Δc_p of 0.1 J/g°C, and three different mesophases. One persists till 110 °C, followed by a second mesophase that is only stable in a small temperature range. Above 121 °C, a third mesophase appears and the material becomes isotropic at 183 °C. Upon cooling the same phase transitions are observed, except the T_g. For pentafluorphenylureido-*s*-triazine **6b** two phase transitions are observed. A transition of mesophase 1 to mesophase 2 is found at 112 °C, and the clearing temperature is at 152 °C. The DSC results of **5** and **6** are summarised in Table 3.2.

Table 3.2: *Thermotropic properties of compounds **3**, **4**, **5** and **6** obtained from DSC.*

Compound	K	T[a] (*ΔH*)[b]	M_1	T (*ΔH*)	M_2	T (*ΔH*)	I
		°C (*kJ/mol*)		°C (*kJ/mol*)		°C (*kJ/mol*)	
3a	•	74 (*35.2*)	•	152 (*4*)	o	-	•
3b	•	-	•	114 (*1.0*)	•	137 (*2.1*)	•
4a[c]	•	–21	•	111(*1.1*)	•	195 (*18.5*)	•
4b[d]	o	-	o	-	o	201 (*35.6*)	•
5a	•	11 (*14.8*)	•	160 (*2.9*)	•	172 (*1.1*)	•
5b	o	-	•	110 (*4*)[e]	•	183 (*4.5*)	•
6a	•	29 (*20.8*)	•	140 (*0.2*)	•	167 (*2.3*)	•
6b	o	-	•	112 (*1.1*)	•	152 (*2.3*)	•
5a-6a	•	–1 (*6.8*)	•	127 (*1.2*)	•	165 (*1.5*)	•

• The phase is observed; **o** *the phase is not observed; K = crystalline phase; M_1 and M_2 = mesophase 1 and 2, respectively; I = isotropic phase; [a] The maximum was taken as the temperature; [b] The enthalpy could not always be determined accurately due to the broadness of the transition; [c] A very small transition was observed around 25 °C (ΔH = 0.5 kJ/mol). [d] Crystallisation occurs upon heating; [e] This value is the sum of two overlapping transitions.*

Finally, mixtures of **5a** and **6a** were investigated with DSC. The thermal behaviour of a 1/1 mixture of **5a** and **6a** is different from that of the individual compounds, indicating that new mesophases are present in which the units are mixed. Two mesophases were detected with DSC. The first transition, assigned to the crystalline to liquid crystalline phase, is found at –1 °C. The transition to the second mesophase can be observed at 127 °C, and an isotropic liquid is formed at 165 °C. All the transitions reappear upon cooling from the

isotropic phase. The textures observed with OPM are more regular than in separate compounds and the Maltese cross is more well-defined.

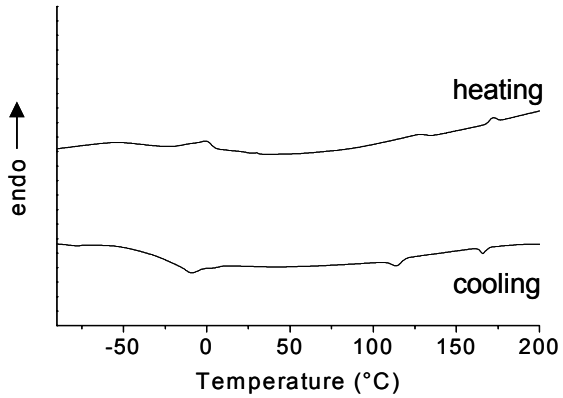


Figure 3.10: *DSC traces of a 1/1 mixture of **5a** and **6a** taken at a rate of 20 °C/min.*

For positive identification of the mesophases as discotic, observation of the textures under the optical polarisation microscope is insufficient and X-ray diffraction measurements are required. For compounds **1b** and **2a** preliminary X-ray measurements were carried out.

3.4 X-ray Diffraction

For X-ray diffraction studies, samples of **1b** and **2** were heated in glass capillaries to their isotropic phase, and then cooled down to the liquid crystalline state. The patterns of compounds **1b** and **2a** obtained at room temperature are depicted in Figure 3.11.

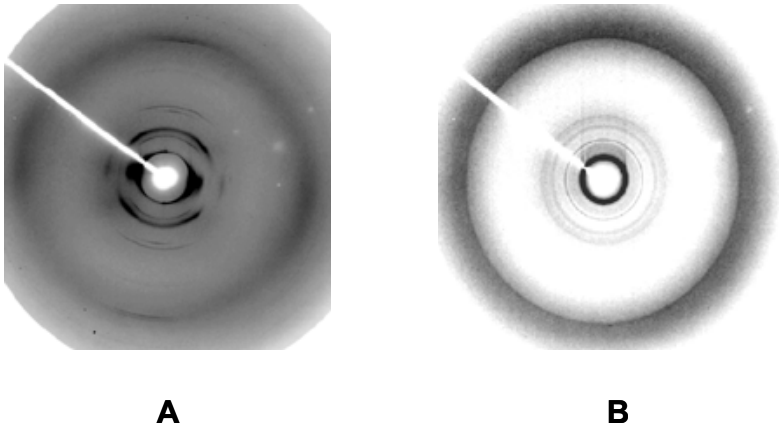


Figure 3.11: *Diffraction patterns observed for monofunctional compound **1b** (left) and bifunctional compound **2a** (right).*

A characteristic pattern splitting in a quadruplet is present in monofunctional compound **1b**. Palmans[19] and Maltête[20] previously observed similar quadruplet splitting of the reflection for their systems. They have attributed this splitting to a helical intracolumnar ordering. In Table 3.3 the observed and calculated spacings together with the corresponding Miller indices are collected for compound **2a**. It was found that the obtained spacings correspond well with the values calculated for an orthorhombic arrangement of the molecules, in which the lattice constants *a* and *b* of the rectangular lattice are in the ratio √3:1.

Table 3.3: *Diffraction spacings (Å) obtained for compound **2a**.*

d_{obs}	d_{calc}	**hkl**
		a = 61.0; *b* = 35.2
30.5	30.48	200; 110
22.9	23.0	210
20.0	20.3	300
17.8	17.6	020; 310
15.2	15.2	400; 220
13.3	13.3	320
12.0	11.7	030
11.2	11.5	420; 130
4.5		halo
35.2		inter-column distance

The obtained spacings of compound **1b** do not correspond with the values calculated for an orthorhombic or a hexagonal arrangement of the molecules. More measurements, especially in the small angle region are required in order to determine the arrangement of the molecules. For compounds **1b** and **2a** the characteristic reflection perpendicular to the intercolumnar direction was not observed, suggesting that the discs are stacked on top of each other in a disordered fashion. From the reflection at small angle, with a d-spacing of 27.7 Å and 30.5 Å for **1b** and **2a**, respectively, an intercolumnar distance can be calculated of 32 Å and 35.2 Å, respectively. For both compounds a broad alkyl halo is present, at 4.3 Å for **1b**, and at 4.5 Å for **2a**.

3.5 Discussion and Conclusion

All compounds synthesised exhibit thermotropic properties, as observed with optical polarisation microscopy and DSC. The mesophases were found to be stable over a reasonably broad (100 degrees for the achiral compounds) to broad (220 degrees for the chiral compounds) temperature range. The replacement of the dodecyl side chains by chiral branched aliphatic chains appears to have great influence on the phase behaviour. Whereas the liquid crystalline mesophase of monofunctional **1a** only exists between 85 °C and 183 °C, the mesophase of its chiral analogue **1b** covers a temperature range of 220 degrees. This can be explained by the less efficient packing of the chiral side chains compared to the dodecyl side chains, resulting in a lower melting point or even formation of a glass upon cooling. In other words, the 3,7-dimethyloctyloxy chains do not crystallise easy.[19,21] For the bifunctional compounds **2** a higher isotropisation temperature was expected due to the stabilisation of π-stacking by the hexamethylene linkage. Both bifunctional compounds **2a** and **2b** have similar phase transitions with two different mesophases. The exact nature of these mesophases has not yet been studied. WAXS measurements at room temperature showed that **2a** has a rectangular packing. The lattice constants *a* and *b* of the rectangular lattice are in the ratio $\sqrt{3}$ which should correspond to a hexagonal structure. However, the (210) reflection that is observed in the pattern is not consistent with a hexagonal packing. Therefore it can be concluded that compound **2a** has an orthorhombic symmetry. This means that the columnar axes are located at the nodes of a hexagonal network. However, the molecules at the centre of the unit cell have a different orientation than those located at the corners. This kind of lattice has been reported for hexagonal columnar phases in which the discs are tilted with respect to the columnar axis.[22] The higher lattice constant in these structures is due to alternation of the tilt direction, resulting in a herringbone arrangement of the elliptical sections of the columns. It is thought that compound **2a** might be present as two different helical columns with opposite helicity (see chapter 4), causing the herringbone arrangement. The transition observed in DSC at 148 °C for **2a** and 139 °C for **2b** may be ascribed to the transition of an ordered phase to a disordered phase. In order to get definite conclusions on the packing of the molecules, more detailed X-ray diffraction measurements need to be performed.

Nevertheless, from the preliminary X-ray measurements, the columnar diameter could be deduced. The diffraction patterns suggest, for compounds **1b** and **2a**, columnar

diameters of 32 Å and 35 Å, respectively. The diameter of **2a** corresponds well with the diameter found by Felix Beijer for monofunctional compound **1a**.[4] The small difference in columnar diameter of **1b** and **2a** is caused by the shorter chiral side chains of molecule **1b** compared to the dodecyl groups of **2a**. From these values it can be concluded that two ureido-*s*-triazine units build up the discs in the columns. In the case of monofunctional **1b** each disc is formed by a dimer. In bifunctional compounds **2a**, a disc cannot be formed from a single molecule, because the hexamethylene spacer is too short to allow intramolecular quadruple hydrogen bonding, nor is the spacer long enough to span the distance between neighbouring columns. An arrangement of the molecules such as displayed in Figure 3.4, therefore, is probable. The two halves of the molecule must reside in different disks. Because the hexamethylene spacer has a limited length, the observed intercolumnar distances are only compatible with an arrangement in which the *s*-triazine moieties of one molecule occupy consecutive layers of the same column. It was previously described by Beijer[4] that 4-amino-2-phenylureido-6-tridodecyloxyphenyl-pyrimidinone has a larger mesophase temperature range and a higher isotropisation temperature than 4-amino-2-butylureido-6-tridodecyloxyphenyl-pyrimidinone. This was explained by the presence of the aromatic substituent, which causes a more extended coplanar core. However, if monofunctional compounds **1b** and **5b** are compared, no dramatic change of the clearing temperature or liquid crystalline temperature range occurs. A large difference between **1b** or **5b**, and **3b** can be observed, however. Compounds **1b** and **5b** have similar temperature ranges, whereas the N-phenylamino substituted *s*-triazine **3b** has a lower clearing temperature and a much smaller temperature range in which the liquid crystalline phase exists. The lower temperature range of the N-phenyl derivatised *s*-triazine is not fully clear to us. The pentafluorphenyl substituent in compound **6** also has a large influence on the thermal properties of ureido-*s*-triazines. The mesophase temperature range decreases, suggesting that the pentafluorphenyl-UTrs do not pack as well as the phenyl-UTrs. In general, the DSC traces of the monofunctional compounds show that the peripheral alkoxy chains have an important effect on the crystalline/liquid crystalline transition temperature. The phenyl substituent in compounds **4a** and **4b** does not have a strong influence on the temperature range and the clearing temperature of bifunctional ureido-*s*-triazine compounds. All bifunctional compounds become isotropic around 185 °C. Apparently, the isotropisation temperature is mainly determined by the hexamethylene spacer that keeps consecutive discs together. Finally, mixtures of **5a** and **6a** do not have broader temperature range of the mesophase, although, the

thermal behaviour has clearly changed. The melting point of the mixture is lower than the one of the individual components. A change in texture was also observed with optical polarisation microscopy. It would be of interest to perform additional X-ray measurements in order to reveal the character of the mesophases of all compounds.

3.6 Experimental Section

General Methods.

All starting materials were obtained from commercial suppliers and used as received. All moisture-sensitive reactions were performed under an atmosphere of dry argon. Dry and ethanol-free dichloromethane was obtained by distillation from P_2O_5; dry tetrahydrofuran (THF) was obtained by distillation from Na/K/benzophenone; dimethylformamide was dried over BaO; pyridine was dried by standing over 4Å molsieves; dry toluene was obtained by distillation from Na/K/benzophenone and triethylamine was dried over potassium hydroxide. Methyl 3,4,5-tridodecyloxybenzoate and methyl 3,4,5-tri((*S*)-3,7-dimethyloctyloxybenzoate were synthesised following previously described procedures.[19] Analytical thin layer chromatography was performed on Kieselgel F-254 precoated silica plates. Visualization was accomplished with UV light. Column chromatography was carried out on Merck silica gel 60 (70-230 mesh) or on Merck aluminum oxide 90 (70-230 mesh, activity II-III). Preparative size exclusion chromatography was performed on BIO RAD Bio Beads S-X1 swollen in methylene chloride or tetrahydrofuran. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a 400 MHz 4-nucleus NMR (Varian Mercury Vx) (400.13 MHz for ^{1}H-NMR and 100.62 MHz for ^{13}C-NMR). Proton chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) and carbon chemical shifts in ppm downfield of TMS using the resonance of the deuterated solvent as internal standard. Electrospray ionisation mass spectrometry (ESI-MS) was carried out on a Perkin-Elmer API 300 MS/MS mass spectrometer. Matrix assisted laser desorption/ionization mass-time of flight spectra (Maldi-TOF) were obtained using indole acrylic acid as the matrix on a PerSeptive Biosystems Voyager-DE PRO spectrometer. IR-spectra were measured on a Perkin Elmer *Spectrum One*. Optical properties and melting points were determined using a Jeneval polarization microscope equipped with a Linkam THMS 600 heating device with crossed polarizers. DSC spectra were obtained on a Perkin Elmer Pyris 1 DSC. X-ray diffraction patterns were recorded at the European Synchrotron Radiation Facility (Installation Européenne de Rayonnement Synchrotron) in Grenoble, France.

6-(3,4,5-Tridodecyloxyphenyl)-*s*-triazine-2,4-diamine (9a). Biguanide sulfate (31.5 g, 0.158 mol) and sodium (7.65 g, 0.33 mol) were added to dry 2-methoxyethanol (400 mL) and the solution was stirred under reflux for 2 h. Subsequently methyl 3,4,5-tridodecyloxybenzoate (72.4 g, 0.106 mol) was added and reflux was continued overnight. After removal of the solvent *in vacuo*, the residue was dissolved in CH_2Cl_2 and treated with active carbon. After filtration the solvents were evaporated *in vacuo* and the product was purified by column chromatography (silica gel, first CH_2Cl_2 followed by methanol/CH_2Cl_2 1:20 R_f 0.46) and crystallisation

from basic ethanol, to yield the pure product (26.4 g, 35.7 mmol, 34%). T_m = 99 °C. IR: ν = 3475, 3401, 3170, 2930, 2852, 1627, 1568, 1545, 1511, 1467, 1417, 1377 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 7.55 (s, 2H, Ar-H), 5.51 (s, 4H, NH), 4.2 (m, 6H, OCH_2), 1.9-1.7 (m, 6H, CH_2), 1.5-1.4 (m, 6H, CH_2), 1.3-1.2 (m, 38 H, CH_2), 0.88 (t, 9H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 172.5, 168.1, 153.5, 142.0, 131.7, 107.3, 74.0, 69.6, 32.5, 30.9, 30.2-29.8. 26.7, 23.2, 19.0, 14.7. Anal. Calcd. (%) for $C_{45}H_{81}N_5O_3$ (740.17): C 73.02; H 11.03; N 9.46. Found (%): C 73.00; H 11.51; N 9.55.

4-Butylureido-6-(3,4,5-tridodecyloxyphenyl)-*s*-triazine-2-amino (1a). Butyl isocyanate (0.23 mL, 2.0 mmol) and 6-(3,4,5-tridodecyloxyphenyl)-*s*-triazine-2,4-diamine (0.74 g, 1.0 mmol) were heated under reflux in pyridine (10 mL). Subsequently the solvent was removed *in vacuo* and the resulting solid was purified by column chromatography (silica gel, CH_2Cl_2/MeOH 97/3) to yield the title compound (0.35 g, 0.42 mmol, 42%). T_{cl} = 183 °C. ^{1}H-NMR ($CDCl_3$): δ 10.16 (s, 1H, NH), 9.78 (s, 1H, NH), 9.29 (s, 1H, NH), 7.37 (s, 2H, Ar-H), 5.49 (s, 1H, NH), 3.96 (m, 6H, OCH_2), 3.30 (br, 2H, NCH_2) 1.75 (m, 6H, CH_2), 1.66 (m, 6H, CH_2), 1.57 (m, 2H, CH_2), 1.5-1.1 (m, 42 H, CH_2), 0.87 (t, 3H, CH_3), 0.80 (t, 9H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 170.3, 167.2, 163.7, 155.9, 153.0, 142.1, 130.2, 106.9, 73.5, 69.2, 40.0, 32.2, 31.9, 30.4, 29.7-29.3, 26.1-26.0, 22.7, 20.3, 14.1, 13.8. IR: ν = 3492, 3419, 3212, 3132, 2921, 2849, 1684, 1638, 1578, 1528 cm^{-1}. Anal. Calcd. (%) for $C_{50}H_{90}N_6O_4$ (839.30): C 71.52; H 10.80; N 10.05. Found (%): C 71.52; H 11.26; N 9.89.

$N^{4\omega}$,$N'^{4\omega}$-(1,6-Hexamethylene)-bis-[6-(3,4,5-tridodecyloxyphenyl)-2-ureido-*s*-triazine-4-amine] (2a). A solution of 2,4-diamino-6-(3,4,5-tri(dodecyloxy)phenyl)-*s*-triazine (2.5 g. 3.38 mmol) and 1,6-diisocyanatohexane (0.162 g, 0.97 mmol) in dry pyridine (15 mL) was stirred at reflux temperature for 2 days. The solvent was removed *in vacuo* and coevaporated twice with toluene (2 × 10 mL) resulting in a yellow gum. Precipitation from chloroform in ethyl acetate and column chromatography (silica gel, $CHCl_3$/EtOH 98/2, R_f = 0.45) yielded the pure title compound as an opaque waxy solid (1.0 g, 63%). T_{cl} = 178 °C. IR: ν = 1691, 1466, 1116, 815 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 10.17 (s, 2H, NH), 9.65 (s, 2H, NH), 9.30 (s, 2H, NH), 7.36 (s, 4H, Ar-H), 5.31 (s, 2H, NH), 4.0 (m, 12H, OCH_2), 3.39 (br, 4H, NCH_2), 1.8-1.5 (m, 68H, CH_2), 1.28 (m, 60H, CH_2), 0.89 (t, 18H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 170.4, 167.5, 163.9, 156.0, 153.1, 142.8, 130.4, 107.8, 73.6, 69.6, 40.0-22.7, 14.0. Anal. Calcd. (%) for $C_{98}H_{174}N_{12}O_8$ (1648.53): C 71.40; H 10.64; N 10.20. Found (%): C 71.34; H 10.62; N 10.16. ES-MS: 825.4 $(M + 2H)^{2+}$ (Calcd 825.3), 1649.8 $(M + H)^+$ (Calcd 1649.6).

6-[3,4,5-Tri-(*S*)-3,7-dimethyloctyloxyphenyl]-*s*-triazine-2,4-diamine (9b). 3,4,5-Tri-(*S*)-3,7-dimethyl-octyloxybenzoic acid (20.3 g, 30.0 mmol) was dissolved in thionyl chloride (100 mL) and the solution was stirred under reflux for 3 h. The solvent was evaporated *in vacuo* and the residue was coevaporated twice with dry hexane (2 x 50 mL) to yield **3,4,5-tri-(*S*)-3,7-dimethyloctyloxybenzoyl chloride** quantitative. The resulting oil was used immediately for the synthesis of **3,4,5-tri-(*S*)-3,7-dimethyloctyloxy)benzamide (7)** and dissolved in diethyl ether (200 mL). While stirring, ammonia was added (150 mL, 25%) followed by ice (50 g) and the mixture was stirred for another hour. The organic layer was separated from the aqueous layer and subsequently washed with water and dried over Na_2SO_4. The solvents were removed *in vacuo* to yield the product as an oil (18.3 g, 27.2 mmol, 91.1%), which was used as such.

To a solution of 3,4,5-tri-(*S*)-3,7-dimethyloctyloxybenzamide (15.5 g, 26.3 mmol) in dry toluene (100 mL) was added $POCl_3$ (20 g, 0.132 mol). The reaction mixture was stirred at reflux temperature for 3 h. The brown oil obtained after removal of the solvents was dissolved in dichloromethane (50 mL). Extraction with water (2 × 100 mL) and brine (100 mL), and drying over $MgSO_4$ gave a yellow oil. Further purification with column chromatography (silica gel, heptane/EtOAc 24/1) yielded 10.5 g (18.4 mmol, 70%) **3,4,5-tri-(*S*)-3,7-dimethyloctyloxybenzonitrile (8)**. IR: ν = 2226 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 6.83 (s, 2H, Ar-H), 3.99 (m, 6H, OCH_2), 1.90-0.86 (CH_2, CH_3, 64H). ^{13}C-NMR ($CDCl_3$): δ 153.2, 142.2, 119.2, 110.2, 106.1, 71.9, 67.7, 39.4-19.7.

A suspension of the benzonitrile (2.3 g, 4.07 mmol), dicyanodiamide (0.37 g, 4.48 mmol) and KOH (0.06 g, 1.02 mmol) in *i*-propanol (10 mL) was prepared and stirred at reflux temperature for 24 h. Diethyl ether (50 mL) was added and the organic layer was washed with water (2 × 50 mL) and brine (50 mL). Drying of the organic layer over Na_2SO_4 and removal of the solvent *in vacuo* yielded a yellow waxy solid. This gave 2.3 g (3.5 mmol, 80%) of the desired product after purification by column chromatography (silica gel, first 100% $CHCl_3$, then $CHCl_3$/THF 97/3, R_f = 0.14). T_{cl} = 89 °C. IR: ν = 3325, 3197, 1463, 1114, 821 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 7.30 (s, 2H, Ar-H), 5.42 (s, 4H, NH_2), 4.08 (m, 6H, OCH_2), 1.90-1.2 (m, 36H, CH_2), 1.0-0.85 (m, 27H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 172.1, 167.7, 153.1, 141.4, 131.2, 106.7, 71.7, 67.4, 39.5-19.7. Anal. Calcd. (%) for $C_{39}H_{69}N_5O_3$ (656.01): C 71.4; H 10.6; N 10.7. Found (%): C 71.2; H 10.5; N 10.5.

4-Butylureido-6-[3,4,5-tri-(*S*)-3,7-dimethyloctyloxyphenyl]-*s*-triazine-2-amine (1b). 6-[3,4,5-tri-*(S)*-3,7-dimethyloctyloxyphenyl]-*s*-triazine-2,4-diamine (2.00 g, 3.05 mmol) and *n*-butylisocyanate (0.91 g, 9.15 mmol) were dissolved in dry pyridine (15 mL). The reaction mixture was stirred, under a flow of nitrogen, at reflux temperature for 2 h. The solvent was removed under reduced pressure and the remaining crude product was coevaporated twice with toluene (2 × 10mL). Precipitation from a concentrated chloroform solution in methanol gave a waxy compound, which was further purified by column chromatography (silica gel, $CHCl_3$/THF 95/5, R_f = 0.7) yielding 1.5 g (1.99 mmol, 65%) pure compound. T_{cl} = 190 °C. IR: ν = 1688, 1465, 1113, 816 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 10.23 (s, 1H, NH), 9.87 (s, 1H, NH), 9.27 (s, 1H, NH), 7.47 (s, 2H, Ar-H), 5.44 (s, 1H, NH), 4.08 (m, 6H, OCH_2), 3.40 (q, 2H, N-CH_2), 1.90-0.86 (CH_2, CH_3, 64H). ^{13}C-NMR ($CDCl_3$): δ 170.5, 167.3, 163.8, 156.0, 153.1, 142.1, 130.4, 106.9, 71.8, 67.5, 40-13.8. Anal. Calcd. (%) for $C_{44}H_{78}N_6O_4$ (755.14): C 69.99; H 10.41; N 11.13. Found (%): C 69.86; H 10.65; N 11.09. ES-MS: 755.8 $(M + H)^+$ (Calcd. 756.1), 1510.6 $(2M + H)^+$ (Calcd. 1511.3).

$N^{4\omega}$,$N'^{4\omega}$-(1,6-Hexamethylene)-bis-{4-ureido-6-[3,4,5-tri-(*S*)-3,7-dimethyloctyloxyphenyl]-*s*-triazine-2-amine} (2b). The title compound was synthesised similar to **2a**, now starting from 6-[3,4,5-tri-(*S*)-3,7-dimethyloctyloxyphenyl]-*s*-triazine-2,4-diamine, giving **2b** in a yield of 32 %. T_{cl} = 187 °C. IR: ν = 1688, 1465, 1113, 816 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 10.23 (2H), 9.89 (2H), 9.28 (2H), 7.44 (4H), 5.44 (2H), 4.08 (12H), 3.38 (4H), 1.90-0.85 (122H). ^{13}C-NMR ($CDCl_3$): δ 170.2, 167.3, 163.7, 156.0, 153.0, 142.1, 130.5, 107.0, 71.7, 67.5, 39.4-19.6. Anal. Calcd. (%) for $C_{86}H_{150}N_{12}O_8$ (1480.21): C 69.78; H 10.21; N 11.36. Found (%): C 69.93; H 10.29; N 11.31. ES-MS: 741 $(M + 2H)^{2+}$ (Calcd. 741.1), 1481 $(M + H)^+$ (Calcd. 1481.2).

