Functional materials based on multiple hydrogen bonding motifs

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Functional Materials
Based on Multiple Hydrogen Bonding Motifs

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de Rector Magnificus, prof.dr.ir. C.J. van Duijn, voor een commissie aangewezen door het College voor Promoties in het openbaar te verdedigen op dinsdag 18 oktober 2005 om 16.00 uur

door

Rudolf Adrian Koevoets

geboren te Rucphen
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Well-Defined Supramolecular Assemblies Using
Bisurea Based Hydrogen Bonding Arrays

Abstract

In this introductory chapter a short review is given on strongly associating bisurea hydrogen bonding arrays. Supramolecular aggregation of low-molecular weight bisurea compounds leads to well-defined supramolecular polymers or organogelators. A scanning tunnelling microscopy study of the multilevel order of these low molecular weight bisurea compounds on solid substrates is described. Finally thermoplastic elastomers with bisurea hard blocks are introduced.
1.1 Introduction

The field of supramolecular chemistry has been defined as ‘chemistry beyond the molecule’ and involves investigating new molecular systems in which the components are held together in a reversible manner by intermolecular forces. It started roughly 30 years ago with the pioneering work of Lehn, Cram and Pedersen, for which they were awarded the Nobel Price in chemistry in 1987. By now, it has grown into a broad field with a wide scope of potential applications.

Since in nature supramolecular chemistry is used at its best, inspiration in this field is often obtained from nature. Although synthetic supramolecular systems cannot meet the standards set by nature, the fundamental aspect of non-covalent interactions can be implemented into new materials to gain control over materials properties. On the other hand, the study of synthetic supramolecular systems can give us valuable information about complicated issues in nature. Great examples from nature whose unique properties are due to secondary interactions consist of DNA, collagen and spider silk. The unique architecture of DNA results from cooperative multiple hydrogen bonding between the bases as well as from hydrophobic interactions. Collagen is formed by the association of tropocollagen fibers that consist of three polypeptides coiled into a helical rod. The interactions responsible for the association of the three strands are cooperative hydrogen bonds. These structural characteristics account for the high tensile strength of collagen.

Whereas in molecular chemistry structures are built up by the covalent connection of small components, in supramolecular chemistry the structures are built up by the non-covalent self-assembly of small components. The main non-covalent binding interactions applied in supramolecular chemistry include coordinative bonding (metal-ligand), dipole-dipole interactions, \( \pi-\pi \) stacking and hydrogen bonding. In general, these forces are relatively weak, resulting in the reversible nature, and therefore multiple interactions have to be combined to form a strong association.

![Figure 1.1. Quadruple hydrogen bond arrays based on ureidotriazines and ureidopyrimidinone.](image)

Hydrogen bonds are the most widely used interactions applied in supramolecular chemistry, because of their strength and directionality. They are for instance much stronger than dipole-dipole interactions, but weaker than covalent bonds. The use of multiple hydrogen bonding is a valuable tool to increase the strength of the interaction. For instance, Gong and coworkers recently reported extremely stable dimers based on six hydrogen bonds with a
dimerization constant of $1.3 \times 10^9 \text{ M}^{-1}$. The use of multiple hydrogen bonding in an array can enhance the strength of the association and the directionality by arranging the hydrogen bonding sites in the proper way. In our group, Beijer and Sijbesma developed a new range of new, self-complementary hydrogen bonding units based on pyrimidine and triazine, featuring a linear array of four hydrogen bonding sites (Figure 1.1). Both molecules are stabilized by an intramolecular hydrogen bond that planarizes the molecule. The weaker binding strength of the quadruple hydrogen bonding ureidotriazines ($2 \times 10^4 \text{ M}^{-1}$) compared to the ureidopyrimidinone ($1.6 \times 10^7 \text{ M}^{-1}$) in chloroform, can be explained by the difference in repulsive and attractive secondary interactions, following Jorgenson’s model. Since the introduction of thermoplastic elastomers (TPE) containing uniform bisurea hard blocks by R. M. Versteegen, bisurea based hydrogen bonding arrays have been studied in more detail in our laboratory to obtain well-defined supramolecular assemblies (Scheme 1.1), including polycaprolactone based TPEs for biomedical applications and block copolymer micelles equipped with bisurea groups on the interface. The effect of the bisurea linkage between the amphiphilic blocks on the self-assembly of these molecules as well as the possibility to functionalise the obtained nanostructures with bisurea functionalized guest molecules was investigated.

![Scheme 1.1. Bisurea based TPEs 1 and 2 and block copolymer 3.](image)

The aim of this thesis comprises the use of multiple hydrogen bonds to obtain functional materials. In the first part of this thesis (Chapter 2 - 5), bisurea based hydrogen-bonding arrays will be used, whereas in the second part (Chapter 6 - 7) the ureidopyrimidinone unit will be used. Since an excellent overview of the ureidopyrimidinone quadruple hydrogen-bonding array has already been published, in this chapter a review is given on the strongly associating bisureas arrays.

### 1.2 Supramolecular polymers based on bisurea groups

Designing self-assembling supramolecular polymers, which can be defined as arrays of small molecules held together by non-covalent interactions, is a fast growing field and attracts considerable attention. Many publications have appeared in literature about supramolecular polymers that self assemble in solution. Most of these systems are based on A-A-type
monomers (like the ureidopyrimidinones and ureidotriazines\textsuperscript{11,12} or A-A and B-B-type monomers.\textsuperscript{13-15} Only a few examples of A - B type monomers have been published in literature.\textsuperscript{16,17} Recently, Li and coworkers and Sijbesma and coworkers have reported the strong complexation of the 6-[1H] tautomeric form of ureidopyrimidinones with 2,7-diamino-1,8 naphthyridines via a quadruple hydrogen bond between ADDA and DAAD arrays.\textsuperscript{18,19}

Urea groups are known to associate strongly via bifurcated hydrogen bonds (Figure 1.2). The two hydrogen atoms bound to a nitrogen atom are hydrogen bonded to the same C=O oxygen atom. Because of this strong association, the self-association of \(N,N\)-dialkyl and \(N,N\)-diarylureas A - B type monomers have been studied in bulk\textsuperscript{20-22} and in solution.\textsuperscript{23}

\[
\begin{align*}
\text{Figure 1.2. Bifurcated hydrogen bonds between urea groups.}
\end{align*}
\]

Jadzyn and coworkers reported the self-association of \(N,N\)-dimethylurea and \(N,N\)-diethylyurea in non-polar solvents. Because of their low solubility, a branched but not too bulky \(N,N\)-di(2-ethylhexyl)urea (Scheme 1.2) was prepared by Bouteiller and coworkers.\textsuperscript{24} This A - B type monomer appeared particularly interesting as a precursor in the field of supramolecular chemistry. It was shown by viscometry and FTIR that the self-assembly of this molecule leads to large supramolecular polymers in non-polar solvents. These interactions, however, where strongly reinforced by the cooperative association of two urea groups in the case of bisureas (EHUT, scheme 1.1) prepared from 2,4 toluene diisocyanate.

\[
\begin{align*}
\text{Scheme 1.2. } N,N\text{-di(2-ethylhexyl)urea and bisurea analogue 2-ethylhexyl-3-[3-(3-(2-ethylhexyl)ureido)-}
\text{4-methyl-phenyl]urea (EHUT).}
\end{align*}
\]

Bisurea based aggregates of EHUT were studied in more detail using capillary viscometry, FTIR, small-angle neutron scattering (SANS) and rheology.\textsuperscript{25} At relatively low concentrations in toluene, EHUT showed remarkable rheological properties. The formation of these visco-elastic solutions was found to be due to strong hydrogen bonding interactions organizing the bisurea molecules into long and rigid fibrillar species as evidenced with SANS. The cross-section of these fibrillar structures likely contains two or three molecules per axial repetition unit. Figure 1.3 shows a tentative bimolecular wire structure, compatible with the SANS data.
The self-association of EHUT and some related compounds having some small structural variations was shown to display cooperativity at two levels. The first level of cooperativity is due to synergistic association of the two urea functions of a single molecule. The second level of cooperativity was revealed from the fact that the formation of dimers was less favored than the formation of long oligomers.\(^{26}\) In chloroform, in which the association is moderate, the association constants were determined with FTIR, and more recently with isothermal titration calorimetry.\(^{27}\)

Polymers based on EHUT are dynamic materials. As a consequence, the chain length of the supramolecular polymer increases continuously as the concentration of monomers is increased (Figure 1.4 a). In other words, their molar mass is concentration dependent. Bouteiller and coworkers recently showed that upon addition of a chainstopper with a high association constant, the concentration dependence of the molar mass of supramolecular EHUT polymers could be blocked over a realistic concentration range: the chain length only increased as function of the overall concentration up to a certain concentration \(C_t\), where the vast majority of the chains is terminated by a chainstopper (Figure 1.4 b)\(^{28}\).
1.3 Bisurea based gelators

Gelation of organic compounds by low-molecular weight compounds has received considerable attention. Most of the gelating molecules have in common that they possess at least one moiety that can participate in highly directional non-covalent interaction with other gelator molecules. Aggregation of these molecules leads to extended one-dimensional arrays of hydrogen bonds. Strands of gelator molecules subsequently assemble into fiber like structures, which in turn form extended three-dimensional networks in the solvent, thereby preventing the liquid from flowing (Figure 1.5). The self-assembly process is completely reversible, and highly efficient, as most organogelators already form gels well below 1 w%. Since the discovery of the aggregation of urea compounds in dilute solutions through intermolecular hydrogen bonding\(^2\), gelation properties of low molecular weight urea compounds, and more specifically bisurea compounds, have been studied extensively during the last 2 decades. Bisurea based gelling agents appeared to be highly efficient, combining easy accessibility with a wide solvent range.\(^\text{29-32}\) Especially 1,2-cyclohexyl\(^\text{29c,e,f,31a,b,g}\) or phenylene\(^\text{29c,30a}\) based bis-ureas with pendant aliphatic, aromatic or ester groups appeared to be very efficient organogelators for organic solvents, such as aliphatic and aromatic hydrocarbons, esters, ketones and alcohols, even at concentrations below 1 (w/v)\(^\%\). Thermal stabilization of these gels up to temperatures above the boiling point of the solvents was obtained by incorporation of methacrylate groups. Polymerization of these functionalities by photo irradiation leads to stabilization as indicated by changes in phase-transition temperature.\(^\text{29b,30d}\)

\[\text{Figure 1.5. Organic gelling agents self-assemble into one-dimensional fibers (right) and finally an entangled network (middle), which causes gelation of the liquid (left) (Image adapted from reference 33).}\]

In order to extend the gelation properties into water and aqueous media, Hamilton \textit{et al.}\(^\text{30c}\) and Van Esch \textit{et al.}\(^\text{29h}\) modified the character of their already proven self-aggregating bisurea based subunits by introducing either hydrophilic amino and hydroxy functionalities (4a and 4b, respectively, Scheme 1.3) or free carboxylic acids (5, Scheme 1.3). The carboxylate groups also imparted a pH and ionic strength dependence on the gelation process.
Hamilton and co-workers also succeeded in the gelation of CO₂.\textsuperscript{30a} For this purpose the character of their self-aggregating bisurea subunit was modified with groups that show affinity for CO₂ to increase the solubility, namely perfluoroalkanes (6, Scheme 1.3). This compound dissolves remarkably well in supercritical CO₂ at higher temperatures and pressure. Upon cooling however, the solution turns into an opaque gel. The most remarkable feature of this system is that except for the organogelators and CO₂ no other compounds or co-solvents are involved.

\begin{center}
\textbf{Scheme 1.3.} Low molecular weight gelling agents for water (4a, 4b and 5) and CO₂ (6).\textsuperscript{29h, 30a, 30c}
\end{center}

1.4 Multilevel order in supramolecular bisurea based assemblies on solid substrates.

Scanning tunneling microscopy (STM) has proven to be a powerful tool for studying physisorbed adlayers of organic molecules on flat conductive surfaces. One of the nice aspects of STM is its ability to distinguish certain functional groups from alkyl groups. The order in two-dimensional films of a broad class of bisurea derivatives (Scheme 1.4) was studied by De Feyter and Van Esch.

\begin{center}
\textbf{Scheme 1.4.} Chemical structures of the bis- and terthiophene derivative (T2 and T3) and the other bisurea containing (CX-Y) derivatives used by Van Esch and coworkers.\textsuperscript{35}
\end{center}
These molecules self-assemble in solution into elongated fibers and form 1-D ribbons on solid substrates. Initial studies of physisorbed monolayers films of C9-12 and C12-12 (Scheme 1.4) in 1-octanol on graphite (HOPG) showed well-ordered two-dimensional monolayers, which could be imaged with sub-molecular resolution. The position and the orientation of the urea moieties could clearly be determined. It was shown that the conformation of the molecules was dependent on the number of carbon atoms in the alkyl spacer (for comparison, see Figure 4.3). Furthermore, the intermolecular distance between the lamellae could be determined (0.462 ± 0.010 nm). This value indicated that hydrogen bonding is involved in the stabilization of the lamellae or monolayers. 34

More recently, two-component self-assembly to 'pattern' organic monolayers at the nanometer scale at the liquid/solid interface was studied. The ability of the scanning probe microscope to investigate structural details in these adlayers was used to obtain insight into the two-component two-dimensional phase behavior. The components used are symmetric alkylated bisurea derivatives (Scheme 1.4). The bithiophene unit acts as a marker and its bisurea derivative (T2) is a component in all the mixtures investigated. By varying the position of the hydrogen bond forming urea groups along the molecule and the length of the alkyl chains of the other components, the effect of 1) hydrogen bonding, 2) molecule length, 3) odd-even effects, 4) shape complementarity on the two-dimensional phase behavior was investigated (Figure 1.6). Insights into the effect of these parameters lead to control of the two-dimensional patterning: from randomly intermixed systems to phase separation. Phase separation appeared to be promoted by an increase in the difference in molecule length while randomly intermixing is optimal when the length of both components is identical (i.e. T2/C14-12 mixture). In addition, the presence and the location of the hydrogen bonding units in the molecules played an important role. Hydrogen bonding can counteract the effect of the difference in molecule length on the two-dimensional phase behavior. 35

Van Esch et. al. also studied the 2D supramolecular organization and electronic properties of two bis(urea)-substituted oligothiophenes (T2 and T3, Scheme 1.4) at the liquid solid interface with STM. T2 and T3 form closely packed arrays enforced by the hydrogen bonding between the urea groups, thereby creating an efficient pathway for charge transport. 36

On SiO$_2$ elongated fibers were observed with lengths up to 100 µm. These fibers are highly birefringent, indicating a high degree of molecular ordering. After annealing, extended mono-layers are formed consisting of upright 1D arrays standing side by side. 37 On HOPG the 1-D arrays tend to lie flat on the surface with tilted thiophene rings allowing partially overlapping π systems. 38 Scanning Tunneling Spectroscopy (STS) on stacks of T2 and T3 indicated that there exists an effective conjugation in the π-stacked ribbons on the surface. 39
Figure 1.6. STM images of the mixtures. Solid (dashed) lines reflect the length, measured perpendicular to the 'lamella' axis, of T2 (CX-12) molecules. A) T2/C6-12 mixture B) T2/C9-12 mixture C,D) T2/C14-12 mixture (Image adapted from reference 35).