N-Phenylamino-6-(3,4,5-tridodecyloxyphenyl)-*s*-triazine-2-amine (10a). In a 100 ml two-neck round-bottomed flask, equipped with a condenser, methyl 3,4,5-tridodecyloxybenzoate (5 g, 7.26 mmol) and phenylbiguanide (1.93 g, 10.88 mmol) were dissolved in 2-methoxyethanol at 60 °C. After cooling, sodium methoxide was added. The reaction mixture was stirred at reflux temperature for 1 h. The reaction mixture was poured in 20 mL 1M HCl solution and washed with 20 mL CH_2Cl_2. The organic layer was extracted with water (2 × 20mL) and brine (20mL), and dried over $MgSO_4.H_2O$. Purification by column chromatography (Al_2O_3, eluent: 7 % THF in $CHCl_3$, product: R_f = 0.8, impurity: R_f = 0) yielded the title compound (69 %). IR: ν = 3460, 3338, 1417, 1121, 810 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 7.62 (d, 2H, phenyl-ortho), 7.6 (s, 2H, Ar-H), 7.35 (t, 2H, phenyl-meta), 7.1 (br, 1H, NH), 7.06 (t, 1H, phenyl-para), 5.2 (br, 2H, NH_2), 4.08 (m, 6H, OCH_2), 1.83-1.2 (m, 60H, CH_2), 0.85 (t, 9H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 171.9, 167.6, 165.1, 153.2, 141.7, 138.8, 131.3, 129.0, 123.6, 120.8, 107.0, 73.7, 69.3, 32.2, 30.6, 30.0-29.6, 26.4, 22.9, 14.4.

2-Butylureido-4-phenylamino-6-(3,4,5-tridodecyloxyphenyl)-*s*-triazine (3a). 4-Phenylamino-6-(3,4,5-tridodecyloxyphenyl)-*s*-triazine-2-amine **10a** (2 g, 2.45 mmol) and *n*-butylisocyanate (0.73 g, 7.35 mmol) were dissolved in dry pyridine (10 mL). The reaction mixture was stirred, under a flow of nitrogen, at reflux temperature for 12 h. The solvent was removed under reduced pressure and the remaining crude product was coevaporated twice with toluene (2 × 10 mL). Precipitation from a concentrated chloroform solution in ethyl acetate gave a waxy compound (1.96 g, 88%). T_{cl} = 157 °C. IR: ν = 3223, 1692, 1428, 1113, 807 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 11.36 (s, 1H, NH), 10.16 (s, 1H, NH), 9.71 (s, 1H, NH), 7.9 (d, 2H, phenyl-ortho), 7.5 (s, 2H, Ar-H), 7.3 (t, 2H, phenyl-meta), 7.1 (t, 1H, phenyl-para), 4.08 (t, 2H, OCH_2), 3.99 (t, 4H, OCH_2), 3.38 (q, 2H, N-CH_2), 1.83-1.2 (m, 72H, CH_2), 0.97 (t, 3H, CH_3 butyl), 0.91 (t, 9H, CH_3 dodecyl). ^{13}C-NMR ($CDCl_3$): δ 170.2, 164.0, 163.6, 155.8, 153.0, 142.3, 139.5, 130.3, 128.3, 123.2, 121.5, 107.2, 73.6, 69.1, 40.0, 32.3-13.8. Anal. Calcd. (%) for $C_{56}H_{94}N_6O_4$ (915.40): C 73.5; H 10.4; N 9.2. Found (%): C 73.7; H 10.4; N 9.2.

$N^{2\omega}$,$N'^{2\omega}$-(1,6-Hexamethylene)-bis-[4-phenyl-6-(3,4,5-tridodecyloxyphenyl)-2-ureido-*s*-triazine] (4a). 4-Phenyl-6-(3,4,5-tridodecyloxyphenyl)-*s*-triazine-2-amine **10a** (2 g, 2.45 mmol) and 1,6-diisocyanatohexane (0.165 g, 0.98 mmol) were dissolved in dry pyridine (10 mL). The reaction mixture was stirred, under a flow of nitrogen, at reflux temperature for 12 h. The solvent was removed under reduced pressure and the remaining crude product was coevaporated twice with toluene (2 × 10mL). A white waxy compound was obtained after precipitation from a concentrated chloroform solution in ethyl acetate. Purification by column chromatography (silica gel, 100% $CHCl_3$, R_f = 0.5) gave 1.05 g (59%) of the title compound. T_{cl} = 205 °C. IR: ν = 3225, 1696, 1428, 1116, 807 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 11.28 (s, 2H, NH), 9.9 (s, 2H, NH), 9.71 (s, 2H, NH), 7.78 (d, 4H, phenyl-ortho), 7.35 (s, 4H, Ar-H), 7.0 (t, 4H, phenyl-meta), 6.75 (t, 2H, phenyl-para), 4.0 (br, 12H, OCH_2), 3.15 (br, 2H, N-CH_2), 2.1 (br, 2H, N-CH_2), 1.83-0.85 (m, 134H, CH_2, CH_3). ^{13}C-NMR ($CDCl_3$): δ 170.0, 163.7, 163.5, 156.0, 152.7, 142.0, 139.5, 130.7, 127.8, 122.5, 120.6, 107.5, 73.6, 69.1, 38.1, 32.0-14.2. Anal. Calcd. (%) for $C_{110}H_{182}N_{12}O_8$ (1800.72): C 73.4; H 10.2; N 9.3. Found (%): C 73.8; H 10.5; N 9.3.

4-Phenylamino-6-[3,4,5-tri-(*S*)-3,7-dimethyloctyloxyphenyl]-*s*-triazine-2-amine (10b). A suspension of methyl 3,4,5-tri-(*S*)-3,7-dimethyloctyloxybenzoate (5 g, 8.3 mmol), phenylbiguanide (2.2 g, 12.4 mmol) and sodiummethoxide (0.67 g, 12.4 mmol) in 2-methoxyethanol (20 mL) was prepared and stirred at reflux temperature for 2 h. After cooling down, the reaction mixture was quenched with 1M HCl (10 mL), and washed with CH_2Cl_2. The organic phase was washed with water (2 × 50 mL) and brine (50 mL), and dried with $MgSO_4.H_2O$. The solvent was removed *in vacuo* to give a yellow oil. The desired highly viscous product (3 g, 50 %) was obtained pure after purification by column chromatography (alumina, CH_2Cl_2/THF 93/7, R_f = 0.6). IR: ν = 3314, 3198, 1412, 1112, 817 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 7.62 (d, 2H, phenyl-ortho), 7.6 (s, 2H, Ar-H), 7.35 (t, 2H, phenyl-meta), 7.2 (br, 1H, NH), 7.06 (t, 1H, phenyl-para), 5.25 (br, 2H, NH_2), 4.1 (m, 6H, OCH_2), 1.83-0.85 (m, 57H, CH_2, CH_3). ^{13}C-NMR ($CDCl_3$): δ 171.7, 167.4, 164.9, 153.1, 141.6, 138.6, 131.2, 128.9, 123.6, 120.6, 106.8, 72.0, 67.6, 40-20.

2-Butylureido-4-phenylamino-6-[3,4,5-tri-(*S*)-3,7-dimethyloctyloxyphenyl]-*s*-triazine (3b). 4-Phenylamino-6-[3,4,5-tri-(*S*)-3,7-dimethyloctyloxyphenyl]-*s*-triazine-2-amine **10b** (0.5 g, 0.68 mmol) and *n*-butylisocyanate (0.7 g, 7.06 mmol) were dissolved in dry pyridine (2 mL). The reaction mixture was stirred, under a flow of nitrogen, at reflux temperature for 6 hours. The solvent was removed under reduced pressure and the remaining crude product was coevaporated twice with toluene (2 × 5 mL). Precipitation from a concentrated chloroform solution in ethanol gave the white title compound (0.45 g, 80%). T_{cl} = 145 °C. IR: ν = 3223, 1692, 1428, 1113, 807 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 11.36 (s, 1H, NH), 10.16 (s, 1H, NH), 9.71 (s, 1H, NH), 7.9 (d, 2H, phenyl-ortho), 7.5 (s, 2H, Ar-H), 7.3 (t, 2H, phenyl-meta), 7.1 (t, 1H, phenyl-para), 4.08 (t, 2H, OCH_2), 3.99 (t, 4H, OCH_2), 3.38 (q, 2H, N-CH_2), 1.83-1.2 (m, 72H, CH_2), 0.97 (t, 3H, CH_3 butyl), 0.91 (t, 9H, CH_3 dodecyl). ^{13}C-NMR ($CDCl_3$): δ 170.3, 164.0, 163.7, 155.9, 153.1, 142.3, 139.4, 130.5, 128.4, 123.3, 121.5, 107.2, 71.9, 67.4, 40.1, 39.5-13.9. Anal. Calcd. (%) for $C_{50}H_{82}N_6O_4$ (831.24): C 72.3; H 9.9; N 10.1. Found (%): C 72.1; H 10.2; N 10.1.

$N^{2\omega}$,$N'^{2\omega}$-(1,6-Hexamethylene)-bis-{4-phenylamino-6-[3,4,5-tri-(*S*)-3,7-dimethyloctyloxyphenyl]-*s*-triazine} (4b). 4-Phenylamino-6-[3,4,5-tri-(*S*)-3,7-dimethyloctyloxyphenyl]-*s*-triazine-2-amine **10b** (1 g, 1.37 mmol) and 1,6-diisocyanatohexane (0.104 g, 0.62 mmol) were dissolved in dry pyridine (2 mL). The reaction mixture was stirred, under a flow of nitrogen, at reflux temperature for 24 h. The solvent was removed under reduced pressure and the remaining crude product was coevaporated twice with toluene (2 × 10 mL). A white waxy compound was obtained after precipitation from a concentrated chloroform solution in ethyl acetate. Purification by column chromatography (silica gel, 100 % $CHCl_3$, then CH_2Cl_2/THF 96/4, R_f = 0.5) gave 0.6 g (60 %) of the desired product. T_{cl} = 195 °C. IR: ν = 3217, 1689, 1428, 1113, 807 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 11.25 (s, 2H, NH), 9.9 (s, 2H, NH), 9.71 (s, 2H, NH), 7.68 (d, 4H, phenyl-ortho), 7.55 (s, 4H, Ar-H), 7.0 (t, 4H, phenyl-meta), 7.75 (t, 2H, phenyl-para), 4.0 (m, 12H, OCH_2), 3.5 (br, 2H, N-CH_2), 2.1 (br, 2H, N-CH_2), 1.9-0.9 (m, 116H, CH_2, CH_3). ^{13}C-NMR ($CDCl_3$): δ 170.3, 163.9, 163.7, 156.1, 153.1, 152.9, 142.2, 139.6, 131.0, 128.0, 122.7, 120.8, 107.7, 72.0, 67.6, 39.6-19.9. Anal. Calcd. (%) for $C_{98}H_{158}N_{12}O_8$ (1632.4): C 72.1; H 9.8; N 10.3. Found (%): C 72.2; H 9.9; N 10.2.

4-Phenylureido-6-(3,4,5-tridodecyloxyphenyl)-*s*-triazine-2-amine (5a). In a two-neck round-bottom flask, equipped with a condenser, 6-(3,4,5-tridodecyloxyphenyl)-*s*-triazine-2,4-diamine **9a** (0.5 g, 0.68 mmol) was dissolved in dry pyridine (5 mL). Part of the pyridine was evaporated under an argon flow in order to remove traces of water. After cooling down the reaction mixture, phenylisocyanate (0.08 g, 0.68 mmol) was added via syringe. The reaction mixture was stirred at reflux temperature for 2 h. The solvent was removed under reduced pressure and the residue was co-evaporated three times with toluene (10 mL). Precipitation from dichloromethane in ethyl acetate followed by column chromatography (silica gel gel gel, eluent: $CHCl_3$, R_f (product) = 0.3) gave 0.23 g (Y = 40%) of the pure desired compound. $T_{C\rightarrow M1}$ = 9 °C (ΔH = 17.2 J/g), $T_{M1\rightarrow M2}$ = 160 °C (ΔH = 3.4 J/g), $T_{M2\rightarrow cl}$ = 172 °C (ΔH = 1.3 J/g). IR (UATR): ν = 3500, 3303, 3211, 3144, 1698, 1654 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 12.14 (br, 1H, NH-intramol. H-bond), 10.39 (br, 1H, NH), 9.24 (br, 1H, NH), 7.58 (d, 2H, phenylureido-ortho), 7.52 (s, 2H, Ar-H), 7.36 (t, 2H, phenylureido-meta), 7.16 (t, 1H, phenylureido-para), 5.53 (br, 1H, NH), 4.05 (m, 6H, OCH_2), 1.8-0.85 (m, 57H, CH_2, CH_3). ^{13}C-NMR ($CDCl_3$): δ 170.6, 167.4, 163.7, 153.8, 153.3, 142.5, 137.5, 130.2, 129.1, 124.6, 121.4, 107.1, 73.6, 69.4, 32.0-14.2. Anal. Calcd. (%) for $C_{52}H_{86}N_6O_4$ (859.29): C 72.68; H 10.09; N 9.78. Found (%): C 72.45; H 10.11; N 9.82.

4-Phenylureido-6-[3,4,5-tri-(*S*)-3,7-dimethyloctyloxyphenyl]-*s*-triazine-2-amine (5b). The title compound was synthesised in the same way as compound **1** starting from 6-[3,4,5-tri-(*S*)-3,7-dimethyloctyloxyphenyl)]-*s*-triazine-2,4-diamine **9b** and obtained pure in 66% yield. T_g = -63 °C (0.1 J/g °C), $T_{g\rightarrow M1}$ = 110 °C and $T_{M1\rightarrow M2}$ = 121 °C overlap each other, $T_{M2\rightarrow cl}$ = 183 °C (ΔH = 4.9 J/g). IR (UATR): ν = 3422, 3303, 3213, 1686, 1645 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 12.12 (br, 1H, NH-intramol. H-bond), 10.40 (br, 1H, NH), 9.2 (br, 1H, NH), 7.58 (d, 2H, phenylureido-ortho), 7.54 (s, 2H, Ar-H), 7.36 (t, 2H, phenylureido-meta), 7.15 (t, 1H, phenylureido-para), 5.52 (br, 1H, NH), 4.1 (m, 6H, OCH_2), 1.83-0.85 (m, 57H, CH_2, CH_3). ^{13}C-NMR ($CDCl_3$): δ 171.7, 167.3, 163.6, 153.8, 153.3, 142.3, 137.4, 130.2, 129.1, 124.6, 121.3, 106.9, 71.8, 67.6, 39.4-19.5. Anal. Calcd. (%) for $C_{46}H_{74}N_6O_4$ (775.13): C 71.28; H 9.62; N 10.84. Found (%): C 71.16; H 9.76; N 10.75.

4-Pentafluorophenylureido-6-(3,4,5-tridodecyloxyphenyl)-*s*-triazine-2-amine (6a). Pentafluoroaniline (0.25 g, 1.35 mmol) was dissolved in $COCl_2$ (8 mL; 10% in toluene) in a 1-neck round-bottomed flask and stirred overnight at reflux temperature. After removal of the solvent and the phosgene in excess *in vacuo* the crude product was co-evaporated with pentane. The isocyanate was characterised with IR (UATR): 2266 cm^{-1}. The pentafluorophenylisocyanate was used as such and dissolved together with 6-(3,4,5-tridodecyloxyphenyl)-*s*-triazine-2,4-diamine **9a** (0.4 g, 0.61 mmol) in dry pyridine (5 mL). The reaction mixture was stirred, under an argon flow, at reflux temperature for 2 h. The solvent was removed under reduced pressure and the remaining crude product was co-evaporated three times with 10 mL toluene. Precipitation from a concentrated chloroform solution in ethanol gave a white, still impure product. The compound was obtained pure (Y = 32%) by column chromatography (silica gel gel, eluent: 3/2 dichloromethane/$CHCl_3$). $T_{C\rightarrow M1}$ = 29 °C (ΔH = 21.9 J/g), $T_{M1\rightarrow M2}$ = 140 °C (ΔH = 0.3 J/g), $T_{M2\rightarrow cl}$ = 167 °C (ΔH = 2.4 J/g). IR (UATR): ν = 3500, 3301, 3208, 3156, 1713, 1646 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 12.11 (br, 1H, NH-intramol. H-bond), 10.76 (br, 1H, NH), 8.86 (br, 1H, NH), 7.44 (s, 2H, Ar-H), 5.55 (br, 1H, NH), 4.02 (m, 6H, OCH_2), 1.8-0.85 (m, 69H, CH_2, CH_3). ^{13}C-NMR ($CDCl_3$): δ 170.7,

167.3, 163.5, 153.9, 153.4, 144.6, 142.7, 142.1, 141.5, 139.3, 136.8, 129.5, 112.0, 107.0, 73.8, 69.3, 32.1, 30.5-29.6, 26.2, 22.8, 14.3. ^{19}F-NMR ($CDCl_3$): δ –144.7, –156.3, –161.8. Anal. Calcd. (%) for $C_{52}H_{81}F_5N_6O_4$ (949.24): C 65.80; H 8.60; N 8.85. Found (%): C 65.75; H 8.40; N 8.63.

4-Pentafluorophenylureido-6-[3,4,5-tri-(*S*)-3,7-dimethyloctyloxyphenyl]-*s*-triazine-2-amine (6b). The title compound was synthesised in the same way as compound **3**, using 6-[3,4,5-tri-(*S*)-3,7-dimethyloctyloxyphenyl)-*s*-triazine-2,4-diamine **9b** and obtained pure with column chromatography (silica gel gel, eluent: $CHCl_3$ of technical quality) in a yield of 48%). T_g = –71 °C (0.05 J/g °C), $T_{M1\rightarrow M2}$ = 108 °C (ΔH = 0.7 J/g), $T_{M2\rightarrow cl}$ = 145 °C (ΔH = 2.5 J/g). IR (UATR): ν = 3498, 3302, 3207, 3150, 1701, 1654 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 12.10 (br, 1H, NH-intramol. H-bond), 10.70 (br, 1H, NH), 8.85 (br, 1H, NH), 7.44 (s, 2H, Ar-H), 5.60 (br, 1H, NH), 4.02 (m, 6H, OCH_2), 1.9-0.80 (m, 57H, CH_2, CH_3). ^{19}F-NMR ($CDCl_3$): δ –144.9, –156.9, –162.2.

3.7 References and Notes

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4

Helical Self-assembled Polymers via Cooperative Stacking of Hydrogen Bonded Pairs*

Abstract

Highly organised self-assembled supramolecular polymers with control over helicity and chain length were obtained in solution. The monomers of these aggregates consist of bifunctional trialkoxyphenyl-s-triazine units connected to each other by a hexyl spacer. Bifunctional molecules ***2a*** *and* ***2b*** *associate via quadruple hydrogen bonds to give linear polymers. Various techniques were employed in order to investigate the aggregation of these compounds in different environments. Compounds* ***2a*** *and* ***2b*** *form lyotropic solutions in dodecane. CD spectroscopy and SANS prove the existence of a columnar architecture in dodecane, whereas in chloroform a random coil like aggregate was found. Complete disruption to molecularly dissolved compounds occurred when methanol is added. The columns formed by* ***2*** *feature a high degree of cooperativity, and a significant amplification of chirality resulted when chiral monofunctional compound* ***1b*** *was added to a dodecane solution of achiral bifunctional* ***2a****.*

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4.1 Introduction

In recent years, substantial progress has been made in the area of self-assembly of synthetic molecules in solution.[1] Whitesides[2] and Lehn[3] have pioneered the study of self-assembled multimolecular complexes and have shown that a high degree of control of macro architectures based on self-assembly is possible. Self-assembly in polymeric systems has drawn a lot of interest. One way to obtain self-assembled polymeric systems is by using stacking interactions of extended π-systems. Usel'tseva *et al.*[4] have described the use of Pd complexes with the intention to extend the rigid core by means of dimerisation of the molecule. As a result, the whole discotic moiety that consists of a dimer, formed via metal-ligand interactions, exhibits thermotropic and lyotropic liquid crystalline behaviour. Palmans[11] has reported on C_3-symmetrical disc-shaped molecules that feature both thermotropic and lyotropic liquid crystalline properties. In addition, the columnar structure of this star shaped molecule persists in diluted apolar solutions. This was achieved by increasing π-stacking interactions and by using hydrogen bonds between the discotic molecules. Also, a number of highly ordered structures in water has been published.[5-9] For instance, Gottarelli reported on the assembly of alkaline folates in water. The aggregates are cylindrical and of finite length, composed of a stacked array of folic acid tetramers. In the columns each tetramer is formed by *Hoogsteen*-bonded folate residues.[7] In our group Luc Brunsveld,[6] following the approach described in this chapter, has reported on bifunctional ureido-*s*-triazines provided with chiral ethylene oxide side chains, that self-assemble in water into helical columns via cooperative stacking of the hydrogen bonded pairs. Following the work of Green for polymers,[10] the role of cooperativity in the self-assembly of chiral architectures has been studied using peripheral chirality.[11,12] Green found that chiral side chains can transmit chirality into a helical polymer backbone. Using the transfer of peripheral chirality and inspired by the secondary structure of proteins, the control over chain folding of synthetic oligomers, so-called foldamers,[13-16] has also become an extensively studied topic. Transfer of chirality of peripheral side chains in supramolecular π-systems has been reported by Palmans.[11]

Our approach is to self-assemble a hydrogen bonded supramolecular polymer that folds into a well-defined secondary structure by using stacking interaction. In the previous chapter it was shown that mesophases of butylureido-*s*-triazine **1** and **3**, and hexamethyl-

bis(ureido-*s*-triazine) **2** and **4**, have discotic hexagonal structures with a columnar structure in which the spacers restrict the relative orientation of the discs. In a regular arrangement, this results in a helical organisation of the columns. In this chapter we are investigating the architecture, and more specifically the persistence of the secondary structure of compounds **1**-**4** in apolar solution. The proposed supramolecular structure is schematically represented in Figure 1 of chapter 3. For the study of the aggregation of these molecules in solution, a range of techniques like rheology, UV and CD spectroscopy, and SANS was applied. Compounds **5** and **6** bearing an additional phenyl group were also studied and compared with compounds **1** and **2**. The compounds studied in this chapter are depicted in Figure 4.1.

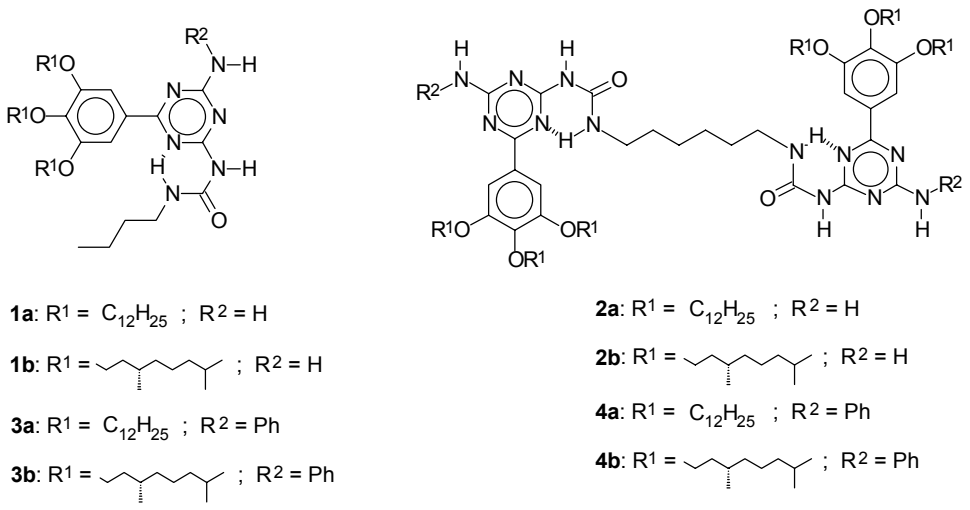

Figure 4.1: *Compounds used in the study described in this chapter.*

4.2 Lyotropic Liquid Crystalline Properties of 1b and 2a

The number of disc shaped molecules that exhibit both thermotropic and lyotropic liquid crystalline behaviour is limited. Lyotropic liquid crystalline behaviour of disc-shaped molecules requires strong stacking interactions between the molecules. This can be achieved by increasing π-stacking interactions in molecules with extended rigid cores. For this purpose we use hydrogen bonds between ureido-*s*-triazine units. When dissolving compounds **1b** and **2a** in dodecane, highly viscous solutions are formed.[17] Above 10 wt% of **1b** in dodecane and above 2 wt% of **2a** in dodecane clear gels are formed. The solutions are birefringent at higher concentrations. The phase behaviour examined with optical polarisation microscopy (OPM) are summarised in the phase diagrams in Figure 4.2 and show that at room temperature,

birefringence occurs for compound **1b** above 25 wt%, and for compound **2a** above 5 wt%, as observed with optical polarisation microscopy. Using DSC for studying the mesophases was not always possible, since the transitions are extremely broad or even absent for the more diluted solutions. In order to elucidate the structure of the lyotropic mesophases, preliminary X-ray diffraction measurements of dodecane solutions of **1a** and **2a** were carried out. However, only diffuse reflections were obtained.

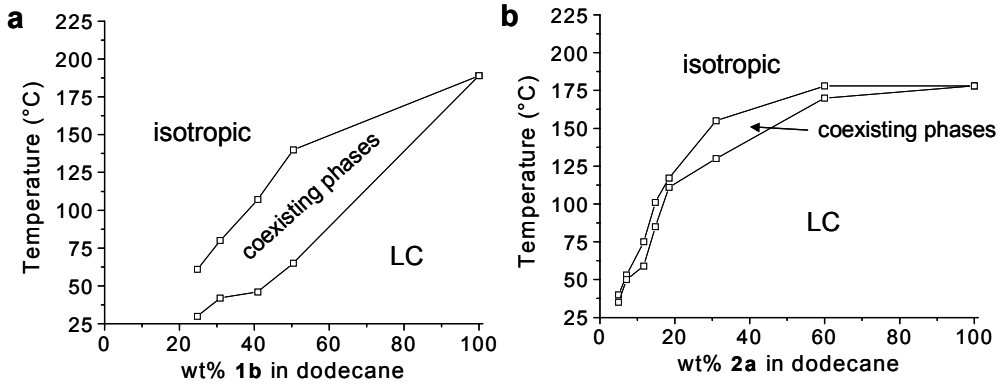

Figure 4.2: *Clearing temperature of solutions of **1b** and **2a** as a function of concentration in dodecane: **a)** compound **1b**, and **b)** bifunctional compound **2a**. The results are obtained by observation with optical polarisation microscopy.*

4.3 Isotropic Solutions of 1 and 2

^{1}H-NMR spectra of compounds **1** and **2** in $CDCl_3$ show that the signals corresponding to the hydrogen bonded protons are found at low field, with chemical shifts at 10.3, 9.9 (intramolecular hydrogen bond) and 9.3 ppm for both compounds (for detailed information the reader is referred to chapter 3). The characteristic position of the NH protons suggests that the ureido-*s*-triazines dimerise in chloroform. In deuterated dodecane, the ^{1}H-NMR signals are broadened beyond recognition. Only when a solution of achiral bifunctional **2a** was heated to 130 °C signals appeared but even then they are extremely broad. This might be explained by the stacking of the aromatic core at lower temperatures as was found before by Palmans[11] and Brunsveld.[6]

4.3.1 Viscosity, Rheology Measurements and Microscopy (TEM)

In contrast to compound **1b**, which does not form viscous solutions, a solution of compound **2a** in chloroform is viscous; a $3.1 \bullet 10^{-2}$ M solution of **2a** has a relative viscosity* of 3.94. As found previously for hydrogen bonded supramolecular polymers the viscosity is highly concentration dependent. Dodecane solutions of **2** are even more viscous. Above 2 wt%, the samples are gel-like, and at high concentration the solution is lyotropic (see previous section).

The viscosity of solutions of **1b** and **2a** in dodecane were determined well below the lyotropic liquid crystalline concentration. Viscosity measurements with an Ubbelohde type viscometer were not successful because the running times were not reproducible. Therefore, the aggregation of compounds **2a** and **1b** in dodecane was studied by measuring viscosity at different shear rates using a fluid rheometer.

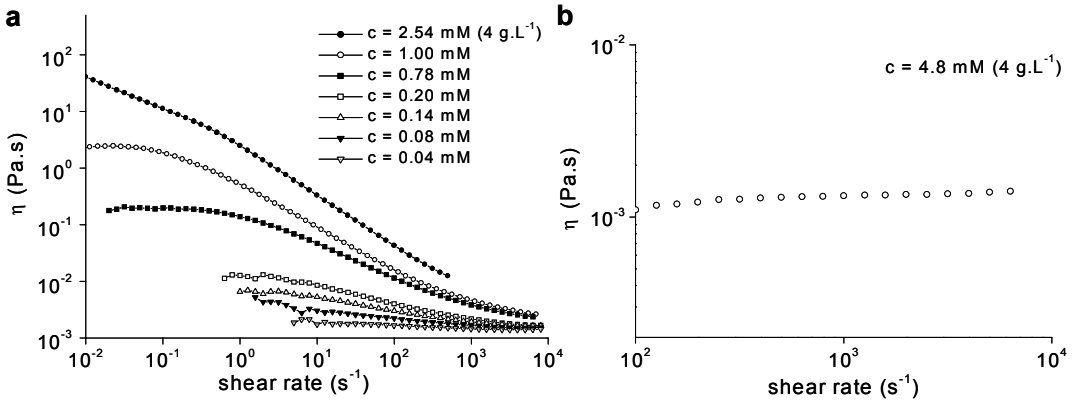

Figure 4.3: *Viscosity in dodecane versus shear rates:* ***a****) for different concentrations of hex-bisUTr* ***2a*** *and* ***b****) for a solution of chiral Bu-UTr* ***1b*** *with a concentration of 4 g.L*$^{-1}$*. The measurements were performed at ambient temperature with parallel-plate geometry.*

It is evident from Figure 4.3 that the viscosity of compound **2a** is orders of magnitude higher than that of **1b** at comparable concentrations. Moreover, dodecane solutions of the bifunctional compound displayed a non-linear behaviour, whereas shear thinning was not observed for the monofunctional compound **1b**, which can exclusively dimerise (Figure 4.3). The rheological properties of dodecane solutions of **2a** indicate gelation. The formation of a

* The relative viscosity is the viscosity relative to the viscosity of pure solvent ($\eta_{rel} = \eta/\eta_{chloroform}$).

network was confirmed with transmission electron microscopy (TEM) on a sample, which was obtained by drop casting from a hexane solution of **2a**. Figure 4.4 clearly shows the presence of entangled aggregates, resulting in a physical network.

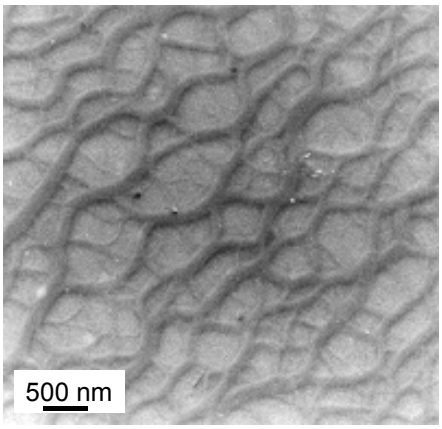

Figure 4.4: *TEM picture of bifunctional **2a**. Sample was drop cast from a 10^{-5} M hexane solution and shaded with carbon.*

4.3.2 Small Angle Neutron Scattering

Small angle neutron scattering was performed to elucidate the aggregation behaviour of compounds **1b** and **2a** in solution. The experiment consists of sending a well collimated beam of neutrons of a certain wavelength λ through the sample, and of measuring the variation of the scattering intensity as a function of the scattering angle θ. The physical parameter is the scattering vector Q.* The resulting scattering pattern is analysed to provide information on the size, the form and the organisation of the particles in the sample. In order to obtain a contrast for neutron experiments, compounds **1b** and **2a** were dissolved in deuterated dodecane.

Scattering intensities of solutions of compounds **1b** and **2a** in deuterated dodecane and deuterated chloroform were measured. The scattering intensities dΣ/dΩ (Q) normalised by the volume fraction ϕ^* for both **1b** and **2a** in dodecane are much higher than in chloroform (see Figure 4.5), suggesting that larger structures are formed in dodecane. Dodecane solutions of bifunctional compound **2a** give higher scattering intensities than solutions of **1b**, indicating

* The modulus of the scattering vector Q can be expressed by: $Q = \frac{4\pi}{\lambda} \sin\frac{\theta}{2}$

that **2a** forms larger aggregates. The SANS measurements also provide information on the shape of the aggregates.

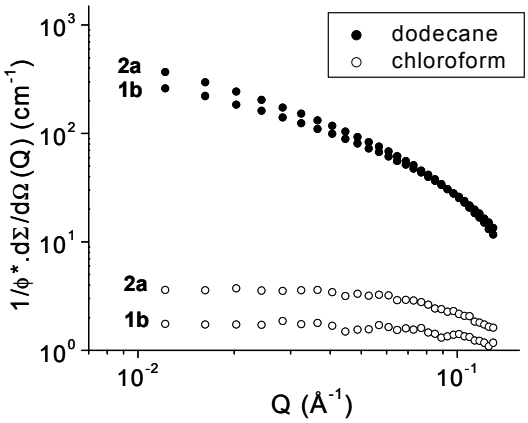

Figure 4.5: *SANS measurements of **1b** and **2a** in deuterated dodecane and chloroform (c = 1 wt%).*

Since compound **2a** was designed to maintain its columnar architecture in solution, it is instructive to plot the scattering results as $Q^2 \times d\Sigma/d\Omega$ (Q) against Q (*Kratky* representation) because in the case of rod-like particles a specific shape is obtained: at low Q the curve goes through a maximum, followed by a horizontal region where the scattered intensity varies with Q^{-2}. At high Q values a line with a slope of 1 is observed.[18] A Kratky representation of the data obtained from solutions of **1b** and **2a** indeed shows curves expected for rod-like cylindrical aggregates (see Figure 4.6).

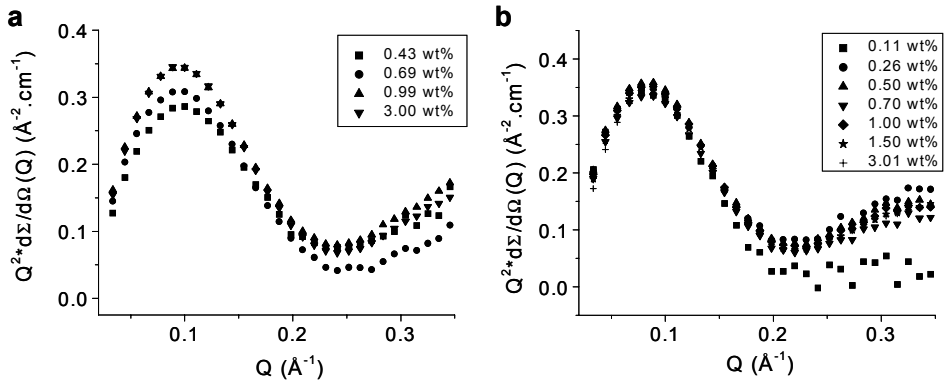

Figure 4.6: *Kratky representation of the SANS data for compounds **1b** (**a**) and **2a** (**b**).*

Quantitative analysis of the scattered intensities was made by fitting a homogeneous cylinder model to the data. In this way, values for the columnar length and the cross-sectional columnar radius of the aggregates were estimated. These values are represented in Figure 4.7

for different concentrations. The data clearly indicate that the diameter of the columns is constant over the concentration range studied. The diameter of the columns formed by **1b** (30 Å) is somewhat smaller than that of the columns formed by **2a** (34 Å), which is in agreement with the shorter side chains of the former compound (C_{10} instead of C_{12}). The values correspond well with those found with X-ray diffraction of the columnar mesophase (see chapter 3). The length of the columns of **1b** increases with increasing concentration from 75 to 191 Å. The cylindrical model cannot be applied to compound **2a** due to a significant contribution of the interference term (the structure factor) in the scattered intensity at higher concentration. In more concentrated solutions of **2a** interparticle interactions are important — this is also expressed by the formation of gel-like solutions— and analysis of the length of the columns is complicated because the unknown structure factor has to be taken into account. An approximate value of the length H of the columns of compound **2a** at low concentration was obtained by fitting the data of 0.1 wt% and 0.25 wt% solutions using only the form factor for cylinders.

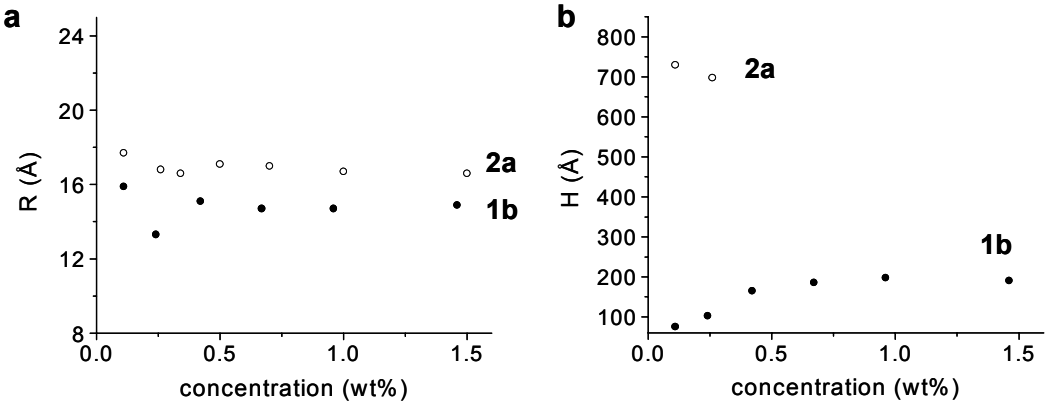

Figure 4.7: *Radii R (**a**) and column lengths H (**b**) at different concentrations. Results obtained from data fitting with a model for rod like structures.*

A strong difference in temperature dependent scattering behaviour is observed between the monofunctional compound **1b** and the bifunctional compound **2a** (see Figure 4.8). The scattering intensity at Q = 0.009 $Å^{-1}$* of solutions of the bifunctional compound is constant between room temperature and 70 °C. From 80 °C to 120 °C the scattering intensity drops by a factor of 2, corresponding to a decrease of the average columnar length. Between 120 °C and 130 °C virtually all scattering intensity is lost. We assume that this is a

* This corresponds to a length scale l of 700 Å.

consequence of the complete loss of the columnar organisation; at 130 °C polymers with a low virtual degree of polymerisation are presumably present. For monofunctional **1b** a gradual decrease of the scattering intensity between 20 and 65 °C was observed. Above 65 °C, scattering intensities are very low, indicating the complete dissociation of columns to dimeric discs.

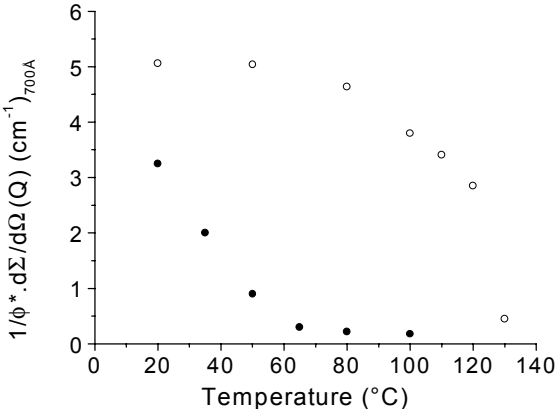

Figure 4.8: *Scattering intensity (at Q = 0.009 Å^{-1}, corresponding to a length scale l of 700 Å) as a function of the temperature for monofunctional compound **1b** (•) and bifunctional compound **2a** (o). The concentration is 1 wt% in deuterated dodecane.*

The low scattering intensities in chloroform as shown in Figure 4.5 indicate that the stacking of the discs to form columns does not occur in this solvent. For compound **1b**, this implies that the molecules do not aggregate beyond the dimeric state. Compound **2a** scatters more strongly than **1b** in chloroform, which is in agreement with small non-ordered (random coil) polymeric aggregates (Figure 4.9).

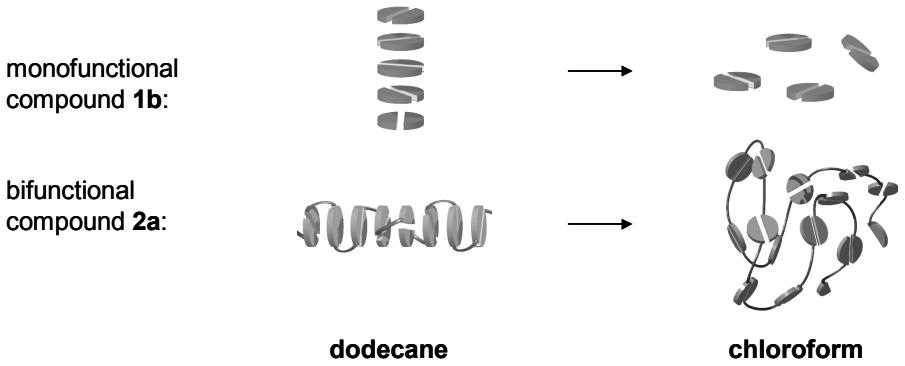

Figure 4.9: *Schematic representation of the suggested mode of aggregation of **1b** and **2a** in dodecane and in chloroform.*

4.3.3 Helicity in the Columns

The aggregation behaviour of the different chiral ureido-*s*-triazine compounds was studied by UV, circular dichroism or/and optical rotation in chloroform and in dodecane. The UV spectra of mono and bifunctional compounds do not change as a function of the concentration. The CD spectra of the columnar aggregates of chiral bifunctional compound **2b** in dodecane display a substantial Cotton effect at the π–π^* absorption band of the aromatic rings at 307 nm and at 237 nm, suggesting the presence of a helical arrangement of chromophores with preferred handedness, determined by the optically pure chiral side chains of **2b** that transfer the chirality into the helix (Figure 4.10). A similar helical arrangement is assumed for achiral analogue **2a**. No Cotton effect is observed in the latter case because equal amounts of *P* and *M* helical columns are present.

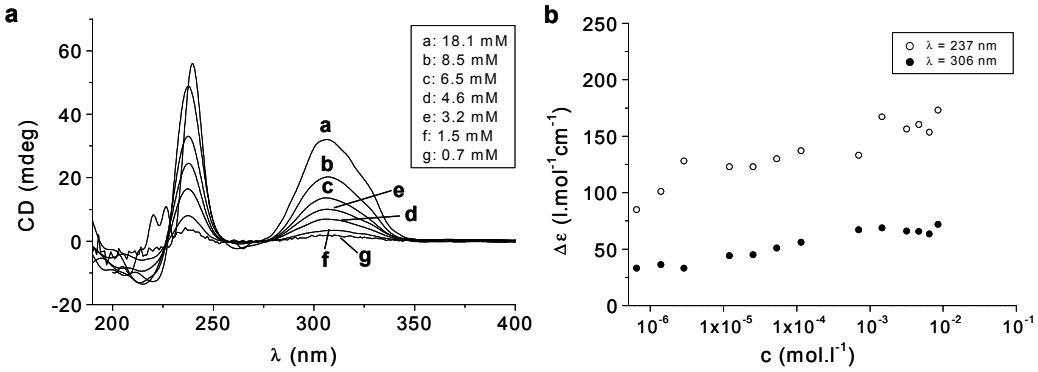

Figure 4.10: *Circular dichroism spectra of **2a** recorded in dodecane. **a)** CD at different concentrations as a function of λ, and **b)** molar ellipticity Δε as a function of the concentration.*

The Δε values* of the CD spectrum decrease slowly upon dilution. When the concentration is lowered from 10^{-3} to 10^{-6} M the Δε value drops by a factor of 2 (see Figure 4.10). Hence, down to 10^{-6} M, most of the molecules are part of helical columns. A plot of the Cotton effect against temperature (Figure 4.11) shows that all helicity is lost over a relatively narrow temperature range from 60 to 90 °C, suggesting that thermal denaturation is a cooperative process. This process is fully reversible and after cooling identical CD spectra without appreciable hysteresis are observed.

* The molar ellipticity Δε was calculated using the following equation: $\Delta\varepsilon = \frac{CD}{32980 \times c \times l}$ with *CD* in mdeg, *c*, the concentration in mol.l^{-1} and *l*, the path length in cm.

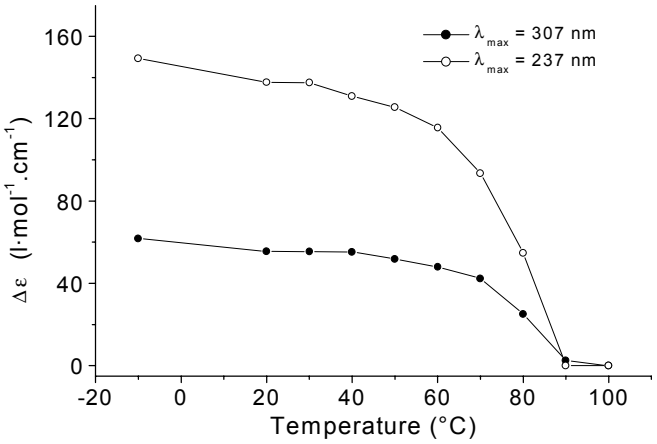

Figure 4.11: *Temperature dependence of Δε at two wavelengths at a concentration of 1.2×10^{-4} M **2b** in dodecane. Samples were kept for 10 min. at the desired temperature before measurement.*

According to the SANS experiments, columns persist above 90 °C, and only disappear above 130 °C. Hence, the loss of the ellipticity corresponds to a transition from helical to non-helical columns. The loss of organisation with increasing temperature is schematically depicted in Figure 4.12.

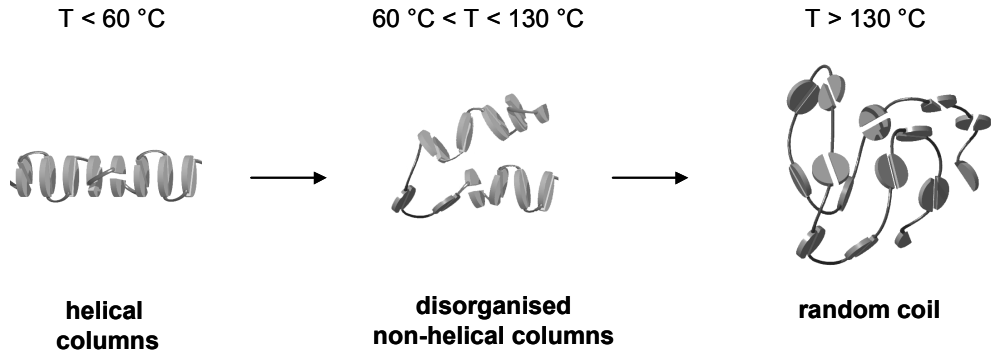

Figure 4.12: *Schematic representation of the aggregation of bifunctional **2a** in dodecane at different temperature regimes.*

The helical order is also disrupted by good solvents. Addition of 2.6 % of chloroform to a dodecane solution of **2b** decreases the Δε by a factor of 10, while in pure chloroform no Cotton effect is observed at all. That the presence of a covalent linker between the disks is important in maintaining supramolecular chirality is shown by the absence of a Cotton effect in solutions of monofunctional **1b** in dodecane. In this solvent the dimers of **1b**

are stacked as can be deduced from the SANS measurements, but the columns lack the hexamethylene chain that induces positional order between disks of **2b**.

4.3.4 Chirality Transfer in Supramolecular Stacks

Addition of chain stopper **1b** to a solution of chiral **2b** (Figure 4.13a) results in a linear decrease of the Cotton effect. In contrast to this, the addition of chiral stopper **1b** to columns of **2a** in dodecane, results in a surprising emergence of a Cotton effect. Both compounds separately are optically inactive in dodecane solution. When chiral stopper **1b** is added to columns of **2a** a steep increase of the CD effect is observed until a maximum is reached at approximately 15% of compound **1b**. Then, the CD effect decreases upon addition of more stopper **1b** (Figure 4.13b).

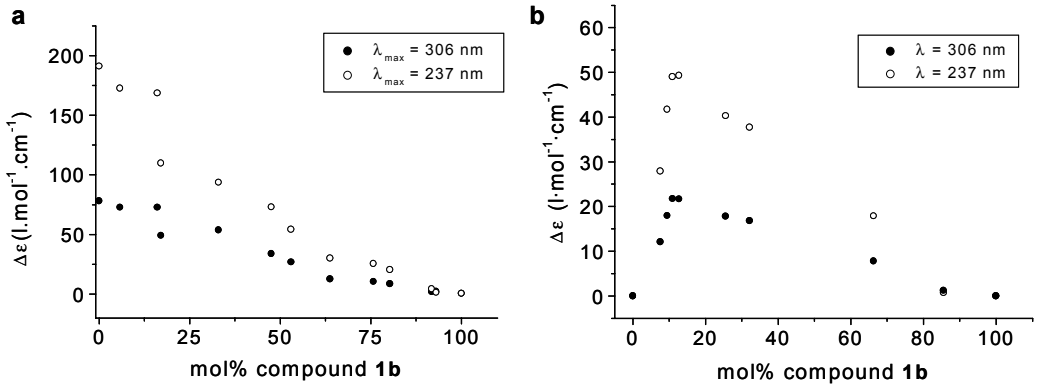

Figure 4.13: *CD measurements of mixtures.* ***a)*** *Δε versus amount of chiral monofunctional compound* ***1b*** *added to a dodecane solution of* ***2b****, and* ***b)*** *Δε versus amount of chiral monofunctional compound* ***1b*** *added to a dodecane solution of* ***2a****.*

Surprisingly, although they form just the ends of the polymer chains, the molecules of **1b** are still capable of transferring their chirality into the column and thus bias their helicity through cooperative interactions, resulting in a significant amplification of chirality. A schematic representation of the organisation of mixtures of **1b** and **2a** is depicted in Figure 4.14.

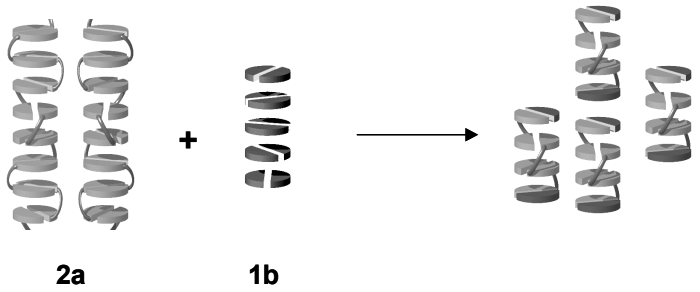

Figure 4.14: *Proposed mode of the organisation of mixtures of mono- and bifunctional compounds **1b** and **2a**, respectively.*

4.3.5 Aggregation Behaviour of Extended-Core Compounds

The CD spectra of monofunctional compound **3b** and bifunctional compound **4b** were recorded in dodecane. For monofunctional compound **3b** a Cotton effect is observed at the π-π* transition of the aromatic chromophores (Figure 4.15), in contrast to chiral monofunctional compound **1b** bearing the free amino group. Indeed, due to the enhanced π-π stacking the rotational freedom is restricted and as a consequence a chiral column is obtained.

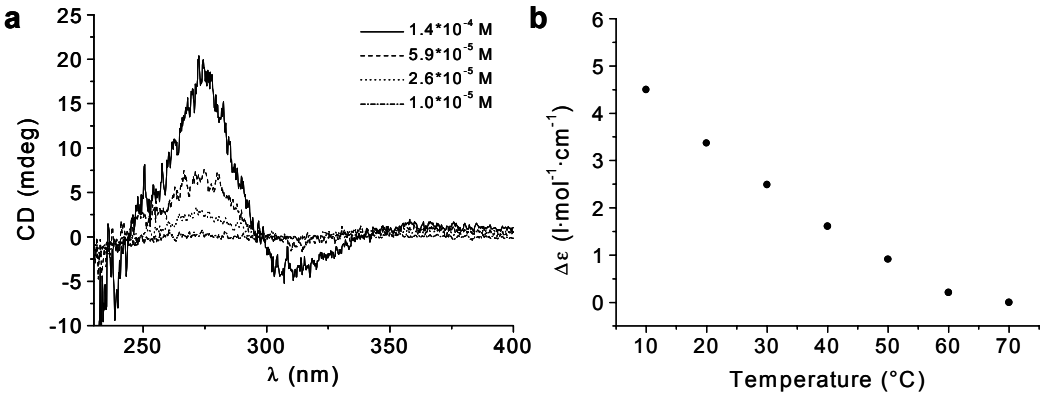

Figure 4.15: *CD measurements on monofunctional compound **3b**: **a)** CD versus the wavelength (λ), and **b)** Temperature dependence of the Cotton effect at a concentration of 5.9×10^{-5} M in dodecane.*

For bifunctional compound **4b** a Cotton effect was observed at the π-π* transition of the aromatic core. The molar ellipticity (Δε) of 7.5 $mol.l^{-1}.cm^{-1}$ at λ_{max} = 275 nm calculated for **4b** is much lower than the one of compound **2b** that exceeds 50 $mol.l^{-1}.cm^{-1}$ at λ_{max} = 306 nm.