Due to the bulky nature of oEDOT, no stable monolayers could be obtained from pure bisurea derivatives of oEDOT (Scheme 1.5), a model compound for poly(EDOT), which is one of the most successful materials among the numerous electrically conductive polymers that have been developed in the last 30 years. However, De Feijter et. al. showed that it is possible to obtain stable monolayers on graphite of this bulky compound by co-adsorption with a mono-urea compound (Scheme 1.5), resulting in unique co-deposition patterns.40

Scheme 1.5. Structure of bisurea derivative of oEDOT and a mono-ureum compound used as co-adsorbant.
1.5 Bisurea based thermoplastic elastomers

Thermoplastic elastomers (TPEs) are elastic materials that owe their properties to phase separation of hard and soft segments. Because of the excellent aggregating properties of bisureas via bifurcated hydrogen bonds, there are numerous examples of TPEs containing bisurea groups in the hard segments. Most of these TPEs however, have hard blocks consisting of urethane-ureas. TPEs possessing hard blocks comprising solely urea groups have only been reported occasionally. In the 80’s Yilgor and coworkers described siloxane-urea containing segmented copolymers, prepared from α,ω-bis(aminopropyl)poly(dimethylsiloxane) oligomers and various aromatic and cycloaliphatic diisocyanates such as MDI, TDI and H-MDI. The mechanical and thermal behavior of these copolymers was studied in detail. These copolymers possessed highly elastic properties. Riess et al. recently showed the gelation properties of such segmented siloxane-ureas in silicone fluids such as dimethylcyclosiloxanes. Bouteiller and coworkers reported the synthesis and mechanical properties of poly(dimethyl)siloxanes grafted with bisurea hydrogen bonding arrays. These “1-D cross-linked” thermoplastic elastomers are physically cross-linked at room temperature by aggregation of the strong but reversible bisurea hydrogen bonding arrays, but can be easily processed at higher temperatures. By adjusting the structure of the polymer (molecular weight, grafting density and nature of the bisurea) a wide control of the mechanical properties of these materials has been achieved.

Recently Yilgor et al. reported poly(ethylene oxide) based urea copolymers. Interactions between urea and ether functionalities lead to phase mixing and thus to relatively poor mechanical properties (especially compared to the siloxane-urea containing segmented copolymers).

Versteegen et al. recently reported the synthesis of segmented block-copolymers possessing uniform hard blocks based on urea groups (Scheme 1.1, 1). The soft blocks consist of poly(tetrahydrofuran) (pTHF). The synthesis as well as an overview of the thermal and mechanical properties are given in Chapter 2.

1.6 Aim and Outline of this thesis

In this thesis functional materials based on multiple hydrogen bonding motifs are described. In the first part of this thesis (Chapter 2 - 5), the strongly aggregating bisurea hydrogen-bonding unit is used to obtain well-defined thermoplastic elastomers (TPEs), whereas in the second part the self-complementary quadruple hydrogen bonding ureidopyrimidinone (UPy) unit is employed to obtain highly ordered supramolecular polymers (Chapter 6 – 7). These ordered structures are obtained by combining the concept of linear supramolecular polymers formed by bifunctional molecules, with the columnar organisation of tri(alkoxy)phenylureido-pyrimidinone.

In Chapter 2 of this thesis, an overview is given of the synthesis, mechanical and thermal properties of the thermoplastic elastomers containing bisurea groups. Attempts to
improve the mechanical properties of these TPEs are discussed and a new way of processing them via electrospinning is presented. In Chapter 3, the mechanical properties of these TPEs are combined with the optical properties of polydiacetylenes. A reactive diacetylene group was incorporated within the hard segment domain of the TPEs. It appeared possible to modify the optical and mechanical properties of these materials by the controlled solid-state cross-polymerization of the diacetylene group. The mechanochromic as well as thermochromic behavior are studied using infrared linear dichroism spectroscopy in combination with polarized UV spectroscopy. In Chapter 4, supramolecular and selective incorporation of various kinds of functional groups in thermoplastic host materials via the bisurea recognition unit is shown. By varying the length of the spacer between the urea groups of the guest, the selectivity of the incorporation of these guests in the TPEs is studied with polarized UV spectroscopy. Furthermore differences in extractability of the guests from the TPE host material due to differences in spacer length between the urea groups are investigated. In Chapter 5 the selective incorporation of guest molecules as demonstrated in Chapter 4 is used to supramolecularly anchor bisurea functionalized phosphine ligands to electrospun meshes of the TPEs via the bisurea recognition unit. These supramolecular complexes are used as mono- and bidentate ligand systems for rhodium catalyzed hydroformylation reactions of 1-octene in apolar solvents like cyclohexane and toluene. The activity, selectivity and recyclability of these systems are investigated and compared to unsupported systems.

Finally, in Chapter 6 the self-assembly of liquid crystalline mono- and bifunctional ureidopyrimidinone derivatives is studied. The effects of length and preorganisation of the spacer on the aggregation behavior is investigated. In Chapter 7 the thermotropic behavior of a monofunctional ureido-pyrimidinone is studied in detail using DSC, optical microscopy and X-ray diffraction. Temperature dependent IR and solid state NMR is used to establish the presence of both keto and enol tautomeric forms in columns of the phases observed with X-ray diffraction.
1.7 References and Notes

Well-Defined Supramolecular Assemblies using Bisurea based Hydrogen Bonding Arrays


General Properties of Segmented Block Copoly(ether urea)s

Abstract

The mechanical and thermal properties of segmented block copoly(ether urea)s 1 - 8 with poly(tetrahydrofuran) (pTHF) soft blocks of various lengths and uniform hard blocks consisting of two urea groups separated by a methylene spacer of various lengths are described. These materials are highly elastic and depending on the molecular weight of their soft block can be elongated up to 23 times their original length. The morphology was studied with Atomic Force Microscopy (AFM) and shows long stacks of hydrogen bonded urea groups embedded in a soft pTHF matrix. As a result of the co-continuous hard phase as observed with AFM, segmented block copoly(ether urea)s show large amounts of tensile set. Attempts were carried out to change the co-continuous hard phase to a disperse hard phase, by incorporation of association inhibitors into the hard domains of 8. This appeared unsuccessful in the bulk: no significant decrease in tensile set could be observed upon incorporation of 5 – 25 mol% of association inhibitors 9 – 11. In solution however, a decrease in viscosity could be observed upon addition of 9 – 11 to viscous solutions of 8 in chloroform. Finally a new way of processing segmented block copoly(ether urea)s is described. Electrospinning was employed on segmented block copoly(ether urea) 6, resulting in thin fibers with a diameter of approximately 4 µm, with a very narrow distribution in fiber diameter.
2.1 Introduction

Thermoplastic elastomers (TPEs) constitute a commercially relevant and fundamentally interesting class of polymeric materials. They combine the properties of irreversibly crosslinked elastomers, such as impact resistance and low-temperature flexibility, with the characteristics of thermoplastic materials, e.g. the ease of processing. In general, TPEs are phase-separated systems consisting of a hard phase, providing physical crosslinks, and a soft phase, contributing to the elastomeric properties. The hard phase is characterized by a high glass transition temperature (Tg) or a high melting point for semicrystalline systems, whereas the soft phase usually exhibits a low Tg. In many cases the phases are chemically linked by block or graft copolymerization. Because of the covalent linkage(s) between the chemically dissimilar segments, the rigid domains can form physical crosslink sites, resulting in a three-dimensional network. Consequently, TPEs exhibit mechanical properties that are, in many ways, comparable to those of a vulcanized (covalently crosslinked) rubber, with the exception that the network and hence the properties of the TPEs are thermally reversible. This feature makes TPEs ideally suited for high-throughput thermoplastic processes, such as melt extrusion and injection molding.

Mainly three classes of commercial TPEs can be distinguished: The first and largest group of TPEs consists of the ABA triblock copolymers like polystyrene-block-polybutadiene-block-polystyrene (PS-b-PB-b-PS) and polystyrene-block-polysoprene-block-polystyrene (PS-b-PI-b-PS). Because of the incompatibility between the hard and soft component microphase separation occurs, whereby the polystyrene minority phase forms dispersed spheres or cylinders in a rubbery matrix of the middle block. The second group consists of thermoplastic polyolefins blended with an elastomer, e.g. a blend of polypropylene and EPDM rubber and are officially called TPVs (thermoplastic vulcanisates). The third group concerns segmented copolymers. These multiblock copolymers comprise an alternating structure of hard and soft segments within the polymer chain. In the first part of this thesis (Chapter 2 - 5), focus will be on this class of TPEs.

Figure 2.1. Schematic representation of the morphology of a segmented block copolymer: (—) hard block, (~) soft block (Image adapted from reference 2).

Today it is well established that the specific properties of segmented copolymers are a result of their morphology (Figure 2.1). At room temperature, low melting soft segments are
incompatible with polar and high melting hard segments, which leads to microphase separation. In many cases part of the driving force for the phase separation is the development of crystallinity in the hard segments. On heating above the melting temperature of the hard segments, the polymer forms a homogenous viscous melt that can be processed by thermoplastic techniques such as injection molding, extrusion, blow molding, and so forth. Subsequent cooling leads again to segregation of hard and soft segments and recovery of the elastic properties.\textsuperscript{3}

Usually, the soft segments form an elastomeric matrix, giving rise to the elastic properties of the TPE. The hard segments on the other hand act as multifunctional tie points that function both as physical crosslinks and reinforcing fillers. These crosslinks can be removed by heat or solvation. On subsequent cooling or desolvation the TPE network is reformed.

The hard blocks in segmented copolymers are generally based on polyester\textsuperscript{4}, polyamide\textsuperscript{5} or polyurethanes\textsuperscript{6}. In multiblock copolymers with polyurethane, polyester, and polyamide hard segments, frequently short chain polyethers are used as a soft component. In some cases polyesters (poly(\(\varepsilon\)-caprolactone)) are incorporated. The polymers having polyester soft segments are tougher and show a higher resistance to oils, solvents, and thermal degradation. Analogue polymers with polyether soft segments exhibit better hydrolytic stability and an increased flexibility at low temperatures.

Among segmented copolymers, thermoplastic elastomeric polyurethanes (TPUs) are the most widely used. They are often prepared via a one-pot procedure, in which a long-chain diol (polyether or polyester) is first reacted with an excess of diisocyanate resulting in a isocyanate functionalized prepolymer, which then reacts with a chain extender, resulting in a high molecular weight polyurethane. One disadvantage of this procedure is that it leads to a statistical distribution in the hard segments length, resulting in an incomplete phase separation of these block copolymers. As a result, these TPUs feature a broad melting range and a rubbery plateau that is dependent on temperature. To improve the properties of these materials, TPUs featuring uniform hard blocks have been prepared in the past.\textsuperscript{7} It was shown that uniform hard blocks leads to polymers, that are less temperature dependent.