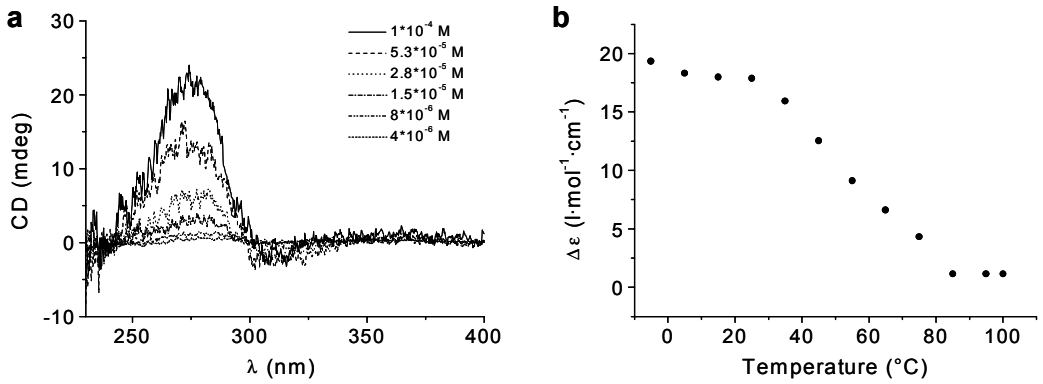

Figure 4.16: *CD measurements on bifunctional compound **4b**: **a)** CD versus the wavelength (λ), and **b)** Temperature dependence of the Cotton effect at a concentration of 5.3 × 10^{-5} M in dodecane.*

Thermal denaturation is shown by performing the CD measurements at different temperatures. Till 30 °C, the helicity of **4b** is constant (see Figure 4.16). Above 30 °C the helicity is gradually lost, and it has completely disappeared at 80 °C. Columns of bifunctional compound **4b**, which have lost half of their maximal helicity at 50 °C, are more stable than those of **3b** which have lost half of their maximal helicity already around room temperature. However, compound **4b** is less stable than compound **2b**. This might be rationalised as follows. The introduction of an additional aromatic ring enhances π-π stacking, as observed in oligo(phenylenevinylene) functionalised ureidotriazines by Schenning and coworkers.[19] However, competition exists between the favourable π-π stacking and the restricted conformation that is imposed by the presence of the hexamethylene linker. For this reason consecutive discs cannot stack in an appropriate way in order to allow a helical packing of the coplanar cores.

4.4 Conclusions

Highly organised self-assembled linear supramolecular polymers with control over helicity and chain length were obtained. The bifunctional molecules **2a** and **2b** associate via four hydrogen bonds to give a linear polymer, whereas solvophobic interactions and π-stacking lead to a helical columnar superstructure in dodecane. Compounds **2a** and **2b** are lyotropic in dodecane above 5 wt%, whereas **1b** forms a birefringent solution in dodecane above a concentration of 25 wt%. At concentrations lower than 5 wt% and 25 wt% for **2a** and **2b**, and **1b**, respectively, the solutions are isotropic. Films cast from solution showed a gel-

like structure in TEM. The presence of cyclic dimers, formed from the association of two bifunctional compounds **2a**, can be excluded because columnar structures consisting of π-stacked dimers would exhibit similar Newtonian behaviour as monofunctional **1b**. Additional proof for the existence of columnar architectures in dodecane comes from CD spectroscopy and SANS experiments. With CD spectroscopy no Cotton effect was observed in chloroform for both mono- and bifunctional chiral compounds. The only important secondary interactions are the four hydrogen bonds, because chloroform not only solvates the aliphatic side chains but also the aromatic core. CD spectra of dodecane solutions of chiral bifunctional compound **2b** display a substantial Cotton effect at the π–π^* absorption band of the aromatic rings suggesting the presence of a helical arrangement of chromophores with a preferred handedness. The origin of this process can be rationalised by the preferential organisation of the chiral side chain, in which all methyl groups attached to the chiral centre are oriented in one direction. The columnar superstructure persists between 90 °C and 130 °C, shown with SANS, although the helicity is completely lost above 90 °C. SANS data suggest that monofunctional **1b** also aggregates in a columnar fashion, but due to the rotational freedom of the discs, no cooperative effect is observed. Complete disruption to molecularly dissolved compounds also takes place when methanol is added. Furthermore, the columns formed by **2**, feature a high degree of cooperative order, and a significant amplification of chirality was found when chiral monofunctional compound **1b** was added to a dodecane solution of achiral bifunctional **2a**. It was shown that by introducing an additional aromatic substituent, π-stacking is enhanced. This is evidently expressed by the presence of a Cotton effect at the π–π^* transition of the extended aromatic core of monofunctional compound **3b**. The favourable π-stacking of the aromatic moiety in bifunctional compounds is probably in competition with the restricted conformational freedom imposed by the hexamethylene spacer. As a consequence, half of the maximal Cotton effect of **4b** is lost at 50 °C compared to 75 °C for bifunctional compound **2b**.

4.5 Experimental Section

General Methods.

The synthesis of all compounds is described in chapter 3. Solvents were obtained from commercial suppliers and used as received. Optical properties and melting points were determined using a Jeneval polarization

microscope equipped with a Linkam THMS 600 heating device with crossed polarizers. Viscosity measurements were performed using an Ubbelohde micro-viscometer equipped with a suspended level bulb of different capillary tube diameters. Before measurements were run, low viscosity samples were passed through a filter of 5 μm. Dynamic mechanical measurements were performed on a Rheometrics fluid spectroscopy RFSII, with a plate-plate geometry (50 mm). Plate-plate distances were taken between 0.3 mm and 0.25 mm. All samples were measured a couple of days after being heated and were filtered before measurements. UV-Vis spectra were recorded on a Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer. Circular dichroism spectroscopy measurements were recorded on a Jasco J-600 spectropolarimeter. All solutions were prepared by dissolving the compounds at elevated temperatures and subsequent equilibration at the temperature of measurement for 30 minutes. Depending on the concentration of the measurement, cells of different path lengths were used (typically 10, 1, 0.1 and 0.01 mm), ensuring an optical density below 1. Small angle neutron scattering experiments were performed using spectrometer PACE of Laboratoire León Brillouin (CE-Saclay), France. The covered scattering vectors vary between 0.01 $Å^{-1}$ and 0.35 $Å^{-1}$. The scattering patterns were obtained using two different spectrometer configurations: λ = 5 Å, D = 3.2 m and λ = 5 Å, D = 1.25 m, with D equal to the sample-detector distance, corresponding to two partially overlapping ranges of the scattering vectors Q = 0.01-0.03 and 0.033-0.35 $Å^{-1}$. Samples were recorded in deuterated solvents ($CDCl_3$ or $C_{12}D_{26}$). The temperatures of the samples were kept constant in a circulating temperature bath with an accuracy of 0.5 °C.

4.6 References and Notes

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5

Well-Ordered Supramolecular Polymers Based on Ureidopyrimidinone

Abstract

*Liquid crystalline mono- and bifunctional compounds **1-6** based on the pyrimidinone unit were synthesised. Bifunctional compounds with different spacer lengths, compounds **2-5**, were studied and the influence of the spacer length on aggregation of these compounds was investigated. Also, compound **6** bearing a preorganised m-xylylene spacer was synthesised in order to favour the formation of columns in apolar solvents. Compounds **1-6** exhibit thermotropic liquid crystalline properties as evidenced by DSC and OPM. ^{1}H-NMR spectroscopy showed that compounds **1-6** are present predominantely in the keto form both in the bulk and in chloroform solutions. In chloroform, no Cotton effect was observed for any of the compounds synthesised. Dodecane solutions of compounds **2**, **3b**, and **6b** featured a Cotton effect at the absorption band of the phenyl-pyrimidinone core. The Cotton effect is lost upon increasing the temperature. Half of the helicity is lost at 25 °C for **2** and 65 °C for **3b** suggesting that **2**, bearing the shorter spacer forms less stable columns than **3b**. Compound **6b** loses half of its helicity at 50 °C. Compounds **1b**, **4** and **5** do not exhibit a helical organisation as evidenced by an absence of the Cotton effect. Finally, (–)-cystine was provided with two tridodecyloxyphenylpyrimidinone groups with the purpose to investigate the transfer of chirality from the chiral spacer into the phenyl-pyrimidinone moiety. The molecule is liquid crystalline between –28 °C to 240 °C, and forms helical columns in dodecane. In chloroform no Cotton effect was observed.*

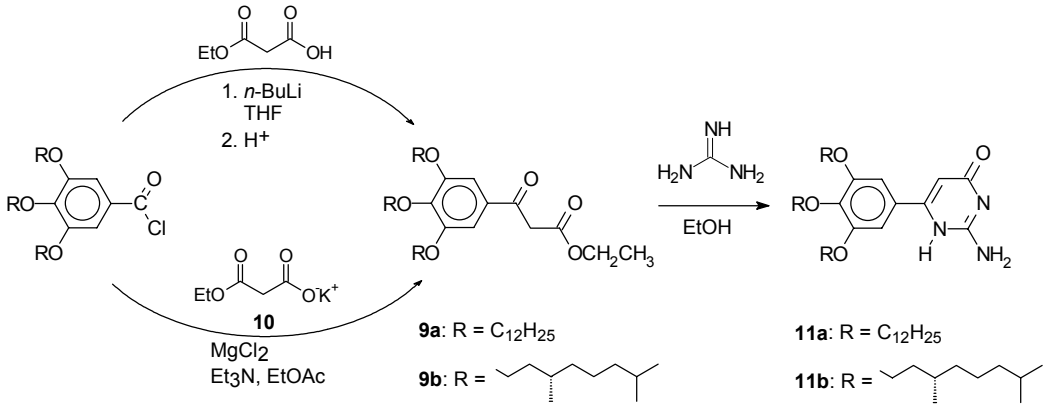
5.1 Introduction

The high strength of quadruple hydrogen bonding units ureidotriazines[1] and ureidopyrimidinones[2] has been employed to obtain linear supramolecular polymers with high degrees of polymerisation in bulk as well as in solution from monomers containing two of these units.[3] The directionality and the selectivity of multiple hydrogen bonds have allowed us to obtain a high degree of control over polymer architecture with respect to chain length — which can be adjusted by mixing monofunctional and bifunctional compounds— and with respect to the degree of cross-linking in reversible networks —which can be controlled by the addition of trifunctional compounds. Even greater control over polymer architecture can in principle be achieved by employing additional non-covalent interactions between monomeric units in order to strongly favour a specific conformation of the polymeric chain. Conformational control is fundamental to the functionality of biomacromolecules like DNA and proteins, and has become a fruitful area of research in synthetic covalent polymers. Here the conformational preferences of monomeric units in combination with inter-residue hydrogen bonds or stacking interactions have been used to obtain macromolecules that are folded into a well-defined secondary structure ("foldamers").[4,5] This concept has been applied by us to supramolecular polymers by using solvophobic interactions between ureidotriazine units connected by a spacer and provided with solubilizing trialkoxyphenyl groups to obtain supramolecular polymers with a helical columnar architecture in dodecane (see chapters 3 and 4).[6] The structure of the columns was shown to be biased towards a single helicity by the use of homochiral side chain. The compounds form random coil polymers in $CHCl_3$, a solvent in which solvophobic interactions between aromatic groups are much weaker, but the hydrogen bonding between ureidotriazine groups is still relatively strong ($K_{dim} = 2 \times 10^4$ M^{-1}).[1] Ureidopyrimidinones have a much higher dimerisation constant ($K_{dim} = 6 \times 10^7$ M^{-1} in $CHCl_3$)[7] and bifunctional compounds containing this unit would in principle allow the construction of polymers with a much higher degree of polymerization in either dodecane or chloroform. Another important difference between the ureidopyrimidinone unit and the ureido-*s*-triazine unit is the presence of additional double hydrogen bonds in the latter. In the present work, the aggregation of mono- and bifunctional ureidopyrimidinones **1-6**, provided with a trialkoxyphenyl group is investigated as a function of solvent and the structure of the spacer moiety of the bifunctional compounds.

In addition to chiral molecules having peripheral chiral side tails, we have studied a bifunctional compound that bears two stereocenters in the spacer. For this purpose (–)-cystine dimethyl ester was used as the linkage between the two pyrimidinone units. The advantage of using (–)-cystine is the presence of the S-S linkage that can be easily broken and restored if appropriate.

5.2 Synthesis and Characterisation

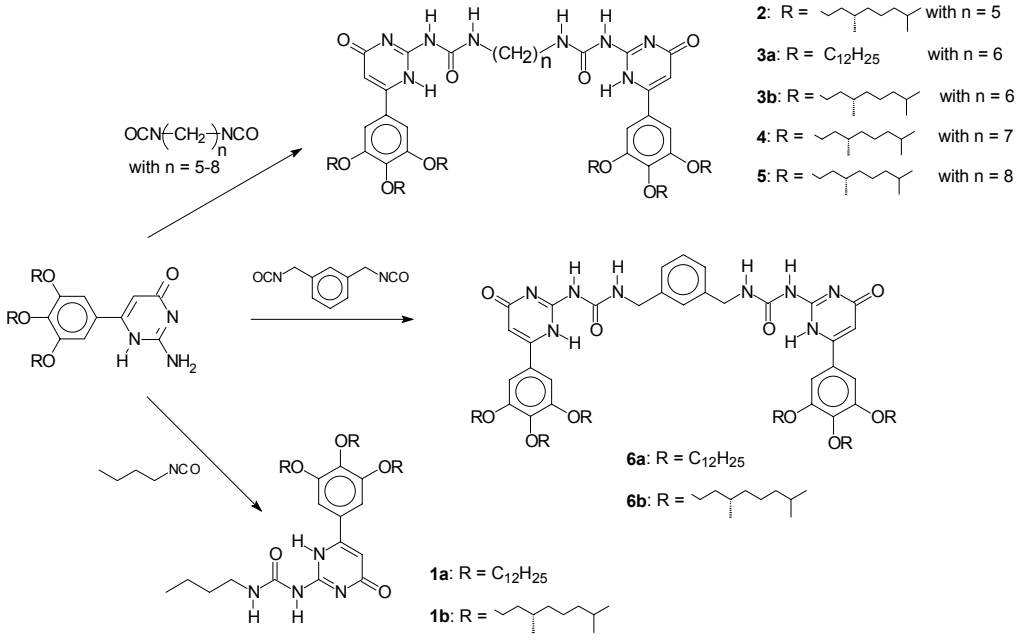
Compounds **1**-**6** were synthesised via an acylation of the isocytosine **11** with the appropriate isocyanate as shown in Scheme 5.2. Achiral and chiral isocytosine **11a** and **11b** respectively were synthesised via a procedure as depicted in Scheme 5.1. Ethyl 3,4,5-trialkoxybenzoylacetates **9** can be synthesised in two different ways. In the first method a dianion of monoethyl malonic acid was prepared with *n*-butyllithium at –78°C, as described in chapter 2. The dianion reacts with the corresponding acid chloride and after hydrolysis and decarboxylation the β-keto-esters **9a** and **9b** are afforded. In contrast to this method a safer and more economical method was used for the preparation of β-keto-esters.[8] This method involves a reaction of the acid chloride with potassium ethyl malonate **7**. A base system that is strong enough to deprotonate the malonate salt is needed. Magnesium has long been recognized as the counter ion of choice in malonate based preparation of keto-esters.



Scheme 5.1: *Two different synthetic routes toward the isocytosines **11**.*

Rathke *et al.*[9] have shown that the combination of anhydrous magnesium chloride and triethylamine provides a useful base system for metalating potassium ethyl malonate and that the corresponding magnesium malonate complex derived in this manner can be acylated with

acid chlorides. β-Keto esters **9** in turn were reacted with guanidinium carbonate to afford isocytosines **11a** and **11b**. The β-keto esters were used as such without further purification in the following reaction. The condensation of **9** with guanidinium carbonate occurred in ethanol to afford the isocytosines. Monofunctional compounds were prepared via an acylation with *n*-butylisocyanate. Various bifunctional compounds bearing different spacers were synthesised following the synthetic route depicted in Scheme 5.2. 1,6-Diisocyanatohexane, 1,8-diisocyanatooctane and *m*-xylylenediisocyanate are commercially available. 1,5-Diisocyanatopentane and 1,7-diisocyanatoheptane, however, had to be prepared from a reaction between the corresponding diamines and di-*tert*-butyl-tricarbonate.



Scheme 5.2: *Synthetic route toward monofunctional compounds **1** and bifunctional compounds **2-6**.*

All compounds were purified with column chromatography and were fully characterized by ^{1}H NMR, ^{13}C NMR, IR spectroscopy, MALDI TOF mass spectroscopy and elemental analysis.

5.3 Thermotropic Liquid Crystallinity

Upon dimerisation, the UPy derivatives **1a** and **1b**, form disk shaped structures, with a rigid, planar core, surrounded by flexible alkyl groups. This architecture is conducive to the

formation of a columnar discotic mesophase in bulk. In bifunctional derivatives **2-6**, similar columns of UPy dimers may be formed when each spacer moiety connects two stacked disks. Depending on the arrangement of the spacers, the columns are either polymeric, or they consist of stacks of cyclic dimers of the bifunctional molecules. In order to investigate the presence of columnar discotic mesophases, the thermal behaviour of the compounds was studied with polarisation microscopy and DSC. Under the polarisation microscope, all compounds feature strongly birefringent textures at room temperature. Textures were grown for compounds **1b**, **2**, and **3a-6** by slowly cooling from the clearing point. In all cases, only tiny homeotropic monodomains were present in the liquid crystalline state; these domains were sensitive towards pressure changes, but could not be identified with the eye. Compound **3b**, however is only thermotropic after precipitation from methanol or ethanol; cooling down from its isotropisation phase at 160 °C an amorphous material was obtained. DSC traces of all compounds feature a large endotherm in the first heating run. This endotherm is due to the transition from the liquid crystalline mesophase to the isotropic state. For all compounds except for chiral compound **3b** an exotherm was observed upon cooling from the clearing point. Indeed, it was observed with optical microscopy that once compound **3b** had been cooled down from its clearing point the material remained amorphous.

Table 5.1: *Thermotropic properties of compounds **1b** and **2-6**, determined with DSC.*

Compound	K	T	M	T (*ΔH*)	I
		°C (*kJ/mol*)		°C (*kJ/mol*)	
1b	o	–50[a]	•	98 (*1.5*)	•
2	o	–53[a]	•	173 (*2.2*)	•
3a	•	–11 (*14*)	•	164 (*3.7*)	•
3b	o	-	•[b]	160[c]	•
4	o	-	•	147 (*2.2*)	•
5	o	-	•	207 (*12.3*)	•
6a	•	–17 (*18*)	•	242 (*7.1*)	•
6b	o	-	•	239 (*7.5*)	•

• The phase is observed; **o** *the phase was not observed; K = crystalline phase; M = mesophase; I = isotropic phase; [a] Uncertain whether this is a transition; [b] Only observed after precipitation in MeOH; [c] Value obtained from the first heating run.*

For the chiral compounds **1b**, **2**, **3b-5** and **6b** no melting of the peripheral chiral groups was observed. Compounds **3a** and **6a** bearing the achiral dodecyl groups exhibit much more pronounced melting transitions. The phase transition temperatures and the corresponding enthalpies were determined from the DSC traces and are summarised in Table 5.1.

5.4 Aggregation in Solution

5.4.1 ^{1}H NMR Spectroscopy

In solution ureidopyrimidinones have been shown[1] to exist as a mixture of strongly dimerizing tautomers, a 4[1H]-pyrimidinone (keto) tautomer and a pyrimidin-4-ol (enol) tautomer (Figure 5.1, inset). The position of the keto-enol equilibrium has been studied by ^{1}H-NMR, and was shown to be substituent and solvent dependent. The ^{1}H-NMR spectrum of monofunctional compound **1b** in $CDCl_3$ is shown in Figure 5.1 and shows signals of the keto and the enol tautomer in a 87:13 ratio. The NH signals of the keto tautomeric form are found at 13.90, 12.06, and 10.24 ppm. The second set of signals, assigned to the enol tautomer of **1b**, can be found at 13.58, 11.32, and 10.02 ppm. The assignment of the ^{1}H-NMR signals is presented in Figure 5.1.

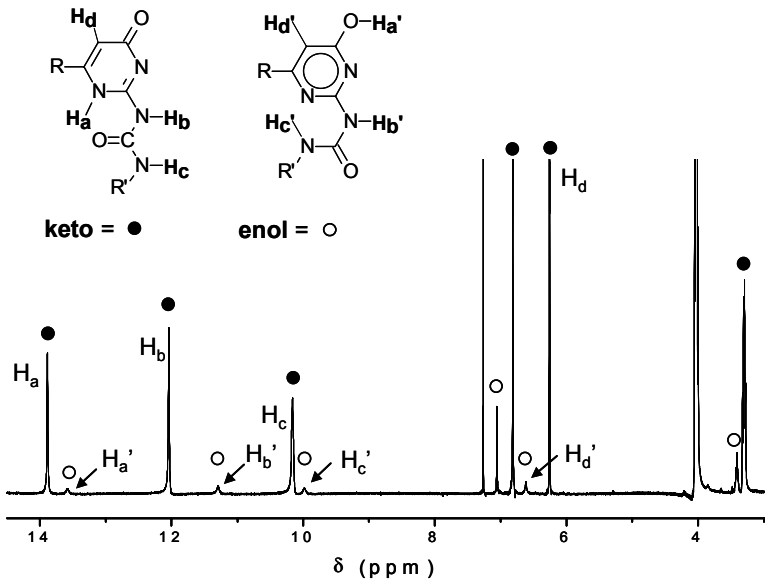


Figure 5.1: *^{1}H NMR spectrum of compound **1b** recorded in chloroform.*

^{1}H-NMR spectra of dilute solutions of bifunctional compounds **2-6** in $CDCl_3$ are much more complex, but simplify dramatically upon addition of a small amount of trifluoroacetic acid, which disrupts the hydrogen bonds between ureidopyrimidinone units. For example the ^{1}H-NMR spectrum[10] of bifunctional compound **3b** in chloroform also showed two sets of signals corresponding to the keto and enol tautomer, but each set of signals consists of a large number of peaks (see Figure 5.2). The most abundant set of NH signals was found at approximately 13.8, 12.0 and 10.2 ppm. These are typically shifts found for dimerised hydrogen bonded 4[1H]-pyrimidinone. The NH-signals at 13.6, 11.2 and 9.9 ppm are assigned to the dimerisation of pyrimidin-4-ol tautomer. As the concentration is increased from 10 mM to 140 mM, one of the peaks of each NH signal of the keto form is becoming more abundant. DOSY-NMR (Diffusion ordered 2D NMR spectroscopy) experiments were performed in order to determine the nature of the different species in a 20 mM chloroform solution. The DOSY NMR spectra show that the set of peaks that dominates at higher concentration comes from aggregates with a low diffusion rate, while all other peaks feature high diffusion rates. Therefore, the former signals are ascribed to the polymeric form of the keto tautomer.[11,12]

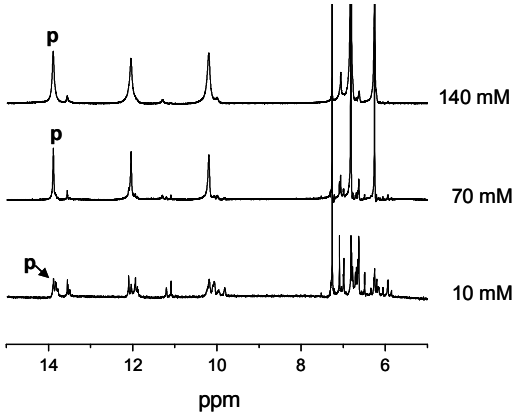


Figure 5.2: *^{1}H NMR spectrum of compound **3b** recorded in chloroform at different concentrations; **p** = polymeric form.*

^{1}H-NMR spectra of compound **2** in $CDCl_3$, on the other hand do not change much with the concentration. DOSY-NMR experiments on a 100 mM solution of **2** shows that all the peaks have similar diffusion rates, which are relatively high, suggesting the absence of polymeric structures.

^{1}H-NMR spectra of **1** and of bifunctional compounds **2-6** in deuterated dodecane showed broad unresolved signals for the alkyl chains and broad signals for the phenyl-pyrimidinone core of the molecules, indicating the formation of large aggregates in this solvent. No signals assigned to the NH hydrogens could be observed, hampering the study of tautomerism in dodecane. Upon increasing the temperature from 20 °C to 125 °C, the intensity of the signals for the aromatic core increased and the peaks became sharper.

5.4.2 Circular Dichroism (CD) Spectroscopy

CD spectra of chiral compounds **1b**, **2**, and **3b**-**6b** were recorded in chloroform and dodecane in order to probe the degree of order in these compounds. In chloroform at a concentration of 1 mM none of the studied compounds showed a Cotton effect. In dodecane the situation is different, although monofunctional **1b** does not feature a CD effect, in 1 mM solutions of bifunctional compounds, a CD effect is present depending on the spacer. In the series of bifunctional compounds, Cotton effects at the π-π^* transition of the phenyl-pyrimidinone moiety were observed in dodecane for compounds **2**, **3b**, and **6b**, while compounds **4** and **5**, with C-7 and C-8 spacers, respectively, showed no activity in CD. Temperature dependent CD measurements were performed with 1 mM dodecane solutions of **2**, **3b** and **6b** in order to study the stability of the aggregates (see Figure 5.3b). A plot of the molar ellipticity versus the temperature shows, that the temperature at which half of the maximal helicity is lost depends on the spacer. For compounds **2**, **3b** and **6b** this happens at 38 °C, 60 °C and 45 °C, respectively.

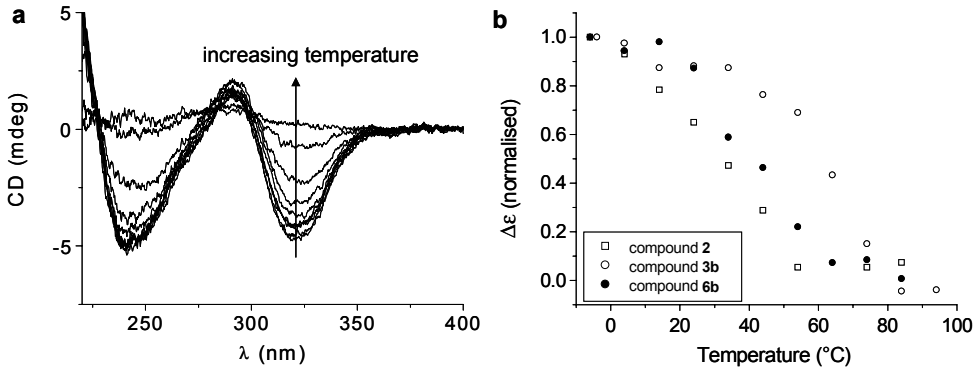


Figure 5.3: *CD spectra of compound **3b** in dodecane (1 mM) at different temperatures (**a**). Normalised molar ellipticity Δε versus the temperature calculated for compounds **2**, **3b** and **6b** (**b**).*

In order to investigate the cooperativity within the stacks of the molecules, a "Sergeant and Soldiers" experiment was performed by adding chiral monofunctional compound **1b** (the sergeants) to a solution of achiral bifunctional compound **3b** (the soldiers). However, at a concentration of 10 mM no Cotton effect was observed. A similar experiment was performed by mixing chiral with achiral bifunctional compounds **3b** and **3a**, respectively. In order to ensure complete mixing of the components, solutions were prepared in $CHCl_3$, evaporated to dryness and finally redissolved in dodecane by heating. Unfortunately, no amplification of chirality occurred as expressed by the linear dependence of the Cotton effect on the amount of chiral **3b**.

5.5 Discussions and Conclusions

Like their ureidotriazine analogues,[6] ureidopyrimidinone derivatives, which are provided with trialkoxyphenylgroups, form liquid crystalline mesophases in which dimeric units are stacked in columns with hexagonal order. This arrangement of Upy units is compatible with the presence of polymeric chains of bifunctional molecules in the columns, although the possibility that the columns consist of stacks of cyclic dimers in the thermotropic mesophase cannot be ruled out with the present knowledge. ^{1}H-NMR and CD spectroscopy in $CDCl_3$ and dodecane give valuable information that sheds additional light on the mode of aggregation in solution. ^{1}H-NMR spectra of the UPy derivatives in $CDCl_3$ are much more complex than those of the corresponding *s*-triazine derivatives, due to keto-enol tautomerism. However, study of the concentration dependence of the spectra, in combination with measurement of the diffusion constants of the different species, have shown that in $CDCl_3$ compounds **1-6** are present as cyclic dimers in the millimolar concentration range; for compound **2** cyclic structures persist till 100 mM. In the chiral bifunctional triazine analogue, both stacking of dimerised units induced by solvophobic interactions and preorganisation by spacer moieties, is required for the observation of a Cotton effect in CD spectroscopy, because only a helically, stacked arrangement of dimers results in transfer of the chiral information of the side chains to the central chromophore. The absence of a Cotton effect for chiral monofunctional Upy derivative **1b** in chloroform as well as in dodecane shows that the same requirements hold for ureidopyrimidinones. The absence of a Cotton effect in chloroform solutions of bifunctional UPy derivatives **2-6** shows that even when the spacers that connect the two layers of the cyclic dimers enforce a stacked arrangement, there is no

bias in the supramolecular chirality. In dodecane, however, the observation of Cotton effects for compounds **2**, **3b**, and **6b** shows that there is enantioselectivity in the self-assembly process. No Cotton effect is observed for dodecane solutions of **4** and **5**. Melting experiments, analogous to thermal denaturation experiments performed on double-helical DNA show that the stability of the helical arrangement of **3b** is similar to that of its direct ureidotriazine analogue (60 vs. 75 °C). No amplification of chirality was observed when the chiral monofunctional compound **1b** is mixed with the achiral bifunctional molecule **3a**, in contrast to the behaviour of the corresponding ureido-*s*-triazine analogue (see chapter 4). Amplification of chirality in mixtures of bifunctional compounds **3a** and **3b** was also not observed. This suggests that either there is no cooperativity within helical stacks or the bifunctional molecules do not form mixed aggregates. Further experiments are needed to answer this question.

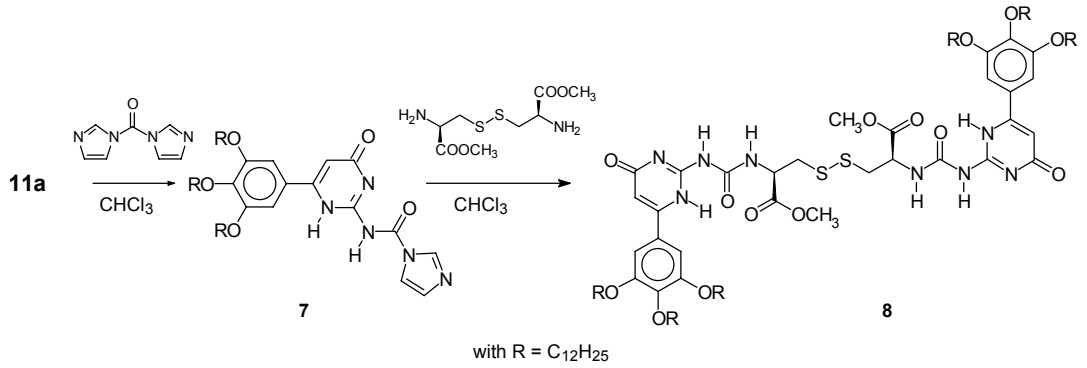
5.6 Bis-ureido-*s*-triazine with Chiral (–)-Cystine Spacer

In the previous chapters and sections, peripheral homochiral tails have shown to be able to transfer their chirality into the backbone of a columnar polymer, resulting in a helical arrangement of the columnar structure. We have investigated the possibility to synthesise a bifunctional compound that bears a stereocenter in the spacer. For this purpose (–)-cystine dimethyl ester was used as the linkage between the two pyrimidinone units.

5.6.1 Synthesis and Characterisation

Bifunctional **8** compound bearing chirality in the spacer was synthesised as shown in Scheme 5.3. The activation occurred with carbonyl diimidazole in chloroform at 60 °C resulting in imidazolylcarbonylamino-isocytosine **7**. This compound is then reacted with the dimethyl ester of (–)-cystine to yield bifunctional molecule **8**. Because imidazole acts as a good leaving group, the reaction can take place at room temperature and only needs a few hours. After precipitation in acetone, the product only contained minor impurities that were removed easily with column chromatography. After precipitation from methanol compound **8** became isotropic at 240 °C as shown with OPM and DSC. When cooling down from the clearing point, no exotherm was observed. However, in contrast to the DSC measurements, textures were grown as observed with the optical polarisation microscope. The material

became isotropic again at 215 °C upon heating; this transition, however, is extremely small in the DSC traces.



Scheme 5.3: *Synthesis of imidazolylcarbonylamino-isocytosine **7** for the preparation of (–)-cystine-derived bis(ureidopyrimidinone) **8**.*

The ^{1}H NMR spectrum of compound **8** recorded in $CDCl_3$ clearly shows three sets of signals (Figure 5.4). DOSY-NMR experiments were performed in order to obtain information about the size of molecules. DOSY NMR of a 30 mM solution of **8** in $CDCl_3$ clearly shows that the three sets of peaks have similar diffusion rates, which are relatively high.

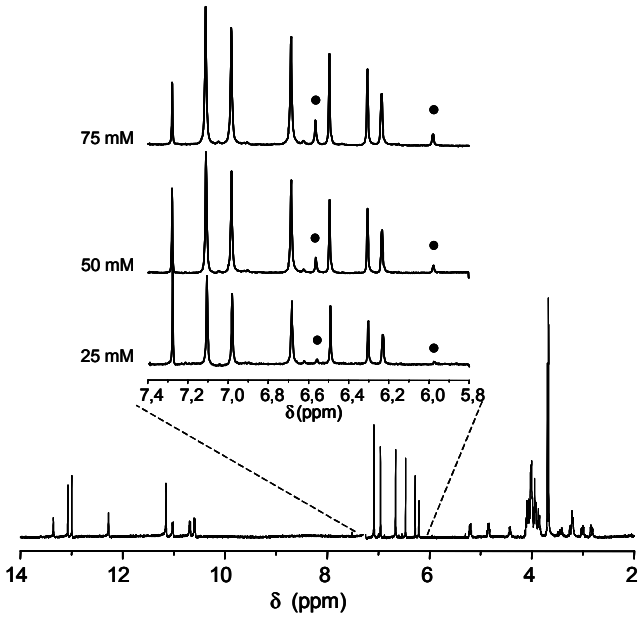


Figure 5.4 *^{1}H NMR spectrum of compound **8** recorded in $CDCl_3$. Inset (from 5.8 to 7.5 ppm): different concentration of **8** in $CDCl_3$. ● = polymeric form.*

Concentration dependent ^{1}H-NMR studies were performed to see whether polymeric structures would arise at the expense of cyclic structures. The spectra were recorded of 25 mM, 50 mM and 75 mM chloroform solutions of **8**. The spectra between 5.8 to 7.5 ppm are depicted in the inset of Figure 5.4. Upon increasing the concentration two additional peaks for the aromatic protons and the alkylidene proton arise at 6.55 and 5.98 ppm respectively. Similar results are found in the area of the NH protons. ^{1}H-NMR spectra recorded in dodecane featured extremely broad signals.

5.6.2 Helical Arrangement in Solution

No Cotton effect was observed for compound **8** in a 1 mM chloroform solution. However, helical aggregates of **8** are present in a 1 mM dodecane solution as evidenced by a positive Cotton effect at the π-π^* transition of the phenyl-pyrimidinone core. A plot of the Cotton effect against the temperature shows no change until 25°C. Starting from 25 °C a gradual decrease of the Cotton effect can be observed. At 100 °C all helicity is lost.

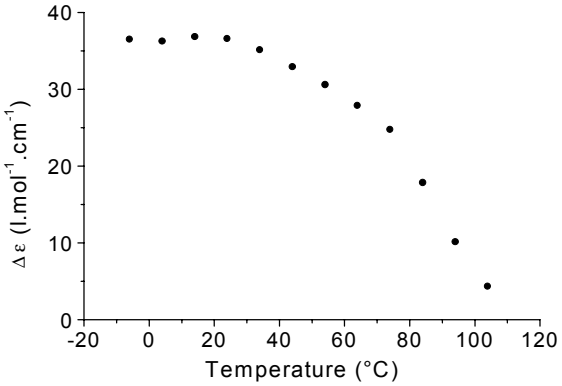


Figure 5.5: *Molar ellipticity versus the temperature for a 1 mM dodecane solution of compound 8 at λ = 237 nm.*

5.6.3 Conclusion

The synthesis of **8** by a reaction of imidazolylcarbonylamino-isocytosine with dimethyl ester of (–)-cystine was successful and a yield of 64% was obtained. Compound **8** is liquid crystalline and the mesophase is stable between –28 °C and 215 °C. The ^{1}H NMR spectrum of **8** recorded in $CDCl_3$ shows three sets of peaks. With DOSY NMR of **8** in $CDCl_3$ (30 mM) it was observed that the three sets of peaks have similarly high diffusion rates,

which suggests that all aggregates are cyclic dimeric structures. Since three sets of signals are observed, caused by cyclic structures, it is presumed that one homo dimer and one hetero dimer (this dimer consists of two identical asymmetric molecules in which one half is 4[1H]-pyrimidinone tautomer and the other half is the pyrimidin-4-ol tautomer) are present. Upon increasing the concentration additional peaks arose at 6.55 and 5.98 ppm. Similar results were found in the area of the NH protons. These might be ascribed to polymeric structures. In dodecane solutions (1 mM), compound **8** forms helical structures as evidenced by a Cotton effect in the absorption band of the phenyl-pyrimidinone core. In this case the helicity is biased by the chiral cystine spacer instead of the peripheral chiral chains. At 100 °C no positional order is present between the discs as evidenced by the absence of a Cotton effect at and above 100 °C.

5.7 Experimental Section

General Methods.

General methods concerning purification of solvents, spectroscopic techniques and mass spectroscopic techniques can be found in chapters 2, 3 and 4. 3,4,5-Tridodecyloxybenzoyl chloride and 3,4,5-tri((*S*)-3,7-dimethyloctyloxybenzoyl chloride were synthesised following previously described procedures that can be found in chapter 3.

Ethyl 3,4,5-tri(dodecyloxy)benzoylacetate (9a). Mono ethyl malonic acid (5.1 g, 38.4 mmol) was dissolved in freshly distilled tetrahydrofuran (100 mL) and the solution was cooled to –78°C. A trace of 2,2-dipyridyl was added. A 2.5 M solution *n*-butyl lithium in hexane (30.6 mL, 76.7 mmol) was added dropwise over 30 min, while the temperature was kept below –65°C. As soon as the colour of the solution changed from yellow to red, the temperature was raised to –40°C to see whether the colour still persisted. Subsequently a solution of crude 3,4,5-tri(dodecyloxy)benzoyl chloride (16.17 g, 23.4 mmol) in 200 mL freshly distilled tetrahydrofuran was added dropwise and the resulting transparent yellow solution was stirred overnight at room temperature. Then, the solution was poured into a mixture of 400 mL ether and 200 mL 1M hydrochloric acid. The layers were separated and the organic layer was washed twice with a saturated sodium bicarbonate solution and twice with water. The solution was dried over sodium sulphate, filtered and evaporated to dryness resulting in a brown oil (17.8 g, 90%). ^{1}H-NMR ($CDCl_3$): δ 7.17 (s, 2H, Ar-H), 4.23 (q, 2H, O-C*H*$_2$-CH_3), 4.04 (m, 6H, O-CH_2), 1.7-1.9 (m, 6H, O-CH_2-C*H*$_2$), 1.50 (m, 6H, O-CH_2-CH_2-C*H*$_2$), 1.28 (br, 51H, CH_2, CH_3), 0.88 (t, 9H, CH_3).

Potassium mono ethyl malonate (10). Diethyl malonate (50 g, 0.312 mol) was dissolved in 200 mL ethanol. A solution of potassium hydroxide (17.5 g, 0.312 mol) in 200 mL ethanol was added dropwise over one h. A white precipitate was formed during the addition, and stirring was continued for another 12 h at room temperature after addition of all the hydroxide. The solution was evaporated to dryness, and then the sticky residue was taken up in ether. The salt was collected by suction filtration, washed with ether and dried under reduced pressure at room temperature resulting in pure **10** (45.6 g, 86 %). ^{1}H NMR ($CDCl_3$): δ 4.06 (q, 2H, OCH_2), 3.15 (s, 2H, $CH_2C{=}O$), 1.12 (t, 3H, CH_3).

Ethyl 3,4,5-tri((*S*)-3,7-dimethyloctyloxy)benzoylacetate (9b). Potassium ethyl malonate (**10**) (1.6 g, 9.4 mmol) and ethyl acetate (15 mL) were transferred to a 25 mL flask. The mixture was stirred and cooled to 0°C. To this mixture was added Et_3N (2.56 g, 3.5 mL) followed by dry $MgCl_2$ (1.17 g, 12.3 mmol). The mixture was heated to 35°C over 30 min and then maintained at 35°C for 6 h. The mixture was cooled to 0°C, and 3,4,5-tri((*S*)-3,7-dimethyl octyloxy)benzoyl chloride (4.2 g; 6.9 mmol) was added dropwise over 15 min. The mixture was allowed to stir overnight at room temperature and then cooled to 0°C before adding 13% hydrochloric acid (20 mL) cautiously while keeping the temperature below 25°C. The aqueous layer was separated and then back-extracted with toluene. The combined organic layers were washed with 12 % hydrochloric acid (2x10 mL) followed by H_2O (2x10 mL) and a 5 % $NaHCO_3$ solution (20 mL) and then concentrated under vacuum to give the product as a solid (3.9 g). ^{1}H NMR ($CDCl_3$): δ 7.21 (s, 2H, Ar-H), 4.24 (q, 2H, O-C*H*$_2$-CH_3), 4.06 (m, 6H, O-CH_2), 1.75-1.93 (m, 6H, O-CH_2-C*H*$_2$), 1.75-0.9 (multiple peaks, 54 H, CH, CH_2, CH_3).

6-[3,4,5-Tri(dodecyloxy)phenyl]isocytosine (11a). A solution of ethyl 3,4,5-tri(dodecyloxy)benzoylacetate **9a** (17.6 g, 21.0 mmol), and guanidium carbonate (4.7 g, 26.25 mmol) in absolute ethanol (200 mL) was boiled and stirred overnight at reflux temperature. Then, the solution was evaporated to dryness and the residue was dissolved in chloroform (400 mL). The solution was washed with water (300 mL). The aqueous layer was back-extracted with chloroform (150 mL). The combined organic layers were washed with a saturated sodium chloride solution, dried over sodium sulphate and filtered. Evaporation gave a white solid that was further purified by column chromatography (eluent: dichloromethane, then 2% ethanol in dichloromethane, and finally 5% ethanol in dichloromethane) (6.04 g, 39%). IR: ν = 3155, 1652, 1467, 1120 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 12.35 (br, 1H, NH), 7.13 (s, 2H, Ar-H), 6.19 (s, 1H, alkylidene H), 5.84 (br, 2H, NH_2) 4.02 (m, 6H, O-CH_2), 1.7-1.9 (m, 6H, O-CH_2-C*H*$_2$), 1.49 (m, 6H, O-CH_2-CH_2-C*H*$_2$), 1.28 (br, 48H, CH_2), 0.89 (t, 9H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 159.7, 154.1, 153.5, 151.7, 142.4, 123.6, 106.0, 100.4, 72.0, 67.9, 32.0, 30.6, 29.7-29.3, 26.2, 26.0, 22.4, 13.9 ppm. Anal. Calcd. (%) for $C_{46}H_{81}N_3O_4$ (740.35): C 74.63; H 11.03; N 5.70. Found (%): C 74.6; H 10.7; N 5.7.

6-[3,4,5-Tri((*S*)-3,7-dimethyloctyloxy)phenyl]isocytosine (11b). A solution of ethyl 3,4,5-tri((*S*)-3,7-dimethyloctyloxy)benzoylacetate, (**9b**), (3.77 g, 5.71 mmol), and guanidium carbonate (1.44 g, 8 mmol) in absolute ethanol (100 mL) was boiled and stirred overnight at reflux temperature. The solution was evaporated to dryness and the residue was dissolved in dichloromethane (50 mL). The solution was extracted with water (50 mL). The water layer was extracted with dichloromethane (40 mL). The combined organic layers were washed

with a saturated sodium chloride solution, dried over sodium sulphate and filtered. Evaporation gave a white solid, which was further purified by column chromatography (eluent: 1/3 ethyl acetate/hexane, and then 8% methanol in dichloromethane) (1.68 g, 45%). IR(UATR): ν = 3148, 1649, 1120 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 12.35 (br, 1H, C=C-N<u>H</u>-C=N), 7.13 (s, 2H, Ph-H), 6.18(s, 1H, <u>H</u>-C=C-N), 5.82(br, 2H, N=C-N<u>H_2</u>) 4.07m, 6H, O-C<u>H_2</u>), 1.7-1.9 (m, 6H, O-CH_2-C<u>H_2</u>), 1.7-0.8 (multiple peaks, 51H). ^{13}C NMR ($CDCl_3$) δ: 159.8, 135.9, 153.5, 151.4, 142.7, 123.6, 105.7, 100.3, 71.9, 67.7, 39.6, 37.8, 37.6, 36.6, 30.1, 28.2, 24.9, 22.9, 22.8, 19.8 ppm.

***N*-Butylaminocarbonyl-6-[3,4,5-tri(dodecyloxy)phenyl]-isocytosine (1a).** A solution of 6-[3,4,5-tri(dodecyloxy)phenyl]isocytosine **11a** (1 g, 1.35 mmol) and *n*-butyl isocyanate (0.77 mL, 6.76 mmol) in dry pyridine (7 mL) was boiled and stirred overnight at reflux temperature. The solution was evaporated to dryness and the residue was co-distilled twice with toluene (5 mL). The brown residue was dissolved in chloroform and precipitated in ethanol. Thin layer chromatography showed that the product contained 2 minor contaminations. The contaminations were removed by precipitation from ethyl acetate resulting in pure **1a** (0.85 g, 75%). IR(UATR): ν = 3226, 1694, 1120 cm^{-1}. ^{1}H-NMR ($CDCl_3$): for 4[1H]-pyrimidinone tautomer δ 13.90 (s, 1H, NH), 12.06 (s, 1H, NH), 10.24 (s, 1H, NH), 6.83 (s, 2H, Ar-H), 6.29 (s, 1H, alkylidene H), 4.05 (m, 6H, O-CH_2), 3.29 (m, 2H, NH-C*H_2*), 1.86 (m, 6H, O-CH_2-C*H_2*), 1.77 (m, 2H, NH-CH_2-C*H_2*), 1.65 (m, 2H, NH-CH_2-CH_2-C*H_2*) 1.50 (m, 6H, O-CH_2-CH_2-C*H_2*), 1.29 (br, 48H, CH_2), 0.890 (t, 12H, CH_3). For pyrimidin-4-ol tautomer δ 13.58 (s, 1H, NH), 11.32 (s, 1H, NH), 10.02 (s, 1H, NH), 7.04 (s, 2H, Ar-H), 6.65 (s, 1H, alkylidene H), 3.43 (m, 2H), rest of the peaks overlap with peaks of the main tautomer. ^{13}C-NMR ($CDCl_3$): δ 4[1H]-pyrimidinone tautomer 173.6, 156.8, 155.1, 153.8, 149.1, 141.1, 126.0, 104.3, 103.7, 73.7, 69.4, 39.9, 32.0, 31.6, 30.4, 29.8, 29.9-29.4, 26.2, 22.8, 20.3, 14.2, 13.8. Anal. Calcd. (%) for $C_{51}H_{90}N_4O_5$ (839.29): C 72.99; H 9.50; N 6.70. Found (%): C 72.9; H 9.6; N 6.7.

***N*-Butylaminocarbonyl-6-[3,4,5-tri((*S*)-3,7-dimethyloctyloxy)phenyl]-isocytosine (1b).** The title compound was synthesised via the same procedure as used for compound **1a** (Y = 43%). IR: ν = 3226, 1694, 1120 cm^{-1}. ^{1}H-NMR ($CDCl_3$): for 4[1H]-pyrimidinone tautomer δ 13.93 (s, 1H, NH), 12.06 (s, 1H, NH), 10.17 (s, 1H, NH), 6.84 (s, 2H, Ar-H), 6.28 (s, 1H, alkylidene H), 4.05 (m, 6H, O-CH_2), 3.30 (m, 2H, NH-C*H_2*), 1.88-0.95 (m, CH_2), 0.890 (t, 12H, CH_3). For pyrimidin-4-ol tautomer δ 13.57 (s, 1H, OH), 11.30 (s, 1H, NH), 10.0 (s, 1H, NH), 7.07 (s, 2H, Ar-H), 6.64 (s, 1H, alkylidene H), 3.43 (m, 2H), rest of the peaks overlap with peaks of the main tautomer. ^{13}C-NMR ($CDCl_3$): δ 4[1H]-pyrimidinone tautomer 173.4, 156.7, 155.0, 153.8, 149.2, 141.9, 126.0, 104.1, 71.8, 67.7, 39.7-13.8. Anal. Calcd. (%) for $C_{45}H_{78}N_4O_5$ (755.13): C 71.58; H 10.41; N 7.42. Found (%): C 71.6; H 10.5; N 7.4.

N,N'-(1,5-Pentamethylene)-bis-(2-ureido-6-[3,4,5-tri((*S*)-3,7-dimethyloctyloxy)phenyl]-4-pyrimidinone (2). To a solution of 1,5-pentanediamine (38 µl, 0.32 mmol) in dichloromethane was added di-*tert*-butyl-tricarbonate (0.20 g, 0.77 mmol). The solution was allowed to stir for 1 h at room temperature to afford 1,5-pentane diisocyanate. The solution was evaporated to dryness and the residue was dissolved in pyridine 3 mL. To this solution was added 6-[3,4,5-tri((*S*)-3,7-dimethyloctyloxy)phenyl]isocytosine (**11b**) (0.5 g, 0.76 mmol). The solution was stirred at 90 °C for 12 h. The solution was evaporated to dryness and the

residue was co-evaporated twice with toluene (2 mL). The orange/white residue was dissolved in chloroform and precipitated in ethyl acetate. The impure product was further purified by column chromatography (eluent: 2% tetrahydrofuran in chloroform, then 1/1 hexane/chloroform) and precipitation in methanol, resulting in pure **3** (0.14 g, 30%). IR(UATR): ν = 3222, 1694, 1114 cm^{-1}. ^1H NMR ($CDCl_3$ + TFA): δ 6.87 (s, 4H, Ar-H), 6.64 (s, 2H, alkylidene H), 4.19 (m, 4H, O-CH_2), 4.09 (m, 8H, O-CH_2), 3.37 (m, 4H, NH-CH_2), 1.87 (m, 12H, O-CH_2-CH_2), 1.67 (m, 4H, NH-CH_2-CH_2), 1.66-0.86 (multiple peaks, 104 H, CH_2, CH_3). ^{13}C NMR ($CDCl_3$): δ 173.2, 157.5, 155.3, 153.8, 148.6, 140.9, 132.12, 126.3, 103.9, 71.9, 67.8, 39.6, 39.5, 37.8, 37.5, 36.5, 30.2, 29.9, 28.2, 25.0, 23.0, 22.0, 19.7. Anal. Calc. (%) for $C_{87}H_{148}N_8O_{10}$ (1466.17): C 71.27; H 10.17; N 7.64. Found (%): C 71.58; H 9.80; N 7.39. MALDI-TOF-MS: (MW = 1465.13) *m/z* 1466 $[M]^+$, 1489.16 $[M+Na]^+$.