Ureas are known to associate via bifurcated hydrogen bonds and have therefore often been incorporated in the hard blocks of TPEs. There are, however, only a few examples known from literature of TPEs containing hard block comprising solely urea groups.\textsuperscript{8} Recently a new class of TPEs featuring urea groups has been developed in our laboratory. These segmented block copolymers possess a uniform hard block comprising solely urea groups, whereas the soft blocks consist of poly(tetrahydrofuran) (pTHF). In the remainder of this chapter, the synthesis and an overview of the thermal and mechanical properties of these TPEs are given. Attempts to improve the mechanical properties of these TPEs will be discussed, and a new way of processing them will be presented.
2.2 Synthesis of segmented block copoly(ether urea)s

Recently a new class of thermoplastic elastomers comprising solely urea groups has been prepared in our laboratory.\(^2\) The number of urea groups in the hard segment was varied from 1 to 4 using the di-\textit{t}-butyl tricarbonate reagent, in combination with a protective group strategy for the copoly(ether urea)s with 3 or 4 urea groups. Copoly(ether urea)s having exactly 1 urea in the hard blocks were obtained as viscous liquids without any materials properties. Copoly(ether urea)s having 3 or 4 urea groups in the hard segments resulted in insoluble gel-forming polymers, which were hard to process. Apparently, the association between the hard blocks in these TPEs was too strong. The polymers having exactly 2 urea groups in the hard block possessed an optimal balance between mechanical properties and processability, as they are highly elastic and very soluble. Because of this, these TPEs or analogues of them will be used in this thesis (Chapter 2 – 5).

For the preparation of copoly(ether urea)s having two ureas in the hard block, amine terminated pTHF is required. The prepolymer are obtained by end-group modification as schematically depicted in scheme 2.1.

![Scheme 2.1. Synthesis of amine-terminated prepolymer and copoly(ether urea)s having 2 ureas in the hard blocks.](image)

Prepolymers with nitrile functionalities were obtained by cyano-ethylation of hydroxy end-groups of pTHF. The reaction was catalyzed by 1 mol\% of sodium hydride. The nitrile functionalities were then hydrogenated with borane in THF. After removal of the boron-nitrogen complexes after several coevaporations with methanol and hydrochloric acid, the prepolymer were obtained as white powder. In this way, prepolymer with a molecular weight of 1100, 2000 and 4000 g/mol were prepared. Subsequently, the copoly(ether urea)s were prepared by chain extension of the amine-terminated prepolymer, with the appropriate diisocyanate (either commercially available, or prepared via either the di-\textit{t}-butyl tricarbonate reagent for diamines or the azide and Curtius rearrangement method for diacids). The chain extender was added dropwise to a solution of the prepolymer in CHCl\(_3\), to ensure the exact 1 to 1 ratio of both functional groups in the equivalence point of the reaction, thus obtaining a maximum degree of
polymerization. The extent of the reaction was determined by following the disappearance of the isocyanate band with infrared spectroscopy. For detailed synthetic procedures, see reference 9.

According to the procedure described above, copoly(ether urea)s with various molecular weights and with different numbers of methylene groups between the urea groups were prepared (Table 2.1). The molecular weights of all segmented copolymers were determined with SEC and are depicted in Table 2.1.

### Table 2.1. Copoly(ether urea)s 1-8.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Soft Block</th>
<th>Hard Block</th>
<th>Yield (%)</th>
<th>$M_n$ ($10^3$ g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pTHF$_{350}$U$_4$U</td>
<td>pTHF$_{350}$</td>
<td>88</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>pTHF$_{1100}$U$_4$U</td>
<td>pTHF$_{1100}$</td>
<td>idem</td>
<td>91</td>
</tr>
<tr>
<td>3</td>
<td>pTHF$_{2300}$U$_4$U</td>
<td>pTHF$_{2300}$</td>
<td>idem</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td>pTHF$_{4000}$U$_4$U</td>
<td>pTHF$_{4000}$</td>
<td>idem</td>
<td>90</td>
</tr>
<tr>
<td>5</td>
<td>pTHF$_{1100,md}$U$_4$U$_10^{10}$</td>
<td>Monodisperse pTHF$_{1100}$</td>
<td>idem</td>
<td>96</td>
</tr>
<tr>
<td>6</td>
<td>pTHF$_{1100}$U$_6$U</td>
<td>pTHF$_{1100}$</td>
<td>84</td>
<td>50</td>
</tr>
<tr>
<td>7</td>
<td>pTHF$_{1100}$U$_7$U</td>
<td>pTHF$_{1100}$</td>
<td>91</td>
<td>48</td>
</tr>
<tr>
<td>8</td>
<td>pTHF$_{1100}$U$_7$U</td>
<td>pTHF$_{1100}$</td>
<td>87</td>
<td>52</td>
</tr>
</tbody>
</table>

### 2.3 Thermal properties of segmented block copoly(ether urea)s

The thermal properties of copoly(ether urea)s 1-8 were determined by optical microscopy as well as with Differential Scanning Calorimetry (DSC). Optical microscopy was used to determine the flow temperature, being the temperature at which the material loses its dimensional stability, of the different block copoly(ether urea)s. DSC on the other hand was used to obtain more quantitative data on the thermal transitions of the block copoly(ether urea)s. The results from both techniques are summarized in Table 2.2.

The flow temperature of the block copoly(ether urea)s decreases with increasing soft block length. This is a well-known trend for segmented copolymers and can be explained by the solvent effect as proposed by Flory. The size of the crystals will become smaller upon diluting the crystallizable hard segment. This effect causes the flow temperature to decrease.
Also the influence of the number of methylene groups in the hard domains on the flow temperature was investigated while leaving the soft block length the same. The copoly(ether urea)s with an even number of methylenes have a higher flow temperature compared to the copoly(ether urea)s with an odd number of methylenes. This trend is often observed in homologous series of \([n]\) nylons\(^\text{12}\) and \([n]\)-polyurethanes.\(^\text{13}\)

Table 2.2. Thermal transitions of block copoly(ether urea)s 1-8 as determined with optical microscopy and DSC. Subscript \(s\) denotes the soft block, \(h\) denotes the hard block.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>(T_g) (°C)</th>
<th>(T_{m,s}) (°C)</th>
<th>(\Delta H_{m,s}) (J/g)</th>
<th>(T_{c,s}) (°C)</th>
<th>(T_{m,h}) (°C)</th>
<th>(\Delta H_{m,h}) (J/g)</th>
<th>(T_{flow}) (°C)</th>
<th>(T_{c,h}) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 pTHF(_{350})U(_4)U</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>158</td>
<td>20.0</td>
<td>-</td>
<td>145</td>
</tr>
<tr>
<td>2 pTHF(_{1100})U(_4)U</td>
<td>-68</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>131</td>
<td>14.2</td>
<td>140</td>
<td>102</td>
</tr>
<tr>
<td>3 pTHF(_{2300})U(_4)U</td>
<td>-74</td>
<td>1</td>
<td>20.3</td>
<td>-27</td>
<td>118</td>
<td>3.9</td>
<td>125</td>
<td>101</td>
</tr>
<tr>
<td>4 pTHF(_{4000})U(_4)U(^a)</td>
<td>-73</td>
<td>1</td>
<td>34.9</td>
<td>-37</td>
<td>78</td>
<td>3.6</td>
<td>100</td>
<td>48</td>
</tr>
<tr>
<td>5 pTHF(_{1100,\text{md}})U(_4)U</td>
<td>-74</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>122</td>
<td>14.4</td>
<td>125</td>
<td>94</td>
</tr>
<tr>
<td>6 pTHF(_{1100})U(_5)U</td>
<td>-74</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>106</td>
<td>11.3</td>
<td>105</td>
<td>104</td>
</tr>
<tr>
<td>7 pTHF(_{1100})U(_6)U</td>
<td>-70</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>125</td>
<td>10.5</td>
<td>126</td>
<td>101</td>
</tr>
<tr>
<td>8 pTHF(_{1100})U(_7)U</td>
<td>-69</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>103</td>
<td>10.6</td>
<td>105</td>
<td>100</td>
</tr>
</tbody>
</table>

\(^a\) Random copolymer of tetrahydrofuran and ethylene oxide (9/1).

In the DSC traces of the block copoly(ether urea)s having a polydisperse pTHF soft block of 1100 g/mol (2 and 6-8) no melting- or crystallization peak for the soft block is observed as the molecular weight is too low to crystallize. The amorphous soft phase shows a glass transition temperature around -70 °C. This value is close to the glass transition temperature of pure pTHF. This is a good indication of the absence of phase mixing between hard and soft segments. Furthermore broad melting endotherms are observed, with maxima close to the observed flow temperatures.

For polymer 5 having a monodisperse soft block with a molecular weight of 954 g/mol a melting endotherm was observed at 122 °C. This value is close to the flow temperature as observed with optical microscopy. The melting and crystallization temperature of 5 are slightly lower than for polydisperse analogue 2. The melting enthalpies on the other hand are similar, since both copolymers contain roughly the same amount of hard block.\(^2\)

Increasing the molecular weight of the soft block results in semi-crystallinity of the pTHF phase. In the DSC trace of compound 3 (pTHF\(_{2300}\)U\(_4\)U) a melting peak at 1 °C and a crystallization peak at -27 °C can be observed. Since further increasing the molecular weight of the soft block will result in an increase in crystallinity (pTHF\(_{2900}\)U\(_4\)U has a \(\Delta H_{m,s}\) of 38.3 J/g compared to 20.3 J/g for pTHF\(_{2300}\)U\(_4\)U) and melting temperature, a random copolymer of ethylene oxide and pTHF was incorporated in 4. This successfully reduces the crystallinity and melting point of the soft phase, resulting in a completely amorphous soft block at room temperature.
2.4 Mechanical properties of segmented block copoly(ether urea)s

TPEs generally offer excellent mechanical properties, for example, high tensile strength and elongation. Segmented block copoly(ether urea)s are no exception in this regard. The tensile and elastic properties of the block copoly(ether urea)s with different soft block lengths and with a different number of methylene groups between the ureas were studied. Clear transparent films were solution cast from chloroform/methanol mixtures. Tensile bars were punched from these films and examined by tensile testing. The results are depicted in Figure 2.2 and summarized in Table 2.3.

![Stress-strain curves of block copoly(ether urea)s](image)

Figure 2.2. Stress-strain curves of block copoly(ether urea)s 2-8.

The stress-strain curves of copoly(ether urea)s 2-8 all show all the characteristics of thermoplastic elastomeric materials. They all show Hookean behavior at small deformations, since a linear relationship between stress and strain is observed. Furthermore a trend in Young’s modulus can be observed. It increases with decreasing soft block length as a result of the increased hard block content of the overall material. Also the influence of the number of methylene groups in the hard domains on the Young’s modulus was investigated while leaving the soft block length the same. The copoly(ether urea)s with an even number of methylenes have a higher Young’s modulus compared to the copoly(ether urea)s with an odd number of methylenes (approximately 95 vs. 82 MPa, respectively).

Upon increasing the stress above the yield stress ($\sigma_y$) plastic deformation sets in. Unlike elastic deformation, plastic deformation is not recoverable, i.e. the change is permanent, due to deformation and reorganization of the hard segments. Finally, the TPEs cannot bear the load anymore resulting in failure of the material. The strain at break ($\lambda_{br}$) of these TPEs is remarkably high. This has been observed before for segmented copolyurethanes having a narrow hard block length distribution$^{7a,7c}$ and is the result of the easy deformation and reorganization of thin crystalline lamellae.

In the stress-strain curve of e.g. pTHF$_{2300}$U$_4$U (3) strain hardening can be observed. This is the result of strain-induced crystallization of the pTHF soft block as is evidenced by a
whitening of the material. For pTHF_{4000}U_4U (4) no strain hardening is observed, because the incorporation of ethylene oxide in the pTHF soft block prevents strain-induced crystallization.

Comparison of the mechanical properties of 2 with its monodisperse analogue 5 shows that the Young’s modulus of 5 is lower than that of 2. Furthermore moderate strain softening followed by pronounced strain hardening for 5 is observed, which toughens the material. It is a result of the monodispersity of the soft block of the material: all soft blocks are equally stretched as a function of elongation and the stress is equally distributed over the soft blocks. As the soft blocks are completely stretched a disproportionate amount of force is required to further elongate the material.

Table 2.3. Tensile properties of block copoly(ether urea)s 2-8.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Young’s modulus E (MPa)</th>
<th>Yield Stress $\sigma_y$ (MPa)</th>
<th>Strength $\sigma_{br}$ (MPa)</th>
<th>Strain at Break $\lambda_{br}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 pTHF_{1100}U_4U</td>
<td>95.7</td>
<td>9.8</td>
<td>28.3</td>
<td>1064</td>
</tr>
<tr>
<td>3 pTHF_{2300}U_4U</td>
<td>25.4</td>
<td>4.4</td>
<td>30.6</td>
<td>1409</td>
</tr>
<tr>
<td>4 pTHF_{4000}U_4U</td>
<td>11.2</td>
<td>2.5</td>
<td>12.1</td>
<td>2150</td>
</tr>
<tr>
<td>5 pTHF_{1100,md}U_4U</td>
<td>53.0</td>
<td>6.5</td>
<td>24.3</td>
<td>790</td>
</tr>
<tr>
<td>6 pTHF_{1100}U_6U</td>
<td>82.8</td>
<td>9.8</td>
<td>25.1</td>
<td>1068</td>
</tr>
<tr>
<td>7 pTHF_{1100}U_7U</td>
<td>92.9</td>
<td>9.4</td>
<td>27.2</td>
<td>1063</td>
</tr>
<tr>
<td>8 pTHF_{1100}U_7U</td>
<td>81.8</td>
<td>10.2</td>
<td>29.2</td>
<td>973</td>
</tr>
</tbody>
</table>

By varying the molecular weights of the pTHF soft block, segmented copoly(ether urea)s with a large variety of Young’s moduli are obtained (Table 2.3). When elastomers with a bimodal distribution of network chain lengths are prepared (by simply mixing segmented copolymers with different soft-block lengths) the young’s moduli can be fine-tuned even further. Bimodal elastomers, involving end linking mixtures of very short and relatively long functionally terminated chains, show very large increases in e.g. reduced stress or modulus, because of the very limited extendibility of the short chains present in the networks. The improvements in materials properties obtained from this method are of course the most striking when the ratio $M_s/M_L$ of molecular weights of the short and long chains are very small and when the short chains are as short as possible.14

As an example, bimodal networks of pTHF_{350}U_4U (1) and pTHF_{2300}U_4U (3) having different amounts of 1 (0, 34 and 66 mol%) were prepared. Whereas pure 1 is an extremely brittle material (it appeared impossible to obtain films of 1 which could be used for tensile testing), the bimodal material having 66 mol% of 1 does show relatively good material properties. Furthermore the Young’s modulus could be fine-tuned from 25.4 MPa for pure 3, to 41.7 MPa when 34 mol% of 1 was mixed in, to even 69.8 MPa when 66% of 1 was mixed in (Figure 2.3). Furthermore, strain-induced crystallization as observed for 3 is partly suppressed by adding 1. Not only can this be witnessed by the eye (the bimodal material doesn’t turn white
as much as pure 3), it can also be seen in the stress-strain curves of the bimodal material, that show less strain hardening as compared to pure 3.

![Stress strain curves for pure 3 and bimodal networks having 34 and 66 mol% of 1 in 3.](image)

**Figure 2.3.** Stress strain curves for pure 3 and bimodal networks having 34 and 66 mol% of 1 in 3.

### 2.5 Morphology of segmented block copoly(ether urea)s

The morphology of the segmented block copoly(ether urea)s having different soft block lengths was studied with Atomic Force Microscopy (AFM) in the tapping mode. Thin films were drop or spin cast on silicon wafers or glass substrates from chloroform/methanol mixtures (9/1). It should be noted that in order to dissolve pTHF$_{1100,md}$U$_4$U, which forms an insoluble gel during its preparation in chloroform, 3 w% of hexafluorisopropanol (HFIP) was added. Figure 2.4 shows AFM images of pTHF$_{1100}$U$_4$U, 2 (a), pTHF$_{2300}$U$_4$U, 3 (b), pTHF$_{4000}$U$_4$U, 4 (c) and pTHF$_{1100,md}$U$_4$U, 5 (d) in phase contrast. In all images, the hard phase appears lighter than the soft phase. In all AFM images long fibers can be observed which are embedded in the soft phase. The lengths of these fibers vary from approximately 100-200 nm for pTHF$_{4000}$U$_4$U, 4 and pTHF$_{1100,md}$U$_4$U, 5 to over 500 nm for pTHF$_{1100}$U$_4$U, 2 and pTHF$_{2300}$U$_4$U, 3. The width of the fibrils is approximately 8-10 nm and its determination is limited by the sharpness of the AFM-tip. The difference in fiber length is most probably the result of the way the samples were prepared. Whereas samples of 2 and 3 were prepared by drop casting, samples of 4 and 5 were prepared by spincasting, resulting in kinetic inclusion of the aggregates.

The observed morphologies are in agreement with the proposed mode of aggregation of the copoly(ether urea)s: long stacks of the hydrogen bonded urea groups embedded in the amorphous pTHF matrix as depicted in Figure 2.1.
2.6 Association inhibitors

2.6.1 Association inhibitors in bulk

One characteristic of thermoplastic elastomers is their ability to relax to their original dimensions after being deformed. However, complete elastic recovery is rarely observed. The same holds for copoly(ether urea)s. The presence of a co-continuous bisurea hard phase in our copoly(ether urea)s as observed with AFM causes a significant plastic deformation and hence minor elastic properties of these materials especially upon relatively large elongations. Orientation studies\textsuperscript{15} revealed that upon elongation, the soft segments orient parallel to the direction of the applied stress, whereas the chain axis of the crystalline bisurea hard segments orient transverse to the stress direction for small strain values. Upon higher elongations the chain axis of the crystalline bisurea segments orient parallel to the direction of stress, which is connected with an irreversible disruption of the co-continuous crystalline hard segment phase. This in turn results in the observed high plastic deformations especially at high strains. Finally,
after complete reorientation of the crystalline bisurea phase the stress is submitted through the continuous soft segment phase, until it breaks.

The extent of tensile set of the copoly(ether urea)s was determined by performing cyclic tensile tests. Specimens are prestrained to a certain amount of strain, subsequently unloaded and allowed to relax, followed by again prestraining it to a higher amount of strain. For copolymer 2 a tensile set of 34% after 100% prestrain is observed, compared to e.g. 2% for natural rubber.

![Figure 2.5.](image)

**Figure 2.5.** Schematic representation of a continuous (a) and dispersed (b) crystalline hard phase. (¶) = crystalline hard phase, ~ = pTHF soft phase.

The general idea is that the elasticity of copoly(ether urea)s, and more precisely its high tensile set, can be improved by changing the co-continuous bisurea hard phase to a dispersed phase (Figure 2.5). This can be achieved by intercalating association inhibitors into the hard domains of the elastomer. The association inhibitors act as ‘stoppers’ for the bis-urea stacks, since they can only bind to the bisurea hard domains once, and thus decrease the stack size of the hard domains (Figure 2.6).

![Figure 2.6.](image)

**Figure 2.6.** Schematic representation of the incorporation of an association inhibitor with an odd (a) and even (b) number of methylene groups between the urea groups into long crystalline stacks or the bisurea hard domains of the copoly(ether urea)s. Only association inhibitors with an odd number of methylene groups will result in a decrease of the stack size of the copoly(ether urea)s.
In order to be effective as an association inhibitor, it needs to have an odd number of methylene groups between the ureas, resulting in a cisoïd arrangement of the urea groups (see Figure 4.3). Therefore association inhibitors 9, 10 and 11 were synthesized, all having an odd heptylene spacer (Scheme 2.2). Association inhibitor 11 was synthesized because N-benzoyl-2-ethoxybenzamide is known to associate strongly to ureas as was previously demonstrated by G. B. W. L. Ligthart (Figure 2.7).

Scheme 2.2. Association inhibitors 9, 10 and 11.

Figure 2.7. Association between N-benzoyl-2-ethoxybenzamide and N-butyl-N’-(3-nitrophenyl)urea ($K_a = 220 \text{ M}^{-1}$).

Films containing copoly(ether urea) 8 with a soft-block of 1100 g/mol and 5 and 25 mol% of association inhibitor 9, 10 or 11 were solution cast from chloroform. All films, except films of 8 containing 25 mol% of 11, were clear and transparent. Films of 8, containing 25 mol% of 11, showed small crystallites of 11, which are evenly distributed through the film. To see whether the properties of elastomer 8 improved after incorporation of 9, 10 or 11, cyclic tensile tests were performed on these films. In these tests the samples are elongated to a certain amount of strain, followed by slowly releasing the strain to evaluate the residual elongation of the sample after being stretched. This procedure is repeated for different amounts of strain until the samples fail. The results are depicted in Figure 2.8 (only the results for 8 containing 25 mol% 9 are depicted).

Figure 2.8. Cyclic tensile tests of pTHF$_{1100}$U$_7$U (8) (a) and 25 mol% 9 in pTHF$_{1100}$U$_7$U (8) (b). Similar cyclic tensile tests were performed for 5 and 25 mol% 10 and 11 in pTHF$_{1100}$U$_7$U (8).
As shown in Figure 2.9, in which the prestrain is plotted versus the tensile set, incorporation of 5 or 25 mol% of association inhibitors 9-11 did not lead to improved materials properties. After incorporation of 25 mol% of association inhibitors 9-11 in 8, the tensile set after 100% prestrain was found to be 36.4, 36.6 and 36.2 % respectively, compared to 38.0 % for pure 8. After being subjected to higher prestrains (800%), the tensile set was found to be 491, 494 and 498% respectively vs. 525% for pure 8.

Figure 2.9. Tensile set of pTHF1100UU with 0, 5 and 25 mol% 9 (a), 0, 5 and 25 mol% 10 (b) and 0, 5 and 25 mol% 11 immediately after prestraining to the indicated strain levels.

Infrared Spectroscopy (IR) and differential scanning calorimetry (DSC) were used to study the incorporation of the association inhibitors in the hard domains of 8. In IR, the carbonyl peak of pure 9 and 10 can be found at 1684 cm\(^{-1}\). After incorporation in 8, this peak is expected to shift to lower wave numbers, because of the hydrogen bonds formed. However, the carbonyl peak of 9 and 10 is still present at 1684 cm\(^{-1}\) (even though small). No further peaks at neither lower nor higher wavelengths were observed. DSC traces of pure 8 and 8 containing 5 or 25 mol% 9 or 10 are identical. Only a melting peak of the hard segments at 105 °C was observed. No separate melting peak for 9 or 10 could be observed. From these results it could be concluded, that 9 and 10 are not incorporated in the hard domains of the segmented copoly(ether urea)s, but are most probably molecularly dissolved in the pTHF soft segments.

Films of 8 containing 5 mol% 11 showed similar results as described above: Neither changes in position of the IR signals after incorporations of 11 in 8 nor in the DSC traces could be observed. In the DSC traces of films of 8 containing 25 mol% 11, however, a separate melting peak of 11 at 116 °C could be observed, indicative for the phase separation that could also be observed by eye.

The morphology of mixed films of 8 containing 5 or 25 mol% 9 or 10 and 5 mol% 11 was studied with AFM. The AFM images of the mixed films looked identical to the ones shown in Figure 2.3. No decrease in stack size of the hard segments could be observed. Furthermore no crystallites of 9 or 10 were observed, which is another indication that 9, 10 and 11 are indeed molecularly dissolved in the pTHF soft segments.

The fact that the chainstoppers are dissolved in the soft segments instead of associated with the stacks of the bisurea hard segments, is most probably the result of the crystallization of the crystallites of the bisurea hard segments. The bisurea hard segments form crystals showing
interactions that go beyond 1 dimension. As a result of this, crystallization results in the segregation of the chainstoppers from the stacks.

2.6.2 Association inhibitors in solution

To validate the principle of the association inhibitors, viscometry experiments were performed in solution. In solution, the segregation process from the crystallites should in principle not take place. As the bisurea concentration of the elastomer increases, the self-assembly will lead to larger and larger polymeric structures. Upon complexation of the association inhibitors with the hard domain of the elastomer, a decrease in size of the polymeric aggregate is expected (association of the association inhibitors with the hard domains of the TPE will result in less physical crosslinks and thus smaller polymeric aggregates), thus leading to a decrease in viscosity. This concept was shown before for supramolecular polymers based on bifunctional 2-ureido-pyrimidinone monomers. Upon addition of small amounts of monofunctional end-cappers, the degree of polymerization decreased significantly resulting in a strong decrease in viscosity. Recently, Lortie and coworkers showed that an efficient chain stopper could block the concentration dependence of the molar mass of hydrogen bonded polymers based on bisurea groups (EHUT, Scheme 2.3.). Decreases in viscosity of EHUT solutions were observed upon addition of only a few percent of chain stopper DBUT.

First of all solution viscometry measurements were performed on a series of different weight percentage solutions of 8 in chloroform to see in which regime the mixing experiments need to be performed. The results of these measurements are plotted in Figure 2.10.
Clearly two regimes can be discerned: From 0 to approximately 1 w% of 8 in chloroform, there is just a minor increase in viscosity. Above 1 w% however, there is a steep increase, probably caused by the entanglements of chains that starts to take place in this regime. Based on this experiment, 1.2 weight-percentage solutions of 8 in chloroform containing 9, 10 or 11 with weight-percentages of 0 to 25% (relative to 8) were prepared. Furthermore a 1.6 w% solution of 8 in chloroform containing 11 was prepared. The results of these measurements are shown in Figure 2.11 a - c.

For all three compounds in 1.2 w% solutions of 8 in chloroform a minor decrease in specific viscosity was observed from approximately 15 to 13. A stronger effect was observed in a 1.6 w% solution of 8 containing different w% of 11 relative to 8, namely a reduction in relative viscosity from approximately 35 to 20. These results clearly indicate that all 3 association inhibitors are able to associate to the hard domains of the TPEs, resulting in a decrease in the number of physical crosslinks created by the bisurea motif. As a result of this, the size of the polymeric aggregates will decrease, resulting in a (small) decrease in viscosity. It should be noted however that relatively large amounts of the association inhibitor are needed to get a noticeable decrease in viscosity. This is the result of the large amount of bisurea hard blocks per polymer chain. Only when association inhibitors are associated with multiple bisurea hard blocks per polymer chain, a significant decrease in aggregate size can be expected. Even for supramolecular polymers that aggregate via only one bisurea unit (EHUT, Scheme 2.3), a similar effect has been observed. A dramatic decrease in viscosity was observed upon addition of only a few percent of bis-urea based chain stopper DBUT (Scheme 2.3). Mono-urea based chain stopper DMEU (Scheme 2.3) on the other hand was much less efficient. More than 8 times more DMEU was needed to get the same effect. The two urea groups of DBUT obviously interact cooperatively with EHUT.

Also triphenylphosphine oxides ((TPPO) are good proton acceptors, which are known to form complexes in solution with various hydrogen bond donors. These complexes are stabilized by strong hydrogen bonding between the phosphoryl oxygen and the proton donor of the guest. TPPOs are expected to associate strongly to ureas. Therefore also the addition of
TPPO (12) and bifunctional analogues of TPPO (13) (Scheme 2.4) to solutions of 8 in chloroform was studied with viscometry. The results are depicted in Figure 2.12.