***N,N'*-(1,6-Hexamethylene)-bis-(2-ureido-6-[3,4,5-tri(dodecyloxy)phenyl]-4-pyrimidinone (3a).** A suspension of 6-[3,4,5-tri(dodecyloxy)phenyl]isocytosine **11b** (4 g, 5.4 mmol) in dry pyridine (12 mL) and toluene (2 mL) was heated to reflux temperature. A clear solution was obtained and some solvent was distilled off to remove traces of water. After cooling down to room temperature, 1,6-hexane diisocyanate (0.36 mL, 2.16 mmol) was added via a syringe and the solution was stirred overnight at reflux temperature. The solution was evaporated to dryness and the residue was co-distilled twice with toluene (5 mL). The brown residue was dissolved in chloroform and precipitated in ethanol. A minor contamination was removed by precipitation in ethyl acetate resulting in pure **6** (2.11 g, 59 %). IR(UATR): ν = 3226, 1693, 1117 cm^{-1}. ^1H-NMR ($CDCl_3$ + TFA) δ: 6.91 (s, 4H, Ar-H), 6.37 (s, 2H, alkylidene H), 4.04 (m, 12H, O-CH_2), 3.32 (m, 4H, NH-CH_2), 3.17, 1.81 (m, 12H, O-CH_2-CH_2, 1.75 (m, 4H, NH-CH_2-CH_2), 1.60 (m, 4H, NH- CH_2-CH_2-CH_2), 1.47 (m, 12H, O-CH_2-CH_2-CH_2), 1.26 (br, 96H, CH_2), 0.88 (t, 18H, CH_3). ^{13}C-NMR ($CDCl_3$): 173.3, 156.9, 155.3, 153.8, 149.5, 140.9, 126.0, 104.5, 103.8, 73.4, 69.3, 40.1, 32.1, 31.6, 30.5, 30.0, 29.9-29.4, 26.4, 22.5, 20.4, 14.2, 13.8. Anal. Calcd. (%) for $C_{100}H_{174}N_8O_{10}$ (1648.52): C 72.86; H 10.64; N 6.80. Found (%): C 72.54; H 9.98; N 6.71.

N,N'-(1,6-Hexamethylene)-bis-(2-ureido-6-[3,4,5-tri((*S*)-3,7-dimethyloctyloxy)phenyl]-4-pyrimidinone (3b). A suspension of 6-[3,4,5-tri((*S*)-3,7-dimethyloctyloxy)phenyl]isocytosine (**11b**) (0.5 g, 0.76 mmol) in dry pyridine (4 mL) and toluene (1 mL) was heated to reflux temperature. A clear solution was obtained and some solvent was distilled of to remove traces of water. After cooling, 1,6-hexane diisocyanate (0.05 mL, 0.3 mmol) was added via a syringe. Furthermore a trace of DMAP was added. The solution was stirred at 90°C for 12 h. The reaction mixture was evaporated to dryness and the residue was co-evaporated twice with toluene (2 mL). The red residue was dissolved in chloroform and precipitated in methanol, ethanol and ethyl acetate. Further purification by column chromatography (eluent: 6% tetrahydrofuran in chloroform) and precipitation in methanol, resulted in pure **2b** (0.12 g, 27%). IR(UATR): ν = 3226, 1692, 1115 cm^{-1}. ^1H NMR ($CDCl_3$ + TFA): δ 6.91 (s, 4H, Ar-H), 6.48 (s, 2H, alkylidene H), 4.09 (m, 12H, O-CH_2), 3.33 (m, 4H, NH-CH_2), 1.87 (m, 12H, O-CH_2-CH_2, 1.71 (m, 4H, NH-CH_2-CH_2), 1.66-0.86 (multiple peaks, 106 H, CH_2, CH_3). ^{13}C NMR ($CDCl_3$): δ 173.1, 157.0, 155.2, 153.4, 148.2, 140.9, 126.3, 103.7, 71.5, 67.8, 39.6, 39.5, 37.8, 37.5, 36.5, 30.2, 29.9, 28.2, 25.0, 23.0, 22.0, 19.7. Anal. Calcd. (%) for $C_{88}H_{150}N_8O_{10}$ (1480.20): C 71.41; H 10.21; N 7.57. Found (%): C 71.05; H 9.92; N 7.52. MALDI-TOF-MS: (MW = 1479.14) *m/z* 1480.04 $[M]^+$, 1503.01 $[M+Na]^+$.

N,N'-(1,7-Heptamethylene)-bis-(2-ureido-6-[3,4,5-tri((*S*)-3,7-dimethyloctyloxy)phenyl]-4-pyrimidinone (4). The title compound was synthesised from 1,7-diisocyanatoheptane in the same way as compound **3**. Purification was performed by column chromatography (eluent: 2% tetrahydrofuran in chloroform) and precipitation in methanol, resulting in pure **4** (Y = 29%). IR(UATR): ν = 3222, 1694, 1114 cm^{-1}. ^1H NMR ($CDCl_3$ + TFA): δ 6.88 (s, 4H, Ar-H), 6.62 (s, 2H, alkylidene H), 4.19 (m, 4H, O-CH_2), 4.09 (m, 8H, O-CH_2), 3.33 (m, 4H, NH-CH_2), 1.87 (m, 12H, O-CH_2-CH_2), 1.68 (m, 4H, NH-CH_2-CH_2), 1.66-0.86 (multiple peaks, 108 H, CH_2, CH_3). ^{13}C NMR ($CDCl_3$): δ 171.6, 157.5, 155.3, 153.8, 148.6, 140.9, 132.1, 126.3, 103.9, 71.8, 67.8, 39.5, 37.6, 37.4, 36.5, 36.4, 30.0, 28.1, 24.8, 22.8, 22.6, 19.6. Anal. Calcd. (%) for $C_{89}H_{152}N_8O_{10}$ (1494.23): C 71.50; H 10.25; N 7.50. Found (%): C 71.35; H 10.00; N 7.42. MALDI-TOF-MS: (MW = 1493.16) *m/z* 1494.22 $[M]^+$, 1517.19 $[M+Na]^+$.

N,N'-(1,8-Octamethylene)-bis-(2-ureido-6-[3,4,5-tri((*S*)-3,7-dimethyloctyloxy)phenyl]-4-pyrimidinone (5). The desired compound was synthesised from 1,8-diisocyanatooctane following the procedure of compound **2b**. Purification was carried out with column chromatography (eluent: 2% tetrahydrofuran in chloroform) and precipitation in methanol, resulting in pure **5** (Y = 28%). IR(UATR): ν = 3226, 1692, 1115 cm^{-1}. ^1H NMR ($CDCl_3$ + TFA): δ 6.88 (s, 4H, Ar-H), 6.57 (s, 2H, alkylidene H), 4.08 (m, 12H, O-CH_2), 3.32 (m, 4H, NH-CH_2), 1.87 (m, 12H, O-CH_2-CH_2), 1.69 (m, 4H, NH-CH_2-CH_2), 1.66-0.86 (multiple peaks, 110 H, CH_2, CH_3). ^{13}C NMR ($CDCl_3$): δ 173.0, 157.8, 155.2, 153.8, 149.0, 141.5, 132.1, 126.3, 104.5, 72.3, 69.5, 39.4, 39.3, 37.4, 37.1, 36.3, 29.8, 29.7, 28.0, 24.8, 22.7, 22.6, 19.5. Anal. Calcd. (%) for $C_{90}H_{154}N_8O_{10}$ (1508.25): C 71.67; H 10.29; N 7.43. Found (%): C 71.71; H 10.09; N 7.35. MALDI-TOF-MS: (MW = 1507.18) *m/z* 1508.18 $[M]^+$, 1530.16 $[M+Na]^+$.

N$^{\varpi}$,N$^{\varpi'}$-*m*-Xylylene-bis-(2-ureido-6-[3,4,5-tri(dodecyloxy)phenyl]-4-pyrimidinone (6a). The title compound was obtained from *m*-xylylenediisocyanate in the same way as **2b**. Column chromatography (flash silica, 2/4/94 methanol/tetrahydrofuran/chloroform) gave pure **6a** (Y = 36 %). IR(UATR): ν = 3226, 1695, 1117 cm^{-1}. ^1H NMR ($CDCl_3$ + TFA): δ 7.30 (s, 2H, m-Ph-H), 7.10, 6.89 (s, 4H, Ar-H), 6.61 (s, 2H, alkylidene H), 4.52 (d, 4H, NH-CH_2), 4.15 (t, 4H, OCH_2), 4.06 (t, 8H, OCH_2), 1.81 (m, 12H, OCH_2-CH_2), 1.49 (m, 12H, OCH_2-CH_2-CH_2), 1.29 (br, 96H, CH_2, CH_3), 0.90 (t, 18H, CH_3). Anal. Calcd. (%) for $C_{102}H_{170}N_8O_{10}$ (1668.51): C 73.43; H 10.27; N 6.72. Found (%): C 72.54; H 9.87; N 6.71.

N$^{\varpi}$,N$^{\varpi'}$-*m*-Xylylene-bis-(2-ureido-6-[3,4,5-tri((*S*)-3,7-dimethyloctyloxy)phenyl]-4-pyrimidinone (6b). For the synthesis of the title compound see the procedure for compound **2b**. 2% Tetrahydrofuran in chloroform was used as an eluent for column chromatography, and precipitation in methanol gave pure **6b** (Y = 14%). IR(UATR): ν = 3226, 1692, 1115 cm^{-1}. ^1H NMR ($CDCl_3$ + TFA): δ 7.34 (s, 2H, m-Ph-H), 7.10, 6.87 (s, 4H, Ar-H), 6.62 (s, 2H, alkylidene H), 4.50 (m, 4H, NH-CH_2), 4.13 (m, 4H, O-CH_2 intra), 4.08 (m, 8H, O-CH_2) 1.86 (m, 12H, O-CH_2-CH_2, 1.68-0.86 (multiple peaks, 102 H, CH_2, CH_3). ^{13}C NMR ($CDCl_3$): δ 173.2, 157.6,

155.1, 153.8, 153.5, 148.6, 139.1, 125.4, 125.1, 124.6, 105.0, 103.6, 71.9, 67.6, 39.6, 38.4, 37.8, 37.7, 36.5, 31.5, 30.1, 29.9, 28.2. 25.0, 22.9, 19.7. Anal. Calc. (%) for $C_{90}H_{146}N_8O_{10}$ (1500.19): C 72.06; H 9.81; N 7.47. Found (%): C 71.65; H 9.97; N 7.17. MALDI-TOF-MS: (MW =1499.11) *m/z* 1500.15 $[M]^+$, 1523.13 $[M+Na]^+$.

2-(1-Imidazolylcarbonylamino)-6-[3,4,5-tri(dodecyloxy)phenyl]-4[1H]-pyrimidinone (7). To a solution of 6-[3,4,5-tris(dodecyloxy)phenyl]isocytosine **4** (1.05 g, 1.35 mmol) in chloroform (7 mL) was added carbonyl diimidazole (0.34 g, 2.7 mmol). The solution was allowed to stir overnight at reflux temperature. The reaction mixture was then evaporated under reduced pressure and precipitated from chloroform in EtOAc resulting in pure **27** (0.92 g; 78%). ^{1}H NMR ($CDCl_3$): δ 8.81 (s, 1H, N-C*H*=N), 7.56 (s, 1H, N-C*H*=CH), 6.85 (s, 2H, Ar-H), 6.75 (s, 1H, N-CH=C*H*), 6.13 (s, 1H, alkylidene H), 4.05 (t, 2H, OCH_2), 3.99 (t, 4H, OCH_2), 1.82 (m, 6H, OCH_2CH_2), 1.48 (m, 6H, $OCH_2CH_2CH_2$), 1.27 (m, 30H, CH_2), 0.88 (t, 9H, CH_3).

N^{ω},$N^{\omega'}$-[(1,6-Bis(methoxycarbonyl)-3,4-dithia)hexylene]-bis-(2-ureido-6-[3,4,5-tri(dodecyloxy)-phenyl]-4-pyrimidinone (8). To a solution of (–)-cystine dimethyl ester, dihydrochloride (81.3 mg, 0.24 mmol) in chloroform (7 mL) was added triethylamine (66.8 µl, 0.48 mmol). It was allowed to stir for a few minutes before 2-(1-imidazolylcarbonylamino)-6-[3,4,5-tri(dodecyloxy) phenyl]-4[1H]-pyrimidinone **7** (0.43 g, 0.52 mmol) was added. The solution was stirred for 3.5 h. IR and a ninhydrin test showed that no more free amines were present. The reaction mixture was evaporated to dryness and precipitated in chloroform resulting in a white powder. The impure product was further purified by column chromatography (eluent: 1% methanol in chloroform) and precipitation in acetone, resulting in pure **8** (0.28 g, 64 %). IR(UATR): ν = 3226, 1745, 1670, 1116 cm^{-1}. ^{1}H NMR ($CDCl_3$ + TFA): δ 6.93 (s, 4H, Ar-H), 6.63 (s, 2H, alkylidene H), 4.91 (m, 2H, NH-C*H*), 4.16 (t, 4H, OCH_2), 3.85 (t, 8H, OCH_2), 3.35 (dd, 2H, S-CH), 3.18 (dd, 2H, S-CH), 1.81 (m, 12H, OCH_2CH_2), 1.6-1.2 (multiple peaks, 108H, CH_2), 0.88 (t, 18H, CH_3). ^{13}C NMR ($CDCl_3$): δ 173.2, 171.6, 170.9, 166.5, 157.4, 156.9, 154.8, 153.9, 153.6, 148.9, 141.2, 132.3, 125.8, 124.9, 106.6, 104.2, 73.9, 69.5, 69.2, 53.0, 41.6, 40.7, 38.0, 32.2, 30.7, 30.0, 29.8, 26.6, 22.9, 14.3. Anal. Calcd. (%) for $C_{102}H_{174}N_8O_{14}S_2$ (1800.66): C 68.04; H 9.74; N 6.22. Found (%): C 68.10; H 9.51; N 6.11. MALDI-TOF-MS: (MW = 1799.26) *m/z* 1802.1 $[M]^+$, 1824.67 $[M+Na]^+$, 899.79 (S-S cleavage), 901.77 (S-S cleavage).

5.8 References and Note

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6

Supramolecular Block Copolymers

Abstract

*Poly(ethylene/butylene) (PEB) and polystyrene (PS) were end functionalised with trialkoxyphenyl-ureido-s-triazine (UTr), hydrogen bonding units for their self assembly in supramolecular block copolymers. An increase of the viscosity occurs upon functionalisation of monofunctional PEB **4a** and telechelic PEB **4b**. Telechelic PEB **4b**, bearing two UTr-groups is a transparent solid that exhibits viscoelastic properties. In solution, much larger aggregates of **4a** and **4b** are formed in dodecane than in chloroform. Triblock and multiblock copolymers are formed in solution and in the bulk when hexamethylene-bis(ureido-s-triazine) is added to functionalised **4a** and **4b**. Monofunctional PEB **4a** acts as a chainstopper and the viscosity of dodecane solutions of $C_6(UTr)_2$ is decreased upon addition of **4a**. Significant amplification of chirality is observed in these mixtures as shown with CD. The bulk morphology of the mixtures is highly dependent on the sample preparation. Whereas in spin coated samples aggregates of **4b**-$C_6(UTr)_2$ gave fibre like structures with an average thickness of 42 nm, drop cast samples resulted in a fur like morphology. The sizes of these aggregates range from 17 nm to 42 nm. With AFM it was observed that the morphology does not change when the composition of the blend is varied. Mixtures of PS-UTr (**1**) and $C_6(UTr)_2$ behave much more like a polymer blend than like a supramolecular block copolymer.*

6.1 Introduction

The polymers most commonly used commercially are homopolymers. In the present days more and more sophisticated applications are being developed that require combinations of properties that cannot be implemented with simple homopolymers. Since most polymers are as a rule immiscible, the use of blends to obtain new materials is not often straightforward. The formation of a macrophase morphology usually results in poor mechanical properties. In block copolymers, however, the components are covalently connected and, therefore, macrophase separation is prevented. The interest in block copolymers mainly derives from their specific microstructure and their use as compatibilisers of polymer blends. They are also employed for the control of interfacial properties in multiphase polymer systems. In diblock copolymer (A-B) segregation of the segments cannot lead to macroscopic phase separation, instead, microscopic phase separation occurs. The microdomains are usually arranged regularly, and the type of morphology depends on the total degree of polymerisation N, the fractional composition f_A, and the Flory-Huggins A-B interaction parameter χ.[1] The classical morphologies of A-B diblock copolymers are lamellae, hexagonally packed cylinders and body centred cubic arrays of spheres.[2] Block copolymers in which a fraction of the backbone is rigid and the remainder flexible are also known as rod-coil copolymers. Examples of rigid blocks that have been used in rod-coil polymers include aromatic moieties,[3] conjugated moieties,[4] α-helices[5] and liquid crystalline mesogens.[6] Self-assembly of a block copolymer consisting of different supramolecular polymers might offer materials with novel architecture. Although macrophase separation is not prevented by the association of self-complementary ureido-*s*-triazine units, we expect that hydrogen bonding will inhibit the process, and may freeze in a microphase separated block copolymer. One of the main goals of the present work is to investigate the balance between microphase and macrophase separation in a supramolecular system. The increase of the miscibility in rod-coil copolymers was reported before by employing not only hydrogen bonds,[7,8] but also charge transfer interactions,[9] dipole-dipole, ion-dipole interactions, and ion-ion interactions.[10,11] Due to the reversible nature of the envisaged systems, the properties of the block copolymer can in principle be easily adjusted by varying the composition of the blend. In this work we are aiming at the combination of columnar structures as described in chapters 3 and 4 with an ordinary random coil polymer, such as poly(ethylene/butylene) and

polystyrene. An attempt is made to assemble a triblock and multiblock copolymer, which consists of either a functionalised polystyrene or a functionalised hydrogenated polybutadiene copolymer as the conventional polymer in combination with columnar stacks of hexane-di-(trialkoxyphenyl-*s*-triazine) as the rigid block. In order to enhance the compatibility of the two components the random coil polymer is provided with ureido-*s*-triazine groups. The concept is schematically represented for the case of a triblock copolymer in Figure 6.1. The self-assembly of the building blocks is studied with DSC and AFM.

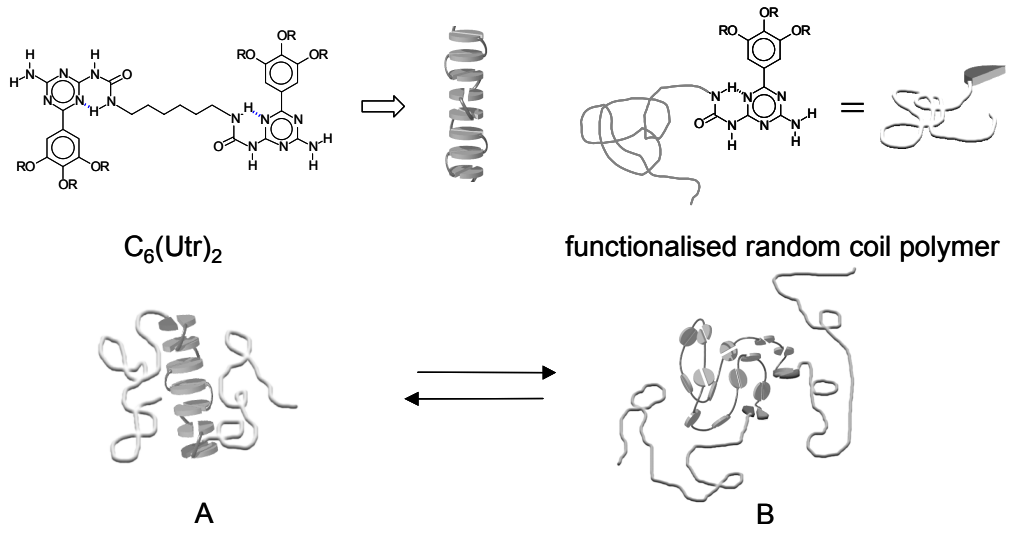


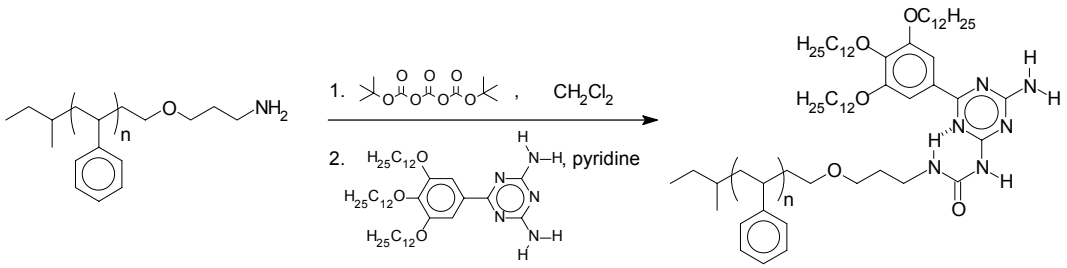
Figure 6.1: *Blends of a helical self-assembled polymer ($C_6(UTr)_2$) and a ureidotriazine functionalised random coil polymer may result in a block copolymer. A schematic representation is depicted of the folding and unfolding of a triblock copolymer in view. Denaturation of a coil-rigid rod **A** into a random coil like block copolymer **B**. Reversibly, conformation **B** can fold back into conformation **A**. In the figure each half disc represents the rigid aromatic phenyl-s-triazine moiety. The curled lines represent an amorphous traditional polymer.*

6.2 End-group Modification of Polystyrene

6.2.1 Synthesis and Characterisation

Amine terminated PS, obtained by a procedure described by van Hest,[12] with an average molecular weight of 3200 g/mol and low dispersity (PD = 1.03), was converted into the corresponding isocyanate either by a reaction with di-*t*-butyltricarbonate, following the procedure of Peerlings,[13] or by a reaction with phosgene dissolved in toluene. Without further purification the PS-isocyanate (PS-NCO) was used in the mono-acylation of 2,4-diamino-2,3,4-tridodecyloxyphenyl-*s*-triazine. We found that high yields in the conversions could only

be reached when the reaction mixture was highly concentrated (approximately 0.5 $g.mL^{-1}$). The product was purified by precipitation of a chloroform solution in ethanol followed by column chromatography.



Scheme 6.1: *Synthesis of monofunctional polystyrene (PS-UTr)* ***1****. The end-group modification from the amine to the isocyanate occurred in the presence of di-t-butyltricarbonate. This could, however, also be performed using phosgene in toluene.*

^{1}H-NMR spectroscopy and size exclusion chromatography (SEC) in chloroform were used to characterise polymer **1**. A ^{1}H-NMR spectrum recorded in $CDCl_3$ shows the three characteristic NH signals at 10.2, 9.7 and 9.1 ppm. From SEC an average molecular weight of 5800 g/mole was found, indicating that the system is dimeric in chloroform, under SEC conditions (10^{-5} M).

6.2.2 Morphology of PS-UTr and its Blends with $C_6(UTr)_2$

The phase behaviour of **1** in the bulk was studied with AFM, optical polarisation microscopy (OPM) and DSC. A sample of **1** obtained from precipitation in methanol is birefringent, and becomes isotropic at 65 °C. The sample remains amorphous after cooling. The morphology was studied in more detail with DSC. For polymer **1** two clear transitions in the DSC traces can be observed. A broad peak expanding from –50 °C to 0 °C can be attributed to the melting of the dodecyl side chains.[14] A second order transition ascribed to the glass transition temperature (T_g) of polystyrene appears at 65 °C. Apart from these changes, no additional transitions are present suggesting that columnar structures formed by aggregation of the phenyl-*s*-triazine core are absent. Furthermore, no contrast was observed with AFM on a sample that was drop cast from a chloroform solution. This is probably due to the small difference in rigidity between the hydrogen bonded block and the PS block. Trialkoxyphenyl-*s*-triazine terminated PS **1** that can act as a chain stopper, was mixed with

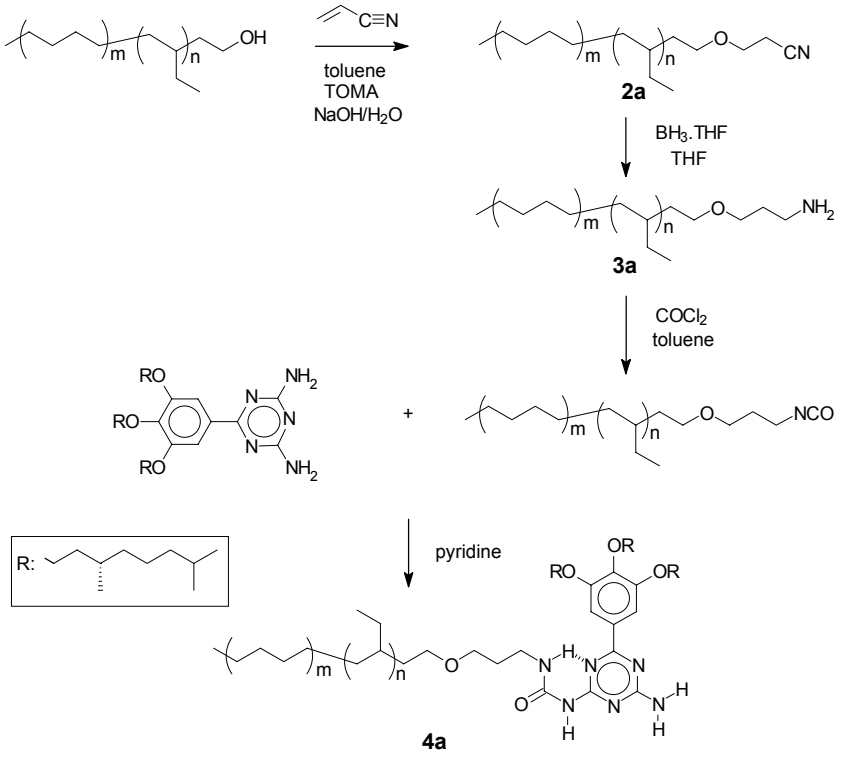
$C_6(UTr)_2$ in order to obtain a triblock copolymer consisting of a central $C_6(UTr)_2$ segment capped by two PS-UTr's. The mixtures were prepared by dissolution of both compounds in chloroform and subsequent removal of the solvent at reduced pressure. Similar patterns as for pure **1** were observed, however, upon cooling at a rate of 0.1 degrees/minute from 200 °C (clearing temperature), indicating the formation of domains consisting of $C_6(UTr)_2$ embedded in a PS matrix. The macrophase separation results from the incompatibility of the two components, and is facilitated by the reversibility of the hydrogen bonding units. Reproducible DSC traces of these mixtures could not be obtained, while no contrast was observed with AFM. Due to the reversible character of the supramolecular block and its incompatibility with PS, it is concluded that this system behaves much more like a polymer blend than like a supramolecular block copolymer.