TPPO (12) shows similar behavior as association inhibitors 9 – 11: A decrease in viscosity can be observed. Upon addition of 25 w% of 12 to a 1.4 w% solution of 8 in chloroform, the relative viscosity decreases from approximately 19 to 9. This is a good indication that 12 associates to the N-H hydrogen bond donor of the urea groups of 8. Compound 13 on the other hand shows an opposite trend. Due to the bifunctional nature of 13 compared to 12 a stronger effect was expected, due to the expected cooperative interaction of 13. Upon addition of 25 w% of 13 to a 1.5 w% solution of 8 in chloroform, the relative viscosity increases from 27 to 33. Apparently 13 does not bind correctly to the bisurea hard domains as depicted in Figure 2.6a. For bis-diphenylphosphine oxides with an odd spacer, it is known that there is a frustration with regard to the molecular conformation, as the preferred all-anti conformation of the aliphatic chain gives rise to an unfavorable parallel alignment of the two P=O dipoles within the molecule.\textsuperscript{19b} Clearly the importance of avoiding a parallel alignment of the P=O dipoles becomes greater as the number of methylenes in the spacer decreases. A crystal structure of tetra-P-phenyl-P'P'-heptanediyl-bis-phosphine oxide (a similar compound to 13, with an heptylene instead of a nonylene spacer), already shows a nearly parallel orientation of the P=O groups (O=P \cdots P=O dihedral angle 5.8 °).\textsuperscript{19b} So the frustration with regard to the molecular conformation is most likely not the reason for the increase in viscosity observed for 13. A good explanation for this behavior however cannot be given so far.
2.7 Processing: Electrospinning

As was already mentioned in the introduction of this chapter, segmented copoly(ether urea)s associate via hydrogen bonding of the hard blocks, resulting in the formation of reversible crosslinks embedded in a soft, rubbery, amorphous matrix. These crosslinks give the material elastomeric properties at ambient temperatures. Above the melting temperature of the hard block the crosslinks disappear and the material can be processed like normal thermoplastic polymers. Processing-techniques include injection molding, extrusion, blow molding and calendering without any pretreatment.

Films of the segmented copoly(ether urea)s have been obtained via extrusion as well as via solution casting from chloroform/methanol mixtures (most generally used technique employed in this thesis). Recently however, a new technique called electrospinning, was applied that provided us a simple and versatile method to generate ultra thin fibers of the segmented copoly(ether urea)s. In this way meshes of our material can be prepared with huge surface-to-volume ratio, offering enormous potential for all kinds of surface interaction effects.

The basis of electrospinning revolves around two main principles: separation of charge and surface tension. In a typical apparatus, a syringe filled with a polymer in solution is set up so that the needle is subject to a large electric potential, on the order of 1 – 25 kV. A grounded "target" is placed facing the syringe. Upon depressing the plunger of the syringe, a droplet of polymer solution will become highly electrified and the induced charges are evenly distributed over the surface. As a result, the drop will experience two major types of electrostatic forces: the electrostatic repulsion between the surface charges and the Coulombic force exerted by the external electric field. Under the action of these electrostatic interactions, the liquid drop will be distorted into a conical object known as the Taylor cone. \(^20\) In the 1880’s, Lord Rayleigh determined that the stabilizing force on the droplet, tension T, was related to the charge Q by the spherical radius a. \(^21\)

\[
T > Q^2 / 16\pi a^3
\]  

When this equation is made invalid due to a decreased radius or increased charge, in other words, when the electrostatic charge is larger than surface tension, liquid is thrown off in fine jets. As the solution is thrown off, it is propelled to the target; the solvent usually evaporates, leaving a pure polymer jet. Polymer strands collected on the target vary from micron to sub-micron diameter. In this way, materials with a high surface to volume ratio can be obtained, with interesting applications ranging from nano-fiber reinforced composite materials \(^22\) to supports for enzymes \(^23\) and catalyst \(^24\) to sensors. \(^25\) A diagram representing a typical electrospinning setup is shown in Figure 2.13.

Although this system does not seem complex, many variables can be altered yielding dramatically different results. Altering the potential, polymer, polymer concentration, solvent, and distance to target all yield different results. In addition, mechanical manipulation of the target can change the way in which the fiber is collected. By varying the parameters above, different results can be achieved.
Even though electrospinning was already patented in 1938, it recently got lots of attention. Last couple of years, more then 20 different polymer fibers have been generated by electrospinning, varying from poly(L-lactide) (PLA) for potential applications as scaffolds in tissue engineering to poly(vinylidene fluoride), a well-known piezoelectric polymer, as nanofibers.

The electrospinning behavior of segmented copoly(ether urea)s in solution was studied. It appeared possible to electrospin fibers of our TPEs. The effect of the electrical field, viscosity of the solution and the distance between nozzle and collection plate on the electrospinning process and morphology of the fibers obtained were investigated. Optimal conditions were found to be: (a) an electric field of 12 kV, (b) a 5 – 6 w% solution of TPE in chloroform and (c) a distance between the nozzle and collection plate of 20 cm. The fibers obtained using these conditions have a uniform distribution of diameters (4 µm), as observed with Scanning Electron Microscopy (SEM) (Figure 2.14 a).

**Figure 2.13.** Schematical representation of an electrospinning setup (Image adapted from reference 20b).

**Figure 2.14.** Electrospun fibers of pTHF$_{1100}$U$_3$U (6) from a 5.0 w% solution of 6 in CHCl$_3$ (a) and a 8.7 w% solution of 6 in CHCl$_3$. 
When lower concentrations of the elastomer in chloroform were used for electrospinning or when the electric field applied to the system was too high, the formation of beads on the fibers could be observed. Beads are known as defect structures, because they disturb the unique property of electrospun fibers and decrease the surface area to volume ratio and should thus be avoided.

When using higher concentrations of TPE in chloroform (8w% or higher) the resulting fibers obtained from electrospinning exhibit curly and wavy structures (Figure 2.14.b). The reason for this behavior, although not dramatic, is not understood by us at the moment.

2.8 Discussion and Conclusions

Block copoly(ether urea)s 1 – 8 with pTHF soft blocks of various lengths and uniform hard blocks consisting of two urea groups that are separated by a methylene spacer varying from butylene to heptylene were prepared. The thermal properties were determined with optical microscopy and DSC. The flow temperature of the segmented block copoly(ether urea)s increased with decreasing soft block length. Furthermore an odd-even effect was observed in the flow temperature of these materials: Copoly(ether urea)s with even number of methylene groups in the hard domain featured a higher flow temperature compared to the copoly(ether urea)s with an odd number of methylene groups while leaving the soft block length the same.

A similar odd-even effect was also observed for the Young’s modulus of these materials as determined with tensile testing. The copoly(ether urea)s with an even number of methylenes have a higher Young’s modulus compared to the copoly(ether urea)s with an odd number of methylenes (approximately 95 vs. 82 MPa respectively). Furthermore an increase in Young’s modulus was observed upon decreasing the soft block length of the material.

The morphology of the copoly(ether urea)s with different soft block lengths was studied with AFM. All materials showed long stacks of hydrogen bonded urea groups embedded in the soft pTHF matrix in a co-continuous way. The co-continuous hard phase of the segmented copoly(ether urea)s resulted in high plastic deformations of these materials, especially at high strains, as determined with cyclic tensile testing. Attempts were carried out to improve the elasticity and more precisely its large plastic deformation by changing the co-continuous hard phase to a dispersed hard phase by incorporation of association inhibitors in the bulk. Upon incorporation of 5 – 25 mol% of association inhibitors 9 – 11 no significant decrease in tensile set could be observed. IR and DSC indicated that the association inhibitors were not incorporated in the hard domains of the elastomers, but were most likely dissolved in the pTHF soft blocks of the segmented copolymers. This is most likely the result of crystallization of the bisurea hard segments in 2 or even 3 dimensional crystallites, resulting in the segregation of the association inhibitors from these crystals.

To validate the principle of the association inhibitors, viscometry experiments were performed on viscous solutions of 8 in chloroform to which different amounts of 9 – 11 were added. Upon addition of all 3 association inhibitors a decrease in viscosity was observed, indicating that the size of the polymeric aggregate decreased as a result. Stronger effects were
observed in more viscous solutions of 8. However, in all cases, large quantities of the association inhibitors had to be added (approximately 5 w% compared to 8).

Finally, electrospinning was applied to the segmented copoly(ether urea)s. After optimization of variables such as solvent, polymer concentration, the electrical field applied and the distance to the grounded collection plate, very thin fibers (4 µm) with uniform fiber diameter distribution were obtained.

Having all the knowledge of these well-defined segmented block copoly(ether urea)s as described in this chapter, we are now able to incorporate functionalities into these materials. Two approaches are described. First of all, functionality in the form of diacetylenes, which can be topochemically crosspolymerized, are covalently incorporated within the hard domains of the segmented block copoly(ether urea)s (Chapter 3). Finally, functional groups functionalized with a complementary bisurea unit are selectively incorporated into the hard domains of these segmented block copolymers in a non-covalent manner via a modular approach (Chapter 4 and 5).
2.9 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 P₂O₅; dry tetrahydrofuran (THF) was obtained by distillation from Na/K/benzophenone; dimethylformamide was dried over BaO; pyridine was dried by standing over 4Å molsieves and dry toluene was obtained by distillation from Na/K/benzophenone. Di-tert-butyl tricarbonate was synthesized following previously described procedures.²⁸ 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). ¹H-NMR and ¹³C-NMR spectra were recorded on a 500 MHz Varian Unity Inova 500, a 400 MHz Varian Mercury Vx and a 300 MHz Varian Gemini-2000. Proton and carbon chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) using the resonance of the deuterated solvent as internal standard. Elemental analysis was performed on a Perkin Elmer 2400 series II CHNS/O Analyser. DSCs were taken on a Perkin-Elmer DSC-7 under a nitrogen atmosphere, with heating and cooling rates of 10 °C min⁻¹. 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 α-cyano-4-hydroxycinnamic acid as the matrix on a PerSeptive Biosystems Voyager-DE PRO spectrometer. Optical properties and melting points were determined using a Jeneval polarization microscope equipped with a Linkam THMS 600 heating device with crossed polarizers. Solution viscosities were measured using Schott-Geräte Ubbelohde micro-viscometers with suspended level bulb in automated set-ups with Schott-Geräte AVS/S measurement tripods and AVS 350 measurement devices. The micro-viscometers were thermostatted in a water bath at 20 °C. Samples were filtrated over 5 µm filters before measurement. SEM was carried out using a JEOL JSM 840 A microscope.

Tensile testing. Dumbbell-shaped tensile bars with a parallel length of 18 mm and a width of 5.0 mm were cut from solution cast films with a thickness of approximately 0.2 - 0.3 mm. Tensile tests were performed on a Zwick Z010 Universal Tensile Tester at an elongation rate of 100%/min, using a minimum of 8 samples for each material.

Atomic Force Microscopy (AFM). Samples for the atomic force microscopy (AFM) study were prepared by drop casting 1 mg/ml solutions in chloroform/methanol on silicon wafers or by spin casting 1 mg/ml solutions in chloroform/methanol on glass-plates. AFM experiments were performed using a NanoScope III A instrument operating in the tapping mode, utilizing NanoSensor tapping tips. The amplitude of oscillation at free vibration, A₀, was set to 4.0V. The operating setpoint ratio (A/A₀) was set to relatively low values (A/A₀~0.7).

Electrospinning. A 5.0 and 8.7 w% solution of 6 in chloroform was pumped (15 µl/min) through a nozzle that was subjected to a voltage of 12 kV. Under the applied electrostatic force, the polymer was ejected from the nozzle and was collected on a grounded collection plate 20 cm below the nozzle.


Bis(1-methyl-2-imidazolidinone)-1,7-heptane (9). 1-methyl-2-imidazolidinione (14, 1.0 g, 10 mmol) was added to a stirred suspension of sodium hydride (60 wt% in paraffin oil, 0.92 g, 23 mmol) in dry THF (20 ml) at 20 °C under an argon atmosphere. After 30 min at room temperature, 1,7-
di(iodo)heptane (15, 1.76 g, 5 mmol) in 2.5 ml dry THF was added drop wise, and the reaction mixture was stirred overnight at room temperature. Most of the solvent was removed in vacuo, and 15 ml ice water was added. The precipitated solids were collected by filtration, washed with water and extracted with chloroform. Final purification was performed using column chromatography (1) 2% MeOH/CHCl₃, (2) 1% MeOH/CHCl₃, resulting in a slightly yellowish solid (0.62, 41.8%). δ 3.31 (s, 8H), 3.20 (t, 4H), 2.82 (s, 6H), 1.51-1.43 (m, 4H), 1.40-1.30 (s, 4H), 1.32-1.26 (m, 6H). 13C-NMR (CDCl₃): δ 161.6, 45.1, 44.1, 42.4, 31.4, 28.9, 27.5, 26.5. FT-IR (ATR): ν 2929, 1680 cm⁻¹. Anal. Calcd. (%) for C₁₅H₂₈N₄O₂: C 60.78, H 9.52, N 18.90. Found (%): C 60.41, H 9.58, N 18.72.