6.3 Functionalisation of Poly(ethylene/butylene)

For the formation of supramolecular rod-coil block copolymers, a supramolecular polymer $C_6(UTr)_2$ and a conventional random coil like polymer with similar χ parameters are required. Poly(ethylene/butylene) (PEB) is highly apolar and is suitable for this purpose. PEB has not only the advantage of being highly soluble in almost any apolar solvent, it is also available as a monofunctional and bifunctional polymer. Both triblock and multiblock copolymers can, therefore, be obtained.

6.3.1 Synthesis and Characterisation

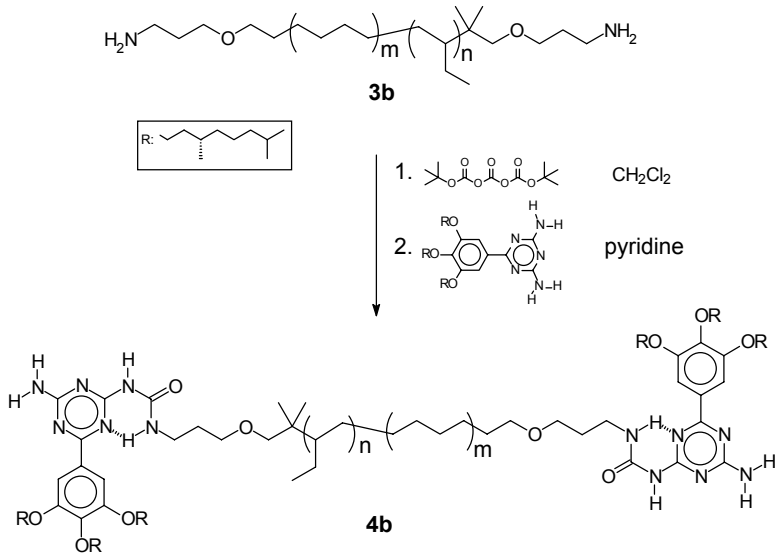
The simplest method to obtain the functionalised polymers PEB-UTr **4a** and PEB-$(UTr)_2$ **4b** is by end-group modification of available OH terminated PEB as depicted in Scheme 6.2 and Scheme 6.3. The OH terminated polymers (3800 $g.mol^{-1}$) first underwent a cyanoethylation via a Michael addition with acrylonitrile. The reaction was performed at the same conditions as described by van Hest[12] and van Aert.[15] Purification was performed at room temperature in order to prevent the retro-Michael reaction. Since reduction of the nitrile by catalytic hydrogenation was not successful, a procedure reported by Brown *et al.*[16] was followed, using borane-tetrahydrofurane (BH_3.THF). In this way both mono-amine **3a** and bis-amine **3b** were synthesised in high yields. Column chromatography on silica was used to separate the relatively polar NH_2 terminated PEB from the less polar impurities.



Scheme 6.2: *End group modification of poly(ethylene/butylene) copolymer for the synthesis of monofunctional poly(ethylene/butylene)* ***4a*** *(PEB-UTr).*

Conversion of the amine into the corresponding isocyanate with phosgene was not successful since the isocyanate reacted instantaneously with unreacted amine yielding the corresponding urea. PEB-bisNCO was, therefore, synthesised with di-*t*-butyltricarbonate in freshly distilled CH_2Cl_2, using the method of Peerlings *et al.*[13] Finally, acylation of the chiral 2,4-diamino-6-(3,4,5-tri((*S*)-3,7-dimethyloctyloxy)phenyl)-*s*-triazine afforded the desired polymers **4a** and **4b**. The use of chiral side chains permits the study of superstructures with circular dichroism (CD) spectroscopy. The acylation can only be performed under strict exclusion of water. Therefore, the reaction was carried out by dissolving the diaminotriazine in dry pyridine and subsequently azeotropically drying the reaction mixture by partial removal of the solvent at reflux temperature under a flow of argon. Omitting this procedure resulted in formation of bis(PEB) urea as was concluded from the presence of a NH-signal at 4.6 ppm in the ^{1}H-NMR spectrum. It was also found that low conversions occur when the concentration of the reaction mixture is below 0.1 g/mL. The crude product was precipitated in ethyl acetate and futher purified with column chromatography in order to remove the excess of diamino-*s*-

triazine. Final purification with preparative size exclusion chromatography on biobeads (Bio-beads X3) with tetrahydrofuran as eluent, gave the pure polymers **4a** and **4b**.



Scheme 6.3: *Functionalisation of poly(ethylene/butylene) copolymer towards bifunctional poly(ethylene/butylene)* ***4b*** *(PEB-(UTr)$_2$).*

Both polymers were characterised with NMR, IR and MALDI-TOF MS. The ^{1}H NMR spectra recorded in chloroform showed the characteristic NH signals at 10.2, 9.85 and 9.25 ppm. This proves that the functionalised polymers associate via an array of four hydrogen bonds. Chloroform solutions of telechelic PEB **4b** are notably viscous.

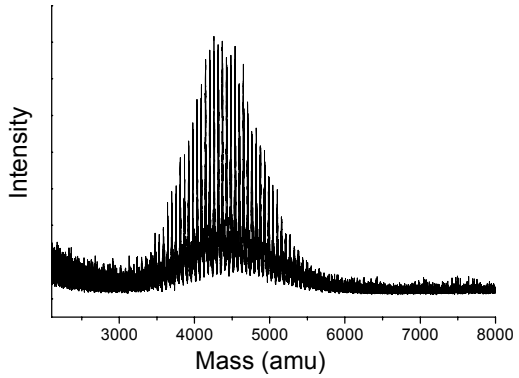


Figure 6.2: *MALDI-TOF MS of PEB-UTr* ***4a*** *gives a M_n = 4372 g.mol^{-1} (DP = 1.13); dimers were not observed.*

With MALDI-TOF (Matrix assisted laser desorption ionisation - time of flight) MS an average molecular weight (M_n) of 4372 g.mol^{-1} was found, and a polydispersity of 1.13 was calculated for **4a** (Figure 6.2). In the MALDI-TOF mass spectrum no starting material (3800 g.mol^{-1}) is observed. Modification of the structures is accompanied by an impressive change in material properties. Monofunctional PEB **4a** is much more viscous than the corresponding OH terminated polymer. The change is even more pronounced in the case of the telechelic polymer; it is a transparent, soft and elastic solid, which is in full agreement with the behaviour of similar telechelic PEB-bisureidopyrimidinone made by Folmer.[17a,b]

6.3.2 Small Angle Neutron Scattering

Solutions of **4a** and **4b** in deuterated chloroform (2 wt%) and dodecane (0.5 wt% and 2 wt%) were studied with SANS. The solutions did not form gels. As shown in Figure 6.4, monofunctional PEB-UTr **4a** and telechelic PEB-$(UTr)_2$ **4b** behave differently. A higher scattering intensity is observed for telechelic **4b**, due to its functionality of 2. Therefore, larger particles are formed than in the case of monofunctional **4a**. As expected, the scattering intensity drops when the concentration is decreased. In both cases more intense scattering is observed in dodecane than in chloroform. This suggests that larger particles are formed in dodecane than in chloroform. Indeed, as was found for $C_6(UTr)_2$ (see chapter 4), the only secondary interaction present in chloroform is hydrogen bonding. This means that dimers of monofunctional PEB-UTr and linear polymers of bifunctional PEB-$(UTr)_2$ are predominantely present in chloroform. However, in dodecane π-stacking of the aromatic core is expected to occur.

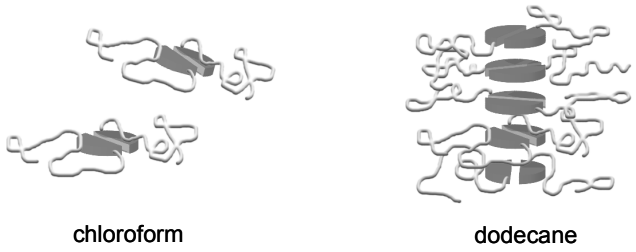


Figure 6.3: *A schematic representation of the organisation of monofunctional **4a** in chloroform and dodecane.*

The formation of a cylindrical structure via combined π-stacking and hydrogen bonding leads to a self assembled hairy rod polymer in the case of the monofunctional **4a** and to columnar structures that are linked to one another via the PEB spacer in the case of the bifunctional polymer **4b**. The organisation of monofunctional **4a** in chloroform and dodecane is schematically illustrated in Figure 6.3.

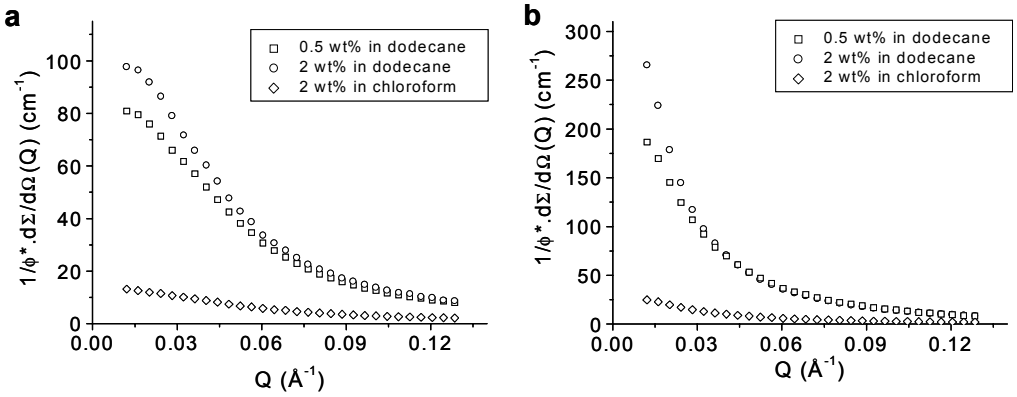


Figure 6.4: *SANS measurements of **a)** monofunctional PEB-UTr **4a** and **b)** telechelic PEB-(UTr)$_2$ **4b** in different deuterated solvents.*

6.4 Block Copolymers: Blends of Functionalised PEB and Achiral Molecule $C_6(UTr)_2$

Blends of a self-assembled polymer with mono- and bifunctional PEB were investigated in solution and in bulk. For this purpose rheology and CD were employed to investigate the behaviour in solution, while DSC and AFM were used for the study in the solid state.

6.4.1 Rheology

The role of monofunctional PEB-UTr **4a** as a chain stopper can be demonstrated clearly by simply observing the drop in the viscosity of solutions of bifunctional $C_6(UTr)_2$ upon addition of the chain stopper. Rheology measurements were performed on dodecane solutions in which the concentration of $C_6(UTr)_2$ was kept constant and the concentration of PEB-UTr **4a** was varied. Viscosity measurement with a Ubbelohde type viscometer was not possible due to the formation of highly viscous or gel like solutions. As a consequence

running times were not reproducible. Steady state shear measurements might give a good indication of the behaviour of $C_6(UTr)_2$ in dodecane upon addition of the chain stopper. As discussed in chapter 3 non-linear behaviour is observed with dodecane solutions of $C_6(UTr)_2$. For polymer **4a**, however, Newtonian behaviour is observed at concentrations below 10^{-3} mol.l^{-1}. A sharp decrease in the viscosity is observed when polymer **4a** is added to a dodecane solution of $C_6(UTr)_2$ (Figure 6.5).

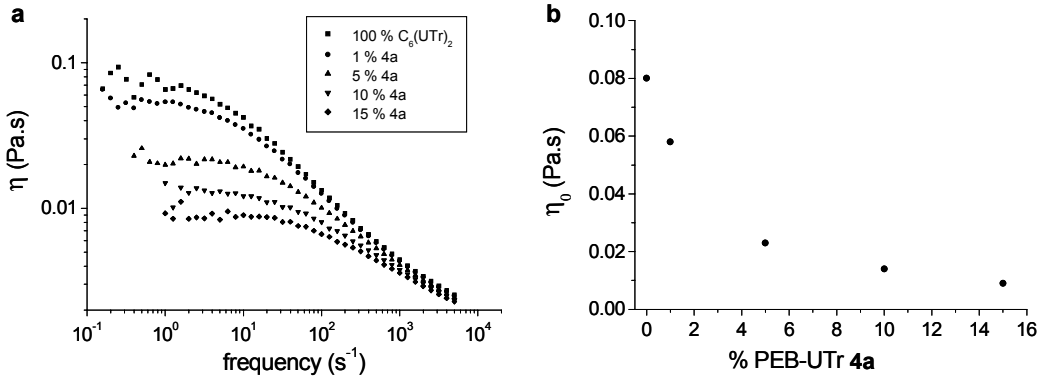


Figure 6.5: *Steady state shear measurements in dodecane at 20 °C. Mixing solutions of $C_6(UTr)_2$ (kept at a constant concentration of 10^{-3} mol.l^{-1}) and chain stopper **4a**. **a)** viscosity η (Pa.s) versus frequency (s^{-1}). **b)** relationship between the zero shear viscosity and the fraction of chain stopper PEB-UTr **4a** mixed with a solution of achiral $C_6(UTr)_2$.*

6.4.2 CD Spectroscopy

Preliminary neutron scattering measurements on polymers **4a** and **4b** suggest that large aggregates predominate in deuterated dodecane, whereas in chloroform only small aggregates are present. The rigid aromatic phenyl-*s*-triazine end groups of polymers **4a** and **4b** can form stacks. When stacking occurs, a column surrounded by the hydrogenated polybutadiene and trialkoxy side chains ('hairy' block copolmer) is formed. The aggregation of the polymers was studied with CD spectroscopy. No Cotton effect is found in chloroform where only random coil like aggregates are expected. In dodecane solutions of **4a** and **4b** no Cotton effect is observed either, indicating the absence of a preferred helical superstructure. In these structures the separate monomers are held together only by hydrogen bonds. In dodecane, stacks are formed, however, lacking the helical arrangement. Blends of chiral, functionalised PEB and achiral $C_6(UTr)_2$ were studied using CD spectroscopy. A "Sergeant and soldiers" experiment was performed by adding chiral **4a** or **4b** to a dodecane solution of

achiral $C_6(UTr)_2$. For the seperate compounds no Cotton effect was observed. However, when **4a** is mixed with $C_6(UTr)_2$, a Cotton effect is observed. Apparently, in this system **4a** is capable of transferring the chirality into the columns (see also chapter 3). As a result the chirality is amplified through cooperative interactions (see Figure 6.6). The maximum CD effect is reached at approximately 50 mol% of the chain stopper.

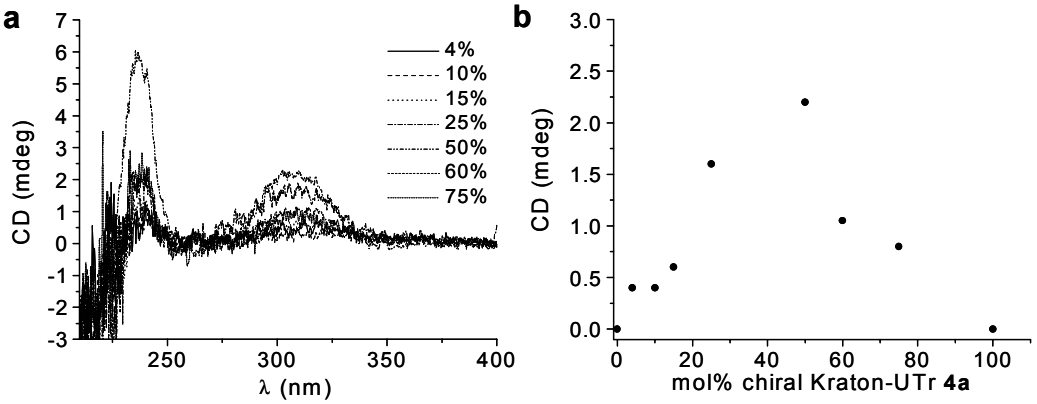


Figure 6.6: *"Sergeant and soldiers" experiment. CD spectra of dodecane solutions containing chiral PEB-UTr **4a** and achiral $C_6(UTr)_2$. CD (mdeg) of blend solutions containing different mol% of **4a**, versus the wavelength λ (nm) (**a**). CD at λ = 306 nm versus mol% of chiral **4a** (**b**).*

6.4.3 Phase Separation in the Solid State

DSC, optical polarisation microscopy (OPM) and AFM of blends of **4a** or **4b** with $C_6(UTr)_2$ were used to investigate the morphology. The blends were prepared by evaporation of mixed hexane solutions containing various ratios of **4** and $C_6(UTr)_2$.

Differential Scanning Calorimetry (DSC)

DSC traces were recorded of pure compounds **4a** and **4b**, and blends of $C_6(UTr)_2$ with **4a** and **4b** (see Figure 6.7). In addition to the T_g at –64 °C another broad transition can be observed for compound **4a**. This broad endotherm can be assigned to the melting of the three dodecyl chains. Similar to telechelic hydrogenated polybutadiene functionalised with two ureidopyrimidone groups,[17] only a glass transition is observed for **4b**. This is in contrast with the OH terminated analogue which features an additional melt transition at –23 °C.

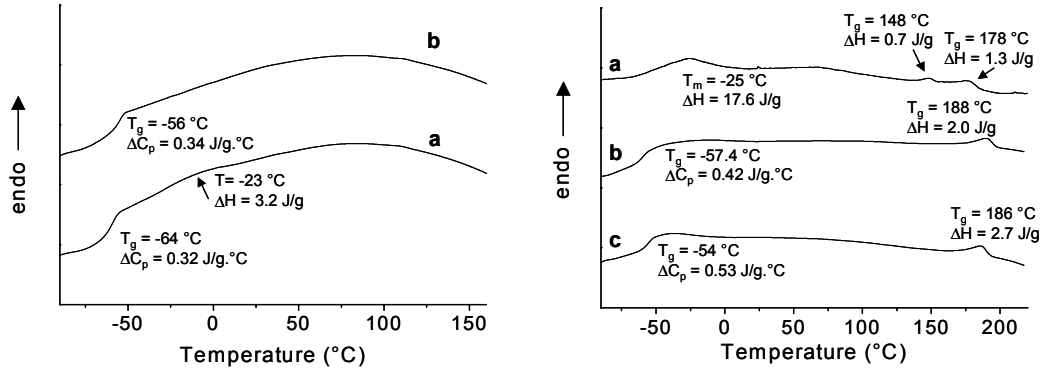


Figure 6.7: *DSC traces recorded at a rate of 40 °C/min. Left: DSC traces of **4a** (a) and **4b** (b). Right: DSC traces of $C_6(UTr)_2$ (a), and mixtures of $C_6(UTr)_2$ with PEB-UTr **4a** 1:1 w/w (b) and mixtures of $C_6(UTr)_2$ with PEB-$(UTr)_2$ **4b** 1:1 w/w (c).*

In blends of $C_6(UTr)_2$ with polymer **4a** or **4b**, the transition from the first mesophase to the second mesophase observed in pure $C_6(UTr)_2$ at 148 °C is absent, while the clearing point shifts from 178 °C to 186 °C and 188 °C for **4a** and **4b**, respectively.

Atomic Force Microscopy (AFM)

Samples for AFM studies were prepared by dissolving $C_6(UTr)_2$ with **4a** or **4b** in hexane using sonication at 60 °C, followed by spin-coating and drop casting on glass plates. With tapping mode no contrast was observed for pure $C_6(UTr)_2$, **4a** or **4b**.

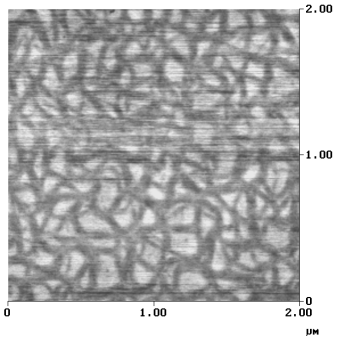


Figure 6.8: *AFM phase images of a 1/1 (g/g) blend of **4a** and $C_6(UTr)_2$. The sample was prepared by spin coating on silica glass plates from a 1 mg/ml hexane solution. Dark domains represent the hard segments, whereas the light domains correspond to the soft segments.*

However, as shown in Figure 6.8, Figure 6.9 and Figure 6.10, in which the phase contrast mode is depicted, hard regions could be distinguished from the soft ones when $C_6(UTr)_2$ is

mixed with either **4a** or **4b**.A 1/1 g/g $C_6(UTr)_2$-**4a** blend spin coated from hexane gave fibre like aggregates with a thickness between 9.5 and 47 nm.* The ratio between hard segments and soft segments in the AFM phase image is in agreement with the relative quantity of the two polymers. The morphology is highly dependent on the sample preparation. Whereas spin-coated samples gave fibre like structures with an average thickness of 42 nm, drop cast samples resulted in a fur like morphology (Figure 6.9A). These aggregates feature sizes between 17 and 42 nm. However, upon annealing the drop cast sample for 1 hour at 60 °C, larger clusters of up to 90 nm of the hard segments are formed (see Figure 6.9D) surrounded by a matrix consisting of soft and hard segments suggesting that macrophase separation occurs.

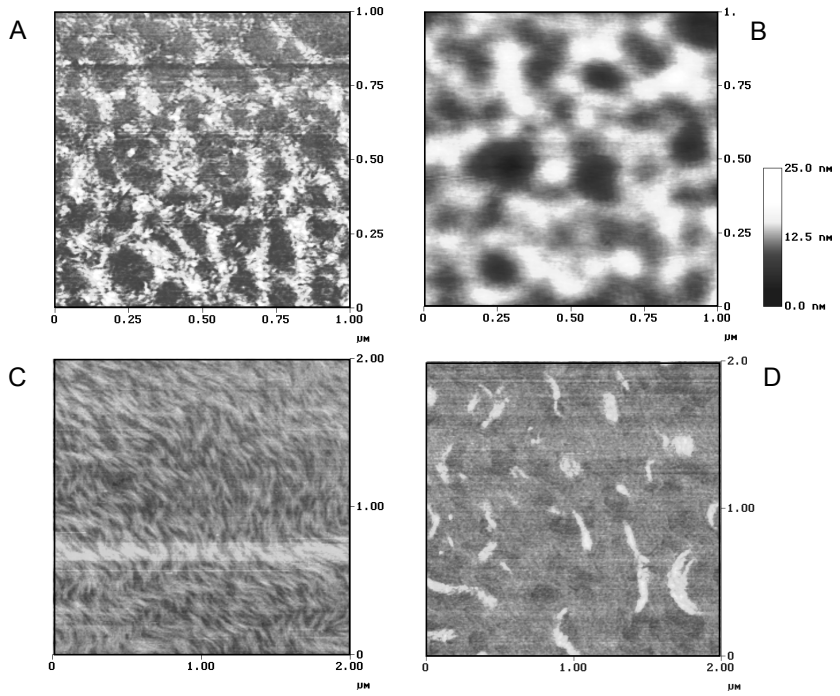


Figure 6.9: *AFM phase image and height image of a 1/1 g/g blend of **4b** and $C_6(UTr)_2$: A) phase image and B) height image of a spin coated sample, C) phase image of a spin cast sample, D) the same sample annealed at 60 °C for 1 hour.*

The morphology of these supramolecular block copolymers does not change when the amount of hard blocks is increased. The same fibre like aggregates are formed, and the volume fraction of the hard segment is increased when more $C_6(UTr)_2$ is added (see Figure

* The estimated size of the aggregates are calculated by the following equation: $r_p = y^2/4r_{tip}$.

6.10). As the amount of soft block is increased smaller and less fibres are observed. In the case of a 1/1.9 g/g $C_6(UTr)_2$-**4b** helical-like structures can be observed (Figure 6.10B).

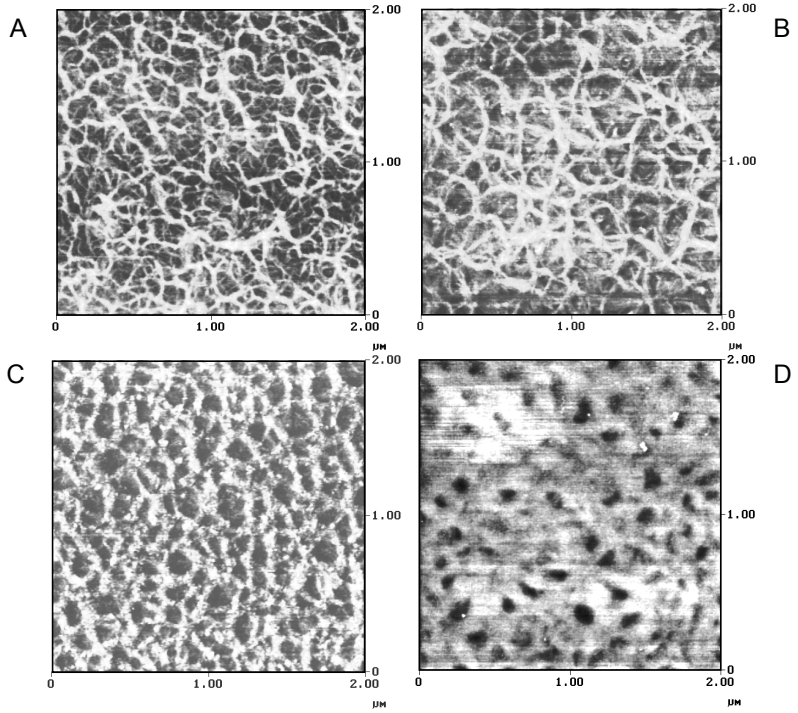


Figure 6.10: *AFM phase images of different blends of **4b** and $C_6(UTr)_2$ spin coated from hexane: A) 1 g $C_6(UTr)_2$/3.2 g **4b** blend, B) 1 g $C_6(UTr)_2$/1.9 g **4b** blend, C) 1 g C6$(UTr)_2$/1 g **4b** blend, D) 3.7 g $C_6(UTr)_2$/1 g **4b** blend. All samples were prepared by either drop casting or spin coating on silica glass plates from a 1 mg/mL hexane solution.*

6.5 Conclusions

Polystyrene and poly(ethylene/butylene) (PEB) were functionalised with one or two trialkoxyphenylureido-*s*-triazine units in order to prevent macrophase separation kinetically during the assembly of block copolymers. Polystyrene functionalised with one tridodecyloxyphenylureido-*s*-triazine unit dimerises in chloroform via an array of four hydrogen bonds. In blends with $C_6(UTr)_2$ macrophase separation predominantly occurs and no experimental evidence for triblock copolymers can be observed. PEB is a more suitable random coil polymer for the assembly of a block copolymer. In chloroform solutions polymers **4a** and **4b** also associate via quadruple hydrogen bonds. In dodecane higher scattering intensities were observed with SANS than in chloroform, suggesting that in the former solvent columnar structures are formed surrounded by the PEB block. These columnar structures can be formed by π-stacking of the phenyl-*s*-triazine moiety. They are, however,

not stacked in a helical way, as evidenced by an absence of a Cotton effect. When $C_6(UTr)_2$ is mixed with **4a** or **4b** a block copolymer rather than a polymer blend is obtained. The viscosity of dodecane solutions of achiral $C_6(UTr)_2$ is strongly influenced by the addition of monofunctional polymers **4a**. The cooperative character of the system is expressed by an amplification of chirality when chiral chain stopper **4a** is added to a dodecane solution of achiral $C_6(UTr)_2$. The transfer of chirality from polymer **4a** to the supramolecular polymer $C_6(UTr)_2$ demonstrates the formation of a block copolymer. Fibre-like structures are formed from samples obtained by spin-coating from hexane solutions of $C_6(UTr)_2$/polymer **4** blends. The morphology, however, does not change when the composition of the blend is varied. Instead, the amount of fibres increases and segregation of the strands occurs when the amount of $C_6(UTr)_2$ is increased. Even more complex supramolecular structures can be assembled when a polymer, grafted with ureido-*s*-triazine groups, is mixed with $C_6(UTr)_2$. In this way a bottle brush-like block copolymer may be obtained.

6.6 Experimental Section

General Methods.

General methods concerning purification of solvents, spectroscopic techniques and mass spectroscopic techniques can be found in chapters 2, 3 and 4. Polystyrene was obtained from van Hest and co-workers.[12] Copolymers of poly(ethylene/butylene) with hydroxy end-groups were obtained by Shell.

Preparation of the blends

All blends were prepared by sonication of both components in hexane at 60 °C.

Rheology. Dynamic oscillatory shear and steady state shear measurements were performed on a Rheometrics RFSII with a plate-plate geometry (50 mm). Plate-plate distances were taken between 0.3 mm and 0.25 mm. Blends were prepared from stock solutions, and were heated till near boiling point. All samples were measured a couple of days after being heated and were filtered before measurements.

AFM

AFM images were obtained from a Nanoscope IIIa, v4.43r8 from Digital Instruments Santa Barbara CA. Tips were used from RTESP. For AFM measurements samples were obtained by either drop casting or spin coating from a 1 mg/ml hexane solution on glass plates.

PS-ethoxyisocyanate (PS-NCO) and PS-(4-amino-2-[N'-(3-oxypropyl)]ureido-6-(3,4,5-tri(dodecyloxy)phenyl)-*s*-triazine) (PS-UTr) (1). PS-NH_2 (1 g, 0.31 mmol, M_n = 3260 g/mol) was weighed and dissolved in a solution of phosgene (4.2 mmol) in toluene. After stirring at reflux temperature for 5 h, the reaction mixture was allowed to cool down to room temperature after which the solvent was removed under reduced pressure. The crude product was co-evaporated three times with pentane (10 mL) in order to remove traces of phosgene. The isocyanate stretching vibrational band was observed at 2263 cm^{-1}. This PS-NCO was used without any further purification for the acylation with diamino-*s*-triazine: in a dry *Schlenk* type reaction flask was dissolved 2,4-diamino-6-tridodecyloxyphenyl-*s*-triazine was in pyridine (5 mL). The solution was stirred at reflux temperature and part of the pyridine was removed under a flow of argon till a volume of approximately 2 mL was reached. Then, the solution was allowed to cool down to room temperature and PS-NCO was added. The reaction mixture was stirred overnight at reflux temperature. Pyridine was then removed and co-evaporation with toluene (3 × 20 mL) gave of the crude product (1.4 g). Precipitation from chloroform in ethanol resulted in a white product, and column chromatography (silica gel, eluent: 2% ethyl acetate in dichloromethane) afforded the pure title polymer (m = 0.95 g, 94 %). T(melting dodecyl side chains) = -10 °C, T_g = 65 °C (Δc_p = 0.26 J/g.°C). IR (UATR) ν = 1694 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 10.21 (br, 1H, NH), 9.71 (br, 1H, NH), 9.05 (br, 1H, NH_2), 7.42 (s, 2H, Ar-H), 7.2-6.3 (m, Ar-H from PS), 5.4 (br, 1H, NH_2), 4.0 (m, 6H, Ar-O-CH_2), 3.2 (br, 2H, N-CH_2), 1.8-0.8 (m, CH_2, CH_3).

1,ω-Poly(ethylene/butylene)-3-oxypropylnitrile (PEB-CN) (2a). In a 250 mL 2-neck round-bottom flask, equipped with a condenser and a thermometer, PEB-OH (10 g, M_n = 3800 g/mol, M_w/M_n = 1.02) was dissolved in 60 mL toluene. A 25 wt% NaOH solution (1.5 g, 9.3 mmol) and methyltrioctylammonium chloride (TOMA) (0.94g, 2.33 mmol) were added while stirring. The two-phase system was stirred vigorously at reflux temperature for 1 h, then cooled down to room temperature. After adding acrylonitrile (3.09g, 58 mmol) dropwise, the reaction mixture was stirred overnight a room temperature. The solvents were then removed without heating, and the desired product was obtained pure with column chromatography (eluent: 100% CH_2Cl_2). Yield: 11g (100%). IR (NaCl) ν = 2251, 1461, 1118 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 3.64 (t, 2H, $\underline{H}C{=}CH_2$), 5.01 (m, 2H, $C\underline{H_2}{=}CH$), 4.20 (q, 2H, OCH_2), 3.45 (s, 2H, CH_2), 2.66 (t, 2H, CH_2), 2.34 (m, 2H, CH_2), 1.30 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 118, 71.8, 70.2, 65.6, 39.0-11.0.

1,ω-Poly(ethylene/butylene)-bis(3-oxypropylnitrile) (PEB-$(CN)_2$) (2b). The same procedure as used for monofunctionalised **1a** was used to yield the title polymer **1b**. Yield: 87 %. IR (NaCl) ν = 2254, 1462, 1119 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 3.65 (t, 4H, $NCCH_2CH_2O$), 3.52 (t, 2H, PEB-CH_2O), 3.16 (s, 2H, PEB-$C(CH_3)_2CH_2O$), 2.60 (t, 4H, $NCCH_2$), 1.3-1.1 (m, CH_2), 0.8 (m, CH_3). ^{13}C NMR ($CDCl_3$): δ 118 80.7, 80.6, 71.8, 70.1, 66.2, 65.5, 39.4-10.6.

1,ω-Poly(ethylene/butylene)-3-oxypropylamine (PEB-NH_2) (3a). Under nitrogen, a 250 mL 2-neck round-bottom flask, dried and equipped with a condenser, was charged with a solution of PEB-CN (3 g) in 40 mL THF. Borane-tetrahydrofurane (BH_3.THF, 10 mL of a 1 M solution in THF, 10 mmol) was diluted with 60 mL THF and added slowly. This reaction mixture was stirred at reflux temperature for 7 h. After cooling to

room temperature MeOH (20 mL) was added dropwise while stirring in an ice bath. After stirring for 45 min at room temperature, concentrated HCl (2 mL) was slowly added and the system was allowed to stir overnight at room temperature. After the removal of the solvents, the remaining residue was co-evaporated three times with MeOH (3 × 30 mL). The opaque oil was then dissolved in diethyl ether, washed with 1 M NaOH (50 mL) and dried with Na_2SO_4. Elution with 100% CH_2Cl_2 then 5% MeOH/1% triethylamine/CH_2Cl_2 gave a transparent oil. Extraction with 1 M HCl then 1 M NaOH yielded pure **3a** (2.1 g, 70 %). IR(NaCl) ν = 1463, 1114 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 3.47 (t, 2H, O$CH_2$$CH_2CH_2NH_2$), 3.42 (t, 2H, PEB-$CH_2$O), 2.8 (t, 2H, CH_2NH_2), 1.7 (quint, 2H, $CH_2CH_2CH_2NH_2$), 1.3-1.1 (m, CH_2), 0.8 (m, CH_3). ^{13}C NMR ($CDCl_3$): δ 69.6, 69.5, 69.1, 39, 38.5, 38, 36, 33.6, 33.5, 30.7, 30, 29.5, 27-26, 11.0, 10.5.

1,ω-Poly(ethylene/butylene)-bis(3-oxypropylamine) (PEB-$(NH_2)_2$) (3b). The title compound was synthesised in the same way as monofunctional PEB-NH_2 **3a**. Yield = 75 %. IR (NaCl) ν = 3378, 1463, 1116 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 3.47 (m, 4H, O$CH_2$$CH_2CH_2NH_2$), 3.4 (m, 2H, PEB-$CH_2$O), 3.1 (s, 2H, PEB-$C(CH_3)_2CH_2$O), 2.8 (t, 4H, CH_2NH_2), 1.7 (m, 4H, $CH_2CH_2CH_2NH_2$), 1.3-1.1 (m, CH_2), 0.8 (m, CH_3). ^{13}C NMR ($CDCl_3$): δ 80.7, 80.6, 70.0, 69.5, 39.1, 38.6, 38.1, 36.4, 33.7, 33.5, 30.9, 30.4, 30.0, 27.0-26.1, 11.1-10.8.

1,ω-Poly(ethylene/butylene)-(4-amino-2-[N'-(3-oxypropyl)]ureido-6-(3,4,5-tri((*S*)-3,7-dimethyl-octyloxy)phenyl)-*s*-triazine) (PEB-UTr) (4a). A solution of PEB-NH_2 (0.5 g) in a 8 mL $COCl_2$ toluene solution (10 %) was stirred at reflux temperature for 2 h. The excess of phosgene was removed under vacuum and co-evaporated with pentane (3 × 10 mL). IR (ATR): ν = 2262 cm^{-1}. PEB-NCO was used as such for the acylation of diaminotriazine: To a solution of PEB-NCO in pyridine (1 mL) was added a solution of diaminotriazine in pyridine (1 mL). The reaction mixture was stirred at reflux temperature for 12 h. The solvent was removed and co-evaporation with toluene (3 times 2 mL) gave a gummy residue. This residue was purified by means of column chromatography (silica) first using chloroform (of technical quality) then 10% EtOAc/pentane as the eluents, followed by preparative size exclusion chromatography (Bio-Beads, THF with stabilizer), yielding the desired monofunctionalised polymer (0.4 g, 68 %). IR (UATR) ν = 3217, 1686, 1646, 1578, 1520 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 10.22 (br, 1H, NH), 9.85 (br, 1H, NH), 9.25 (br, 1H, NH_2), 7.5 (s, 2H, Ar-H), 5.5 (br, 1H, NH_2), 4.08 (m, 6H, Ar-O-CH_2), 3.5 (t, 4H, PEB-CH_2-O-CH_2), 3.4 (t, 2H, PEB-N-CH_2), 1.8-0.8 (m, CH_2, CH_3). ^{13}C NMR ($CDCl_3$): δ 164.02, 153.36, 142.36, 130.52, 107.13, 72.00, 69.91, 69.52, 68.60, 67.70, 39.50, 38.63, 38.13, 37.66, 36.60, 36.35, 33.72, 33.66, 30.87, 30.42, 29.97, 27.0, 26.80, 27.0, 26.37, 26.28, 26.12, 22.94, 19.80, 11.10, 10.9. MALDI-TOF-MS (matrix: α-cyano-4-hydroxycinnamic acid): distribution between 5800 and 2950 $g.mol^{-1}$, PD = 1.13.

1,ω-Poly(ethylene/butylene)-bis(4-amino-2-[N'-(3-oxypropyl)]ureido-6-(3,4,5-tri((*S*)-3,7-dimethyl-octyloxy)phenyl)-*s*-triazine) (PEB-$(UTr)_2$) (4b). The diisocyanate of PEB was obtained by dissolving PEB-$(NH_2)_2$, **3b**, (1 g) in dry dichloromethane (20 mL). Di-*t*-butyltricarbonate (0.3 g, 1.14 mmol) was added and the reaction mixture was stirred for 1 h at room temperature. The solvent was removed under reduced pressure to afford the diisocyanate (PEB-$(NCO)_2$). This diisocyanate was used as such without any further purification. A solution of diamino-*s*-triazine and PEB-$(NCO)_2$ in dry pyridine (10 mL) was stirred for 24 h at

reflux temperature. Pyridine was removed and the remaining crude product was flushed with toluene (3 times with 15 mL). The gummy residue was dissolved in dichloromethane (5 mL) and poured in ethyl acetate (50 mL). Then, the solvent was decanted from the oily product. Column chromatography (silica, $CHCl_3$) followed by preparative size exclusion chromatography (Bio-Beads, THF with stabilizer) gave the title bifunctional polymer (0.81 g, 60 %). IR (UATR) ν =3216, 1686, 1645, 1578, 1520 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 10.24 (br, 2H, NH), 9.87 (br, 2H, NH), 9.25 (br, 2H, NH_2), 7.5 (s, 4H, Ar-H), 5.4 (br, 2H, NH_2), 4.1 (m, 12H, Ar-O-CH_2), 3.5 (t, 8H, PEB-CH_2-O-CH_2), 3.4 (t, 4H, PEB-N-CH_2), 3.1 (s, 2H, PEB-C$(CH_3)_2$CH_2O), 1.8-0.8 (m, CH_2, CH_3). ^{13}C NMR ($CDCl_3$): δ 170.9, 167.5, 164.0, 156.1, 153.4, 142.4, 130.6, 107.1, 80.6, 72.0, 69.9, 69.3, 68.6, 67.7, 39.5-10.5.

1,ω-Poly(ethylene/butylene)-(4-N'-phenylamino-2-[N'-(3-oxypropyl)]ureido-6-(3,4,5-tri((*S*)-3,7-dimethyloctyloxy)phenyl)-s-triazine) (5). A solution of phenylaminotriazine (0.088 g, 0.12 mmol) in pyridine (1 mL) was added to a solution of PEB-NCO (0.25 g) in pyridine (1 mL). The homogeneous solution was stirred at reflux temperature for 12 h. Pyridine was removed and co-evaporation three times with toluene (2 mL) gave a brown and sticky product. This residue was purified by means of column chromatography (silica gel) first using chloroform (of technical quality) then 10 % EtOAc/pentane as the eluents, yielding the title monofunctionalised polymer (0.1 g, 33 %). IR (UATR) ν = 3220, 1731, 1696, 1636, 1563, 1461, 1114 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 11.25 (br, 1H, NH), 10.25 (br, 1H, NH), 9.84 (br, 1H, NH), 7.95 (br, 2H, phenyl-ortho), 7.62 (s, 2H, Ar-H), 7.38 (br, 2H, phenyl-meta), 7.14 (br, 1H, phenyl-para), 4.12 (m, 6H, Ar-O-CH_2), 3.5 (t, 4H, PEB-CH_2-O-CH_2), 3.4 (t, 2H, PEB-N-CH_2), 1.8-0.8 (m, CH_2, CH_3). ^{13}C NMR ($CDCl_3$): δ 172, 164, 163, 157, 153, 142, 139, 130, 129, 123, 122, 107, 72, 70, 69, 67, 39.0-10.0.

6.7 References and Notes

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Summary

Supramolecular polymers are defined as aggregates of low molecular weight compounds that are held together by non-covalent interactions. This new class of supramolecular polymers has the advantage of being reversible, making them, for instance, easily processable at elevated temperatures. The work described in this thesis deals with the combination of multiple hydrogen bonding and π-interactions for the assembly of supramolecular polymers that fold into a well-defined conformation. For these purposes ureidopyrimidinone (UPy) and ureido-*s*-triazine (UTr) units that dimerise via an array of four hydrogen bonds were used. The synthesis and the characterisation of the building blocks of supramolecular polymers are described, and the organisation of the assemblies in the bulk and their aggregation in solution is investigated.

Hexamethyltrisiloxane and telechelic poly(dimethylsiloxanes) were provided with two ureidopyrimidinone (UPy) functional groups, resulting in a strong modification of the properties. Spectroscopic techniques and rheology measurements showed that the ureidopyrimidinone groups in these compounds are associated via quadruple hydrogen bonds in a DDAA array, whereas the O-benzyl-protected analogues do not associate, and therefore, behave like low molecular weight compounds. The amorphous functionalised bifunctional compounds behave like high molecular weight entangled polymers, exhibiting a rubber plateau with a modulus of 10^5 Pa.

Highly ordered structures were obtained by combining the concept of linear supramolecular polymers formed by bifunctional molecules, with the columnar organisation of trialkyloxyphenylureido-*s*-triazine (UTr). Monofunctional Bu-UTr and bifunctional $C_6(UTr)_2$ exhibit thermotropic and lyotropic liquid crystalline behaviour. Optical polarisation microscopy showed focal conic textures typically observed for discotic hexagonal mesophases. With X-ray diffraction it was found that the mesophases of $C_6(UTr)_2$ have a pseudo-hexagonal structure with a columnar diameter of 35 Å. Extending the planar core with an additional phenyl group did not influence the stability of the liquid crystalline mesophases. In dodecane the compounds form columnar superstructures as shown with CD spectroscopy and SANS. The columns formed by $C_6(UTr)_2$ feature a high degree of

cooperativity, and a significant amplification of chirality was the result of adding chiral monofunctional compound Bu-UTr was added to a dodecane solution of achiral bifunctional $C_6(UTr)_2$. The introduction of an additional aromatic substituent enhanced π-stacking, as evidenced by the presence of a Cotton effect of monofunctional phenylamino-butyl-UTr.

Compounds based on the 2-ureido-4-pyrimidinone unit were expected to give more stable columns in apolar solutions due to the higher association constant of this unit. Liquid crystalline mono- and bifunctional compounds based on the pyrimidinone unit were synthesised, and all exhibit thermotropic liquid crystalline properties as evidenced by DSC and OPM. In chloroform, no Cotton effect was observed for any of the compounds. Dodecane solutions of $C_6(Upy)_2$, $C_5(Upy)_2$ and *m*-xylylene-$(Upy)_2$ feature a Cotton effect at the absorption band of the phenyl-pyrimidinone core, whereas $C_7(UTr)_2$ and $C_8(UTr)_2$ do not. The Cotton effect is lost upon increasing the temperature. (–)-Cystine was provided with two tridodecyloxyphenylpyrimidinone groups. The molecule is liquid crystalline and forms helical columns in dodecane. In chloroform no Cotton effect was observed.

In order to obtain supramolecular block copolymers monofunctional poly(ethylene/butylene) (PEB) and polystyrene (PS), and bifunctional poly(ethylene/butylene) were provided with the UTr unit and mixed with $C_6(UTr)_2$. Mixtures of PS-UTr (**1**) and $C_6(UTr)_2$ behave much more like a polymer blend than like a supramolecular block copolymer. An increase of the viscosity occurs upon functionalisation of monofunctional PEB and telechelic PEB. Telechelic PEB, bearing two UTr-groups is a transparent solid that exhibits viscoelastic properties. Triblock and multiblock copolymers are formed in solution and in the bulk when $C_6(UTr)_2$ is added to functionalised PEB. Monofunctional PEB-UTr acts as a chainstopper and the viscosity of dodecane solutions of $C_6(UTr)_2$ is decreased upon addition of PEB-UTr. Significant amplification of chirality is observed in these mixtures as shown with CD. Fibre-like structures were observed with AFM from samples obtained by spin-coating from hexane solutions of $C_6(UTr)_2$/PEB-UTr blends.

The results described above have demonstrated that non-covalent interactions have been used successfully for the assembly of supramolecular polymers, whose organisation and size can be easily controlled.

Samenvatting

Supramoleculaire polymeren kunnen gedefinieerd worden als aggregaten van laagmoleculaire componenten die samengehouden worden via niet-covalente interacties. Een belangrijk aspect van deze nieuwe klasse van polymeren is hun reversibele karakter waardoor ze bijvoorbeeld bij hoge temperaturen gemakkelijk te verwerken zijn. Het onderzoek dat in dit proefschrift beschreven wordt, handelt over het gebruik van de combinatie van meervoudige waterstofbruggen en π-interacties voor het verkrijgen van supramoleculaire polymeren, welke zich kunnen opvouwen tot goed georganiseerde superstructuren. De synthese en de karakterisatie van de supramoleculaire bouwstenen zijn beschreven in dit proefschrift. Tevens wordt de organisatie van deze aggregaten, zowel in de bulk als in oplossing, beschreven.

Een sterke verandering van de materiaaleigenschappen werd waargenomen na het functionaliseren van hexamethyltrisiloxane en telechelische poly(dimethylsiloxanen) met twee ureïdopyrimidinon (UPy) eenheden. Spectroscopische technieken en reologiemetingen hebben aangetoond dat de ureïdopyrimidinon groepen in deze verbindingen via viervoudige waterstofbruggen dimeriseren, terwijl de O-gebenzyleerde analogen niet associëren en zich bijgevolg gedragen als laagmoleculaire verbindingen. De amorfe supramoleculaire polymeren bezitten eigenschappen van hoogmoleculaire polymeren: een rubber-plateau met een modulus van 10^5 Pa werd gemeten.

Door het concept van lineaire supramoleculaire polymeren, opgebouwd uit bifunctionele moleculen, te combineren met de columnaire ordening van trialkyloxyphenylureïdo-*s*-triazine (UTr) werden hooggeordende secundaire structuren verkregen. Bu-UTr en $C_6(UTr)_2$ zijn zowel thermotroop als lyotroop vloeibaarkristallijn. Uit de gecombineerde resultaten van optische polarisatiemicroscopie en röntgen diffractie blijkt dat de mesofase van $C_6(UTr)_2$ bij kamertemperatuur van het columnaire pseudohexagonale type is. Eveneens is gebleken dat de vergroting van de aromatisch coplanaire kern geen invloed heeft op de stabiliteit van de vloeibaarkristallijne mesofasen. CD spectroscopie en SANS metingen hebben aangetoond dat Bu-UTr en $C_6(UTr)_2$, in dodecaan, columnaire structuren vormen. Een voorkeursdraairichting van deze columnaire structuren werd verkregen door chirale zijketens in de moleculen in te bouwen. De co-operativiteit in een

kolom komt goed tot uiting als chirale monofunctionele Bu-UTr bij kolommen, bestaande uit achirale bifunctionele $C_6(UTr)_2$, gevoegd wordt. Eveneens is beschreven dat de introductie van een extra phenylgroep een sterke invloed op de π-stacking heeft: in tegenstelling tot Bu-UTr, werd een CD effect in dodecaan waargenomen voor fenyl-amino-Bu-UTr.

De columnaire structuren kunnen eveneens stabieler gemaakt worden door UTr groepen te vervangen door 2-ureïdo-4-pyrimidinone (UPy) groepen, daar zij veel sterker associëren. Een aantal monofunctionele (Bu-UPy) en bifunctionele verbindingen ($C_n(UPy)_2$, met n = 5-8, en *m*-xylyleen-$(UPy)_2$) werden gesynthetiseerd en gekarakteriseerd. Alle gesynthetiseerde verbindingen zijn vloeibaarkristallijn. In dodecaan, werd een CD effect waargenomen voor $C_5(UPy)_2$, $C_6(UPy)_2$ en *m*-xylyleen-$(UPy)_2$, terwijl in chloroform dit CD effect afwezig was. Vergeleken met de helische structuren, bestaande uit de UTr analogen, vormen deze bifunctionele UPy derivaten minder stabiele kolommen. Voor verbinding $C_7(UPy)_2$ en $C_8(UPy)_2$ werd, noch in chloroform noch in dodecaan een CD effect waargenomen. Naast de inbouw van chirale zijstaarten, werd een bifunctionele verbinding gesynthetiseerd met een chirale (–)-cystine spacer. Dit molekuul is vloeibaarkristallijn en vormt helische superstructuren in dodecaan. In chlorofom werd geen CD effect waargenomen.

Om supramoleculaire blok copolymeren te verkrijgen, werden conventionele polymeren, poly(ethyleen/butyleen) (PEB) en polystyreen (PS) gefunctionaliseerd met UTr groepen, en vervolgens gemengd met $C_6(UTr)_2$. Mengsels van PS-UTr en $C_6(UTr)_2$ gedragen zich eerder als polymere blends dan als blok copolymeren. Een sterke toename van de viscositeit werd waargenomen na functionalisering van PEB met UTr groepen. PEB-$(UTr)_2$ is transparant en bezit visco-elastische eigenschappen. De viscositeit van een oplossing van $C_6(UTr)_2$ in dodecaan nam drastisch af na toevoeging van PEB-UTr. Eveneens werd een sterke toename van chiraliteit waargenomen na toevoeging van chiraal PEB-UTr aan achiraal $C_6(UTr)_2$. Met AFM werd aangetoond dat vezelachtige structuren gevormd worden uit $C_6(UTr)_2$/PEB-UTr blends.

De hier beschreven resultaten tonen aan dat niet-covalente interacties met succes gebruikt werden voor de constructie van supramoleculaire polymeren, en laten zien dat ordening en grootte goed gecontroleerd kunnen worden.

Curriculum Vitae

Ky Hirschberg werd geboren in 1971 te Rach Gia (Vietnam). In 1984 startte hij met het secundaire onderwijs op de “Europese School 1” te Brussel, waar hij in 1991 het Europese baccalaureaat behaalde. Aansluitend werd begonnen aan de studie Scheikundige Technologie aan de Technische Universiteit Eindhoven. Het propedeutisch examen werd in 1992 behaald en het afstudeerproject binnen de vakgroep Organische Chemie (prof.dr. E.W. Meijer) werd in 1997 afgerond. Van juli 1997 tot en met juni 2001 was hij als onderzoeker in opleiding in dienst van de Nederlandse Organisatie voor Wetenschappelijk Onderzoek. Onder leiding van prof.dr. E.W. Meijer en dr. R.P. Sijbesma in de capaciteitsgroep Macromoleculaire en Organische Chemie werkte hij aan zijn promotieonderzoek waarvan de belangrijkste resultaten in dit proefschrift beschreven staan.

Ky Hirschberg was born in Rach Gia (Vietnam) in 1971. In 1984, he started his secondary school at the European School 1 of Brussels where he obtained his European baccalaureate in 1991. In 1997 the author of this thesis graduated with a major in Organic Chemistry (prof.dr. E.W. Meijer). From July 1997 to June 2001 he was employed by the Dutch Foundation for Scientific Research. During this period he worked at the laboratory of Macromolecular and Organic Chemistry at the Eindhoven University of Technology under the supervision of prof.dr. E.W. Meijer en dr. R.P. Sijbesma, on the research described in this thesis.

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Ky

郝士伯爾紀