Bis(1-tert-Butyl-2-imidazolidinone)-1,7-heptane (10). 1-tert-butyl-2-imidazolidininone (16, 2.84 g, 20 mmol) was added to a stirred suspension of sodium hydride (60 wt% in paraffin oil, 1.84 g, 46 mmol) in dry THF (40 ml) at 20 °C under an argon atmosphere. After 30 min at room temperature, diiodoheptane (3.52 g, 10 mmol) in 5 ml dry THF was added drop wise, and the reaction mixture was stirred overnight at room temperature. Most of the solvent was removed under reduced pressure, and 30 ml ice water was added. The precipitated solids were collected by filtration, washed with water and extracted with chloroform. Final purification was performed using column chromatography (1) hexane/ethyl acetate 4/1, (2) Hexane/ethyl acetate 1/1), resulting in a slightly yellowish solid (2.34 g, 61%). δ 3.29 (t, J = 7.7 Hz, 4H), 3.19 (t, J = 7.7 Hz, 4H), 3.12 (t, J = 7.6 Hz, 4H), 1.51-1.43 (m, 4H), 1.34 (s, 18H), 1.32-1.26 (m, 6H). 13C-NMR (CDCl₃): δ 162.0, 52.92, 44.2, 42.4, 40.8, 29.1, 27.5, 27.4, 26.8. FT-IR (ATR): ν 2929, 1680 cm⁻¹. Anal. Calcd. (%) for C₂₁H₄₀N₄O₂: C 66.28, H 10.59, N 14.72. Found (%): C 66.20, H 10.40, N 14.62.

N, N’(nonanedioyl)bis(2-etoxybenzamide) (11). To a solution of 2-ethoxybenzamide (1.5 g, 9.08 mmol) in pyridine at 80 °C was added azelaoylchloride (0.97 g, 4.32 mmol). The solution was stirred overnight at 80 °C. The solvent was removed in vacuo, and co-evaporated three times with toluene. The crude product was dissolved in chloroform and washed with 1N HCl. The organic layer was dried over MgSO₄. Final purification was performed using column chromatography (1) 8% ethylacetate/CH₂Cl₂, (2) 2% MeOH/CHCl₃) resulting in a white solid (0.7 g, 34%). Tm = 118 °C. δ 10.51 (s, 2H), 8.24 (d, J = 7.7 Hz, 2H), 7.32 (t, 2 H), 7.10(t, 2H), 7.05 (d, J = 8.5 Hz), 4.32 (q, 4H), 2.99 (t, 4H), 1.80-1.65 (m, 4H), 1.64 (t, 6H), 1.4-1.2 (m, 6H). 13C-NMR (CDCl₃): δ 175.8, 163.5, 157.0, 134.4, 132.7, 121.5, 112.5, 65.1, 38.1, 29.1, 29.0, 24.1, 14.5. FT-IR (ATR): ν 3312, 2930, 1707, 1693, 1672, 1601 cm⁻¹. MALDI-TOF-MS: (MW = 482.58) m/z 483.00 [M] +, 504.99 [M+Na] +. Anal. Calcd. (%) for C₂₇H₃₄N₂O₆: C 67.20, H 7.10, N 5.80. Found (%): C 67.40, H 7.07, N 5.75.

Tetra-P-phenyl-P’P’-nonanediyl-bis-phosphine oxide (13). hexa-P-phenyl-P,P’-nonanedily-bis-phosphonium bromide (17, 5 g; 6.17 mmol) was heated under reflux for 14 hours in 50 ml 30% aqueous NaOH. The reaction mixture was cooled and diluted with 40 ml water. It was extracted with dichloromethane (2 * 30 ml). The organic layer was dried with magnesiumsulphate and filtered. The solvent was then removed under reduced pressure to afford a colorless oil, that was recrystallized from dichloromethane / hexane (1/1) to afford 13 as a colorless solid (2.5g, 76.7%). δ 7.74-7.68 (m, 8H), 7.51-7.41 (m, 12H), 2.27-2.19 (m, 4H), 1.60-1.54 (m, 4H), 1.34-1.31 (m, 4H), 1.20-1.17 (m, 6H). 13C-NMR (CDCl₃): δ 175.8, 163.5, 157.0, 134.4, 132.7, 121.5, 112.5, 65.1, 38.1, 29.1, 29.0, 24.1, 14.5. FT-IR (ATR): ν 3312, 2930, 1707, 1693, 1672, 1601 cm⁻¹. MALDI-TOF-MS: (MW = 528.58) m/z 528.00 [M] +, 549.99 [M+Na] +. Anal. Calcd. (%) for C₃₇H₃₈O₂P₂: C 76.70, H 7.10, N 5.80. Found (%): C 76.47, H 7.07, N 5.75.

1-methyl-2-imidazolidinone (14). To a solution of 2-imidazolidinone (17.2 g; 200 mmol) in 200 ml of 1,4-dioxane in a 500 ml 3-neck flask equipped with a condenser was slowly added sodium hydride
(60 wt% in paraffin oil, 9.43 g; 235 mmol) under an argon atmosphere with vigorous stirring. The milky solution was heated to 65 °C and stirred at this temperature for 2 hours and then cooled to 0 °C. Methyl iodide (23.1 ml; 371.2 mmol) was added slowly via a syringe and the resulting mixture was stirred overnight. The reaction mixture was filtered through a bed of Celite and the solvent was removed in vacuo. The product was purified using column chromatography (10% MeOH in CH₂Cl₂, Rf = 0.17) followed by crystallization from CHCl₃/hexane resulting in white crystals (7.7 g, 38%). 1H-NMR (CDCl₃): δ 4.6 (br s, 1H), 3.45 (s, 4H), 2.80 (s, 3H). 13C-NMR (CDCl₃): δ 163.2, 47.2, 37.5, 30.3. FT-IR (ATR): ν 3268, 2865, 1700, 1501, 1450 cm⁻¹. Anal. Calcd. (%) for C₄H₈N₂O: C 47.97, H 8.06, N 27.99. Found (%): C 47.70, H 8.13, N 28.10. m.p. 114 °C (lit. 112-115 °C)

1,7-di(iodo)heptane (15). A solution of 1,7-dibromoheptane (7.55 g, 29.3 mmol) in 100 ml of dry acetone was added dropwise to a 500-ml flask equipped with a condenser, containing a suspension of sodium iodide (17.5 g, 117 mmol) in 150 ml of dry acetone at room temperature. The mixture was heated to reflux for 3 hr. After cooling, the reaction mixture was filtered and the solvent was evaporated in vacuo. The crude residue was extracted with CHCl₃. (10.2 g, 99%): 1H NMR (CDCl₃): δ 3.17 (t, 4H), 1.39 (m, 4H) 1.30 (m, 6H). 13C NMR (CDCl₃): δ 33.21, 30.14, 27.81, 27.32, 6.91. EI-MS (m/z, loss fragment): 352 (M + ), 225 (M + -HI), 183 (M + -HI-C₃H₆), 155 (M + -C₅H₁₁I), 97 (C₇H₁₃).

1-tert-butyl-2-imidazolidinone (16). To a 100 cm³ 3-neck flask equipped with a dropping funnel and a thermometer and surrounded by an ice-bath, was added sulfuric acid (98%, 21 ml). Finely powdered 2-imidazolidinone (17.2 g; 200 mmol) was added slowly at a rate such that the temperature remained between 0 and 10 °C, followed by the drop-wise addition of tert-butanol (38 ml, 400 mmol) at 20 °C. After the addition was complete, the reaction mixture was stirred for 30 min, and then poured with stirring into 300 ml ice water. The mixture was brought to pH 6 by slow addition of a solution of 2 M NaOH, while the temperature was kept below 25 °C. The mixture was cooled to 15 °C, and the product was collected as a colorless white solid by filtration (4.2 g). The filtrate was extracted with chloroform (4 * 40 ml) and the obtained organic layers were dried and evaporated under reduced pressure. The filtered product and the organic layer were combined (18.22 g) and recrystallized from ethyl acetate/light petroleum ether giving 1-tert-2-imidazolidinone as colorless plates (15.8 g, 55.6%). 1H NMR (CDCl₃): δ 6.60 (br s, 1H), 2.78-2.60 (m, 4H), 1.36 (s, 9H). 13C-NMR (CDCl₃): δ 163.7, 52.2, 43.4, 37.6, 27.2. FT-IR (ATR): ν 3241, 1714 cm⁻¹. Anal. Calcd. (%) for C₇H₁₄N₂O: C 59.12, H 9.92, N 19.70. Found (%): C 59.23, H 9.89, N 19.75. m.p. 140.5 °C (lit. 135-139 °C)

hexa-P-phenyl-P,P'-nonanedily-bis-phosphonium bromide (17). A mixture of dibromononane (4.0 g; 3.98 mmol) and triphenylphosphine (7.33 g; 27.97 mmol) were heated under reflux overnight in 50 ml dried DMF. The solvent was removed in vacuo and 17 was obtained as a colorless solid (8.87 g; 86.4%). 1H NMR (CDCl₃): δ 7.82-7.66 (m, 30H), 3.75-3.60 (m, 4H), 1.64-1.50 (m, 8H), 1.20-1.31 (m, 4H), 1.11-1.19 (m, 2H). 13C-NMR (CDCl₃): δ 135.0 (d, J = 3.1 Hz), 133.6 (d, J = 10.0 Hz), 130.5 (d, J = 12.3 Hz), 118.1 (d, J = 86.0 Hz), 29.7 (d, J = 16.1 Hz), 28.3, 28.1, 22.6 (d, J = 49.9 Hz), 22.5 (d, J = 4.6 Hz). MALDI-TOF-MS: (MW = 2 * 79.9 + 650.32) m/z 649.30 [M]+, 729.21 [M+Br]+.

2.10 References and Notes

1 M. Niesten, Ph.D. Thesis, University of Twente (Enschede), 2000.


Thermoplastic Elastomers Containing Cross-Polymerizable Hard Blocks

Abstract

Diacetylene-containing segmented copoly(ether urea) 1 was prepared via a polycondensation of 1,10-diisocyanato-deca-4,6-diyne with bis(3-aminopropyl)-poly(tetrahydrofuran) (Mn ≈ 2300 g/mol). The reactive diacetylene spacer, which resides within the hard domains of the segmented elastomer, was cross-polymerized topochemically by means of UV radiation, without disrupting the flexible nature of the material, resulting in an intensely blue colored insoluble material. The extent of cross-polymerization was determined using solid-state $^{13}$C-NMR and was found to be approximately 10%. The optical properties of the cross-polymerized material could be modified in a mechanical and thermal way, as well as by changing the solvent. A study into the mechanochromic behavior, which can be visibly observed as the color changes from blue to yellow as a function of elongation, showed that the polydiacetylene chains orient parallel to the deformation axis and are irreversible at strain levels greater than 80%. Thermochromic and solvochromic behavior of 1 was completely irreversible.

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3.1 Introduction

Since the appearance of the seminal publication of G. Wegner, by which the solid-state reactivity of certain unsubstituted diacetylenes was explained in terms of a polymerization reaction, polydiacetylene (PDA) research has evolved to a multidisciplinary field with many active developments. A unique feature of this polymerization is that it proceeds within the perfect lattice of the monomer crystal. Since it is completely controlled by the packing of the monomer, it leads to perfect crystals of the corresponding polymer. Therefore PDAs can only be structured as bulk single crystals. More recently they have also been applied in multilayer films, vesicles suspended in liquids and as nanocomposite components integrated into inorganic host matrices.

Properties of PDAs that are of interest include their high nonlinear optical susceptibility, ultrafast optical response and strong structural anisotropy imposed by the highly aligned, linear backbones. The most-studied properties of PDAs however are the chromogenic transitions they exhibit. The optical absorption in PDAs occurs via a $\pi \rightarrow \pi^*$ absorption within the linear $\pi$-conjugated polymer backbone. In contrast to unpolymerized films, which do not exhibit absorption in the visible region, upon polymerization, the first chromogenically interesting state of the PDA appears blue in colour, with an absorption maximum in the range of 640 nm. The chromogenic transitions all involve a significant shift in absorption from low- to high-energy bands of the visible spectrum, where the PDA transforms from a blue to a red color, with an absorption maximum in the range of 540 nm.

The mechanism behind the chromatic transitions is still not fully established. Previously, Lee et al. reviewed a number of other mechanisms attempting to explain the transition. They proposed a transformation from the ene–yne structure to a butatrienic structure (three sequential double bonds), which could however be ruled out by crystallographic studies and quantum chemical calculations. Recent investigations on both bulk and thin-film forms of PDA have shed new light. These studies showed that the key to the transition consists of the interplay between the conformation of the pendant side-groups and the backbone. Furthermore the absorption properties of the backbone depend on strain. Rotation about the C–C bond of the polymer backbone is critical in this respect, since it changes the planarity of the backbone (Figure 3.1). Theoretical calculations indicate that a rotation of only a few degrees around this bond drastically changes the $\pi$-orbital overlap, causing a significant blue-shift of the absorption spectrum. Rotation around this bond results in changes in the conformation of the pendant side-groups, which have a preferred packing arrangement, dominated by the intermolecular arrangement in the unpolymerized form. This packing arrangement may be dictated by H-bonding between e.g. urethane groups. The extended backbones will be formed in a strained configuration upon polymerization, because of the geometric restriction imposed by the side-group arrangement. Essentially, the packing energy of the side-groups creates a barrier that prevents the backbone from adopting a more relaxed form. Subsequent application of heat, stress, or other stimuli leads to side-chain fluctuations or reconfigurations and allows the
backbone to adopt a more relaxed conformation that involves rotation around the C–C backbone bonds, and thus leads to changes in the optical absorption spectrum.\(^6\)

**Figure 3.1.** Schematic diagram of the molecular orbitals in the π-conjugated PDA backbone in the planar configuration. Energy levels are affected by the overlap of these orbitals. This overlap is altered by rotation about one of the C–C bonds in the backbone (Image adapted from reference 6).

Another unusual property of polydiacetylenes is that the photo polymerization occurs via a topochemical polymerization from a well-ordered solid state, leading to extremely linear, aligned polymerized domains. A prerequisite for the polymerization to occur is crystalline packing of the monomers. The polymerization successfully proceeds because the monomer spacing, imposed by the van der Waals’ forces between the pendant alkyl chains, is close or close enough to the spacing required for the diacetylene backbone to form.

Polymers exhibiting the optical properties of polydiacetylenes and the mechanical behavior of a tough and highly extensible elastomer are highly desirable materials. As has been previously demonstrated, the reactive diacetylene group can be easily incorporated into many different polymeric structures.\(^7\)-\(^{11}\) In this way it is possible to modify the optical and mechanical properties of these materials by the controlled solid-state cross-polymerization of the diacetylene groups. The ability to couple the optical and mechanical behavior of a TPE presents a world of opportunities, ranging from optically anisotropic materials to mechanooptic sensors. Self-assembled polydiacetylene supramolecules in the form of Langmuir-Schaeffer or Langmuir-Blodgett films have already proven themselves as chemosensors monitoring ligand-receptor interactions involving viruses\(^{12}\), toxins\(^{13}\) and ionic interactions\(^{14}\), even though they function in an irreversible fashion. Recently however, Ahn and coworkers have studied the effect of enhanced hydrogen bonding in polydiacetylene Langmuir-Schaefer films, resulting in reversible color changes, which could be potentially useful for designing reversible calorimetric sensors based on polydiacetylenes.\(^{15}\)
In the late 80’s and early 90’s Rubner and coworkers have studied polyurethane-diacetylene segmented copolymers (Scheme 3.1). By using this combination, the optical properties of diacetylenes were linked with the mechanical properties of polyurethanes. In the copolyurethane-diacetylene copolymers a polydiacetylene network is produced in the hard domains on irradiation in the solid state. The resulting cross-polymerized polyurethanes undergo color changes that are coupled to elastomeric strain (mechanochromism), as well as temperature changes (thermochromism).

Scheme 3.1. Structures of polyurethane diacetylene segmented copolymers prepared by Rubner et al.

In this chapter a bis-urea based thermoplastic elastomer with cross-polymerizable hard blocks (1) is described, based on a new class of TPEs containing urea groups which was recently developed in our laboratory by Versteegen (see Chapter 2). They consist of a uniform bisurea hard block in which the urea groups are separated by a fixed number of carbon atoms. These hard blocks are embedded in a soft amorphous pTHF matrix. Association of the hard segment domains via hydrogen bonding results in the formation of reversible crosslinks embedded in a soft, rubbery, amorphous pTHF matrix.

These copoly(ether urea)s exhibit promising thermal and mechanical properties, as summarized in Chapter 2. Here, a reactive diacetylene spacer was incorporated between the two urea groups in the hard segment domains of the elastomer. In such an arrangement it should be possible to cross-polymerize the diacetylene units to the poly(diacetylene) form by means of heat or UV radiation without disrupting the flexible nature of the elastomeric phase (Figure 3.2). Additional hydrogen bonding in our system compared to Rubner’s polyurethanes results in a more defined geometry of the hard-domain, which might result in increased reactivity of the diacetylene monomers; topochemical polymerizations are restricted to ordered lattices of monomer molecules that are stacked in such a way that the stacking distance and angle between the diacetylene monomer are satisfied.
The mechanical properties as well as the orientation of the different chromophores under tensile conditions were studied with polarized IR and UV spectroscopy. Furthermore, the thermo- and solvochromic behavior of this remarkable material will be discussed.

### 3.2 Synthesis

The synthesis of diacetylene-segmented copolymer 1 is schematically depicted in Scheme 3.2. 1 was synthesized via the oxidative coupling of 5-hexynoic acid (2) to 5,7-dodecadiynedioic acid (3) with CuCl₂. The acid was converted to the 5,7-dodecadiynedioic acidchloride (4) with oxalyl chloride. This was converted to the diisocyanate (5) via a Curtius rearrangement. Compound 1 was finally obtained via a polycondensation reaction of the diisocyanate with amine-terminated polyTHF prepolymer with a Mₙ of approximately 2300 g/mol. After precipitation of 1 in hexane, the polymer was obtained as white fluffy fibers. The molecular weight of 1 as determined with SEC was 56 x 10³ g/mol.
3.3 Cross-polymerization

3.3.1 Requirements for solid-state cross-polymerizations

As already mentioned in the introduction, in topochemical polymerizations of diacetylenes the intermolecular spacing is critical. For polymerization to occur, the diacetylene monomers should be aligned at 4.9 Å, the repeat distance in the final polymer (Figure 3.3). Since this distance is nearly similar to the molecular repeat distance of bisurea model compounds that were synthesized to gain more insight into the way copoly(ether urea)s associate (Figure 3.3), our copoly(ether urea)s could in principle be used to position diacetylenes for topochemical polymerization. Besides the stacking distance, the monomer packing is also characterized by the angle \( \Theta \) between the diacetylene rod and the stacking axis (Figure 3.3).

![Figure 3.3](image.png)

*Figure 3.3. Matching between the repeat distance of bisureas as determined with single crystal x-ray structure of a bisurea model compound (left) and the requirements for the stacking distance for topochemical polymerizations of diacetylenes (right).*

3.3.2 Solid-state crosspolymerization of 1

Clear colorless films of 1 were solution cast from chloroform/methanol mixtures. The films were cross-polymerized by means of 254 nm radiation. The conversion of the diacetylene functionality into polydiacetylenes (Figure 3.2) was followed with UV-Vis spectroscopy. Since the electronic transition of the \( \pi \)-electrons of the backbone occurs in the wavelength region of the visible light, the material becomes intensely blue-colored when the conjugated backbone is formed (Figure 3.3).

The copolymer developed an intense absorption band with a maximum at about 660 nm after a 24 minutes exposure to UV radiation (Figure 3.4). The relatively sharp absorption band at 660 nm can be attributed to exciton formations, which are believed to be localized over only a few backbone atoms. Vibrational sidebands due to coupling of the valence electronic levels with the vibrations of the backbone double and triple bonds can be observed at 616 and approximately 530 nm.
Topochemical cross-polymerization of diacetylenes generally occurs without disrupting the packing and order of the polymer chains. To study this, the extent of hydrogen bonding of the urea groups before and after cross-polymerization of the diacetylenes was investigated with FT-IR. In the IR spectra of copolymer 1 before and after cross-polymerization, the urea C=O stretch vibration can be found at 1615 cm\(^{-1}\), and the urea NH vibration at 3326 cm\(^{-1}\). Coleman and Painter reported a temperature-dependent infrared study of a polyurea and model ureas. They concluded that the frequency of both the N–H and the C=O vibration depend strongly on the hydrogen bonding nature of the urea groups.\(^{23}\) If the hydrogen bonding strength between urea groups increases, the frequency of both the N–H and C=O vibrations decreases (from 3350 to 3325 cm\(^{-1}\) and 1640 to 1615 cm\(^{-1}\) respectively), in contrast to the amide II band (a combined N–H bending and C–N stretching vibration) at approximately 1575 cm\(^{-1}\), which increases in frequency. The position of both bands in the unpolymerized and polymerized films thus indicates that strong hydrogen bonds persist after cross-polymerization. In other words: cross-polymerization does not disturb the organization of the hard domains of the copolymer, which is favorable for the mechanical properties of the material.

### 3.3.3 Extent of solid-state cross-polymerization

In order to understand how cross-polymerization influences the final properties of our material, knowledge of the extent of cross-polymerization is of critical importance. Since cross-polymerized samples of 1 become completely insoluble, solid state NMR was used to estimate the fraction of cross-polymerized diacetylene groups.\(^{11,24}\) Peaks due to the diacetylene groups decrease upon polymerization and their relative intensity was measured as a function of radiation time. Since the carbonyl carbon signal is an isolated resonance, it served as an internal reference against which the diacetylene peak area was followed. \(^{13}\)C-NMR spectra were recorded as a function of spin lock/contact time, showing that neither the carbonyl nor the diacetylene carbons showed a variation in CP rate, thus making the data amenable to quantitative analysis. In the resulting spectra (Figure 3.5), the peaks at 30 and 70 ppm were
assigned to the ether carbons of the pTHF soft block, the peak at 160 ppm to the carbonyl carbon, while the acetylenic carbons appear at 65 and 78 ppm, with the interior carbon resonating at higher field due to additional shielding provided by the π-electrons. Spinning side bands (SSB) are observed at 143, 135, 130, 97 and 91 ppm due to inefficient averaging of the chemical shift anisotropy. This effect is generally larger for sp-carbons, thus explaining the relatively large intensities of the SSBs of the acetylenic carbon compared to the ether carbons.25

![Figure 3.5. Magic Angle Spinning CP \(^{13}\)C NMR spectrum of diacetylene segmented copoly(ether urea) 1. Spectrum was obtained with CP times of 3 ms and recycle times of 10 seconds. Spectrum represents the FT of 16384 FID accumulations (* = spinning side bands).](image)

Strong overlap between the signals of the ether carbon and the two acetylenic carbons hampers the determination of the extent of cross-polymerization. However, after deconvolution, an extent of solid-state cross-polymerization of 10% (± 3%) after 30 minutes irradiation with 254 nm UV radiation was determined.

Upon formation of the polydiacetylene backbone, new resonances due to the sp and sp\(^2\)-hybridized carbons of the conjugated backbone should appear around 130 and 110 ppm. These, however, were not observed. This might be caused by the experimental setup: cross-polymerization yields more rigid network domains with long proton T\(_1\)'s. The recycle delay may have been too short to relax efficiently. Another explanation might be the large dispersion of chemical shifts observed for conjugated carbons chains of varying length. Chemical shift fluctuations were also observed for poly(1,11-dodecadiyne) before and after cross-polymerization.24

### 3.4 Mechanical properties of 1

The mechanical properties of the diacetylene-segmented copolymer can be modified by cross-polymerization and were determined by tensile testing. The resulting stress-strain curves are displayed in Figure 3.6 for a sample before and after cross-polymerization for 30 minutes with 254 nm UV radiation.
The ultimate strain at break of the cross-polymerized copolymer compared to the non-polymerized copolymer decreases from 1060 to 820%, as a consequence of the fact that the permanent cross links created between the hard segments allow less slippage and elongation of the hard domains, giving rise to a more pronounced strain amplification in the material. Furthermore an increased modulus at strains above 100% can be observed, indicating that the material becomes stiffer.\(^{16}\) This demonstrates that the hard domains participate in the deformation process even at low strains. This fact emphasizes the role of the hard domains in providing reinforcement to the soft segment phase and, in particular, how increased hard domain rigidity can increase the copolymer's resistance to deformation. Xue-Hai and coworkers also reported an increase in Young's modulus upon increasing the rigidity of the hard domains via increases in crystallinity or ionic aggregation in PDMS-polyurethane elastomers.\(^{26}\)

### 3.5 Chromic behavior of 1

Upon elongating the cross-polymerized sample of 1, a color change from blue to red to yellow can be observed. This is a result of introducing levels of stress to the hard domains of the material: Polydiacetylenes are known to be highly susceptible to the molecular environment of their polymeric backbone. Changes in the molecular environment result in significant changes in the energy and shape of the absorption bands. In other words, the electronic states of polydiacetylenes are strongly linked to the conformation of the conjugated backbone. It is therefore possible to use the polydiacetylene chains as visible monitors of changes that take place within the polymer matrix. Not only can these chromic transitions be induced by mechanical stress, they are also known to be temperature and solvent dependent. In the remainder of this chapter, the mechanochromic, as well as thermo- and solvothermic behavior of 1 will be studied in detail.
3.5.1 Mechnochromic behavior

The mechanochromic behavior of copolymer 1 was studied in more detail using polarized UV spectroscopy and infrared linear dichroism spectroscopy, a technique that has often been used to study the orientation of functional groups within polymers.\textsuperscript{27} Infrared linear dichroism spectroscopy was used to investigate mechanical orientation of the urea blocks of polymer 1 that was cross-polymerized for 30 minutes. Using this technique, strain induced orientation of hard segments in polyether urethane ureas has been shown to be perpendicular to the deformation axis at strains beyond the yield point.\textsuperscript{28} Similar trends were observed for copoly(ether urea).\textsuperscript{19} In cross-polymerized films of 1, the dichroic ratio of absorption bands due to stretch vibrations was measured with polarized infrared light parallel and perpendicular to the deformation axis. Upon elongation of 10 \(\mu\)m thin tensile bars, the difference in absorption of linearly polarized infrared light on the N-H stretch vibration at 3326 cm\(^{-1}\) and the C=O stretch vibration at 1615 cm\(^{-1}\) was measured. Figure 3.7 shows the dichroic ratio (absorption parallel / perpendicular with respect to the deformation axis) for the 2 bands as a function of elongation.

Up to 80\% strain an increase in the dichroic ratio can be observed, indicating that at low strains, below the yield point (80\% strain), the carbonyl and amine groups orient parallel to the orientation axis. Above the yield point however, the hard blocks break up and the carbonyl and amine orient perpendicular to the deformation axis, as can be concluded from the decrease of the dichroic ratio to below 1 as a function of elongation. This can of course only hold for urea groups that are separated by diacetylene chains instead of polydiacylenes. As a reminder, only approximately 10\% of all diacetylene functionalities were topochemically cross-polymerized.

![Figure 3.7](image)

\textbf{Figure 3.7.} (a) Dichroic ratio\((A_{\text{par}}/A_{\text{perp}})\) as a function of the elongation for the NH (–) and C=O (–) vibrations of 1 that was cross-polymerized for 30 minutes with 254 nm UV radiation. (b) schematic representation of hard block orientation as function of elongation.

The orientation of the polydiacetylenes blocks was studied in further detail with polarized UV spectroscopy. UV-Vis spectra were measured of cross-polymerized samples of 1
at 0° and 90° polarization angles with respect to the deformation axis. The results are depicted in Figure 3.8 and strongly resemble the results obtained for Rubner’s polyurethane-diacetylene segmented copolymers (d in Scheme 3.1). In the spectra recorded with vertically polarized light (parallel to the stretch direction) (Figure 3.8(a)) a continuous shift of the absorption band to higher energies can be observed. Furthermore, it broadens and becomes poorly defined as a function of increasing strain. Even when low strains are applied to 1 there is already a relatively large red shift indicating that stress is transmitted to the hard domain resulting in a change in the molecular environment of the polydiacetylene backbone. Above 240 % strain only a very broad featureless absorption band with a maximum around 490 nm can be observed. This broad band at high strain suggests that the hard domains become highly disordered.

In the spectra recorded with a horizontal polarizer (perpendicular to the stretch direction) (Figure 3.8(b)) the shift of the excitonic peak is less dramatic. However, the intensity of the overall absorption band decreases significantly relative to the band observed for vertically polarized light, indicating that the polydiacetylene chains are oriented along the stretch direction as a function of elongation. The fact that the red shift for the excitonic peak is less dramatic and retains its shape to higher strains in the case of the horizontally polarized light indicates that the polydiacetylene chains that are lying perpendicular to the loading direction are not subjected to such high level of stress as experienced by the chains that are forced to align into the stretch direction.

![Figure 3.8](image.png)

**Figure 3.8.** Visible absorption spectra of 1 as function of increasing strain with (a) vertically polarized light (parallel to deformation axis) and (b) horizontally polarized light (perpendicular to deformation axis). For clarity reasons some spectra have been omitted.

To get a better understanding of residual hard block orientation and the reversibility of the deformation process, visible absorption spectra were recorded of 1 after relaxation from different increasing strain levels with a vertical polarizer (parallel to deformation axis) and a horizontal polarizer (perpendicular to deformation axis). The results are depicted in figure 3.9.
As can be seen, the shape of the original absorption band is more or less recovered after relaxing from strains up to 80%. Only a small decrease in intensity of the excitonic peak as well as the appearance of a very small higher energy band can be observed. As the material is subjected to higher strain levels, the intensity of the excitonic peak decreases significantly and furthermore the intensity of the higher energy absorption band increases strongly and becomes more intense than the excitonic peak. Apparently, the hard domains remain structurally intact up to approximately 80% strain. Above 80% strain, a deformation mechanism sets in resulting in stress being transmitted to the hard domains of the material. Those results are in agreement with the infrared circular dichroism results: up to the yield point (80% strain) the urea groups orient parallel to the deformation axis. This orientation process is reversible. Above the yield point however the hard blocks break up and the carbonyl and amine become oriented perpendicular to the deformation axis. As a result of this mechanism, stress is being transmitted to the polydiacetylene blocks permanently.

3.5.2 Thermochromic behavior

As mentioned before, the conjugated backbone is sensitive to variations in side-group organization. One way to achieve this is with temperature. Therefore, it should be possible to further modify the optical properties of the polydiacetylenes by changes in temperature. UV measurements were performed on a thin film of cross-polymerized elastomer of 1, which was heated to different temperatures and then cooled back to room temperature. An irreversible shift of the absorption band to higher energies can be observed during temperature cycling (Figure 3.10). Even after heating to 40 °C a significant increase of the higher energy absorption band at 530 nm can be observed. A featureless absorption band can be observed when the sample is heated to 120 °C. This high-energy absorption band is similar to that exhibited by a
soluble polydiacetylene when it is dissolved in a thermodynamically good solvent. Therefore it can be concluded that this is an example of a thermally induced disordering process in which the polydiacetylene chains are completely disordered upon heating similar to the solution state.

![Figure 3.10](image)

**Figure 3.10.** Visible absorption spectra of thin films of 1 that were cross-polymerized for 30 minutes with 254 nm UV radiation recorded at 20 °C after being heated to the indicated temperatures for 5 minutes.

### 3.5.3 Solvochromic behavior

A similar irreversible color change was also observed when the material was 'dissolved' in different solvents (Figure 3.11(a)). In hexane, a thermodynamically bad solvent, the material doesn't dissolve at all and the material remains blue, indicating that there are no conformational changes of the hard domains and consequently of the conjugated backbone.

![Figure 3.11](image)

**Figure 3.11.** Solvochromic behavior of 1 in (a) hexane and (b) chloroform.

However, in chloroform, a thermodynamically good solvent, the material swells (Figure 3.11(b)), due to dissolution of the pTHF soft block. Since the molecular environment of the
polydiacetylene changes, they become more disordered, the primary excitonic peak broadens and the higher energy vibronic sidebands become obscured by a broad absorption that dominates the entire spectrum. Therefore the color of the material changes from blue to yellow. Once in the disordered state, it appeared impossible to go back to the ordered state by changing back to hexane. Even upon removal of the solvent, the material remains yellow.

3.6 Discussion and Conclusions

A diacetylene segmented copoly(ether urea) is prepared, with a reactive diacetylene functionality residing in the hard segment domains of the elastomer. The diacetylene groups provide a means to topochemically crosslink our TPE in the solid state using UV radiation. With the development of this diacetylene segmented copoly(ether urea), the behaviour of thermoplastic elastomers has been expanded to include mechano-optic and chromic properties characteristic of polydiacetylenes. In this way, the mechanical properties of the copoly(ether urea) could be altered, without altering its original morphology. The yield of the topochemical cross-polymerization was approximately 10% (± 3%), which is relatively low. The tight packing of the hard blocks via the bisurea groups, might result in restricted side groups mobilities within the spacer, which is necessary in addition to a favourable monomer packing for high reactivities.

The orientation of the polydiacetylenes blocks was studied in detail with polarized UV spectroscopy. Even at low strains a relatively large red shift of the absorption maximum is observed indicating that stress is transmitted to the hard domain resulting in a change in the molecular environment of the polydiacetylene backbone. The decrease in intensity of the overall absorption band observed for horizontally polarized light relative to the band observed for vertically polarized light, indicates that the polydiacetylene chains orient along the stretch direction as a function of elongation. Infrared linear dichroism spectroscopy was used to study the molecular orientation of the bisurea groups of the cross-polymerized material during tensile testing. A deformation process similar to copoly(ether urea)s was observed: Below the yield point (80 % strain), the hard domains tilt in a direction parallel to the deformation axis. Above the yield point however, fragmentation and irreversible reorganization of the hard domains occur, resulting in perpendicular orientation. As a result of this reorganization process, an irreversible mechanochromic transition was observed at strains larger than 80%. As a comparison, Rubner’s diacetylene segmented polyurethanes were found to be reversible up to 350 % strain. This large difference is a consequence of the fact that in their system the disruption of hard domain ordering occurs at much higher strains compared to our system (above 300%).

The optical properties of the diacetylene-segmented copolymer were further modified by temperature. An irreversible shift of the absorption band to higher energies was observed during temperature cycling.

The thermochromic and mechanochromic behaviour could in principle be used to design optical sensors for respectively temperature and stress. One drawback of our system
however, is the irreversible nature of the transitions. However, further molecular design of our diacetylene-segmented system in the future might result in the ability to control the optical and mechanical properties. This may be accomplished by further functionalization of our copoly(ether urea)s, and systematic variation of the chemical structure of both hard and soft blocks to achieve the desired range of chromic response.
3.7 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$_2$O$_5$; dry tetrahydrofuran (THF) was obtained by distillation from Na/K/benzophenone; dimethylformamide was dried over BaO; pyridine was dried by standing over 4Å molsieves and dry toluene was obtained by distillation from Na/K/benzophenone. 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). $^1$H-NMR and $^{13}$C-NMR spectra were recorded on a 500 MHz Varian Unity Inova 500, a 400 MHz Varian Mercury Vx and a 300 MHz Varian Gemini-2000. Proton and carbon chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) using the resonance of the deuterated solvent as internal standard. Elemental analysis was performed on a Perkin Elmer 2400 series II CHNS/O Analyser. IR-spectra were measured on a Perkin Elmer Spectrum One. A shimadzu LC-10-AT, using a Polymer Laboratories Mixed-D column (Particle size 5 µm; Length/I.D. (mm): 300 x 7.5) and UV detection was employed for size exclusion chromatography (SEC), using N-methyl-Pyrollidone (NMP) as an eluent (1 ml/min). Molecular weights were calculated relative to polystyrene standards.

**Film preparation.** Diacetylene segmented copoly(ether urea) 1 was dissolved in chloroform / methanol mixtures (9/1). The solution was poured into silylated petri dishes or Teflon moulds and films were obtained by slow evaporation of the solvents in the dark to prevent cross-polymerization. All films were dried further under reduced pressure at room temperature before analysis.

**Tensile testing.** Dumbbell-shaped tensile bars with a parallel length of 18 mm and a width of 5.0 mm were cut from solution cast films with a thickness of approximately 0.3 mm. Tensile tests were performed on a Zwick Z010 Universal Tensile Tester at an elongation rate of 100%/min, using a minimum of 8 samples for each material.

**Polarized UV spectroscopy.** UV-Vis spectra were recorded on a Perkin Elmer Lambda 900 spectrometer equipped with a polarizer accessory. Films of 1 were elongated and clamped, and spectra were recorded at 0° and 90° polarization angle with respect to the deformation axis.

**Infrared linear dichroism spectroscopy.** Infrared (IR) spectra were recorded by means of a Biorad UMA 500 microscope, coupled to an FTS6000 FT-IR spectrometer. 10 µm thin tensile bars were elongated and clamped. Infrared spectra were recorded in transmission at 0° and 90° polarization angle with respect to the deformation axis.

**Solid State $^{13}$C NMR.** Solid state $^{13}$C NMR spectra were recorded on a Bruker Advance DMX-500 Spectrometer (magnetic field 11.7 T) operating at 500 MHz using a cross-polarization (CP) pulse sequence in combination with magic angle spinning (MAS). Thin slices of the polyurea-diacetylenes or polyurea-polydiacetylenes were packed in a 4 mm rotor and spun at 8 kHz. A cross-polymerization contact time of 3 ms was used in combination with a 10 s recycle time.

**Synthesis of 1 – 5.**

**Diacetylene segmented copoly(ether urea) (1).** Bis(3-aminopropyl)-poly(tetrahydrofuran)$^{18}$, $M_n=2300$ g/mol (6.3 g; 2.77 mmol) was dissolved in dry chloroform (60 ml) and a solution of a solution of
1,10-diisocyanato-deca-4,6-diyne (5, 0.6 g; 2.77 mmol) in dry chloroform (15 ml) was slowly added. The reaction was followed with IR and addition of the diisocyanate was stopped once the isocyanate peak at 2249 cm\(^{-1}\) appeared. The solution was partly evaporated and methanol (5 ml) was added. The product was precipitated in hexane (400 ml), filtered and dried \textit{in vacuo}. It was obtained as white, fluffy, elastic fibers (6.1 g) and was stored in the dark and at \(-10^\circ\)C to prevent cross-polymerization. \(^{1}\)H-NMR (CDCl\(_3\)): 4.8-4.6 (4H, N-H), 3.45 (4H O-C\(_2\)H\(_2\)CH\(_2\)N), 3.42 (96H C\(_2\)H\(_2\)-O), 3.25 (8H, NC\(_2\)H\(_2\)), 2.30 (4H, CC\(_2\)H\(_2\)), 1.77 (8H, OCH\(_2\)C\(_2\)H\(_2\)CH\(_2\)N, CCH\(_2\)C\(_2\)H\(_2\)), 1.61 (96H, OCH\(_2\)C\(_2\)H\(_2\)CH\(_2\)O). FT-IR (ATR): \(\nu\) 3327 (N-H stretching), 2940, 2855, 1615 (C=O stretching), 1581, 1369, 1103 (C-O stretching) cm\(^{-1}\). SEC (NMP, rel. to PS): \(M_n\): 56 x 10\(^3\) g/mol.

5,7-Dodecadiynedioic acid (3).\(^{31}\) A suspension of copper (I) chloride (7.9 g; 80.1 mmol) and ammonium chloride (14.34 g; 0.27 mol) in 40 ml water was added to a solution of 5-hexynoic acid (2) (3 g; 26.7 mmol) in 40 ml water. The green reaction mixture was heated to 60\(^\circ\)C and for 2 hours air was bubbled through the solution while it was stirred vigorously. The reaction mixture was quenched with 46 ml concentrated hydrochloric acid and the resulting precipitate was collected by suction filtration, washed with a 1/1 mixture of hydrochloric acid / water and recrystallized from a water / methanol mixture (2/8), resulting in white crystals (1.8 g, 61%). \(^{1}\)H NMR (CD\(_3\)OD): \(\delta\): 2.43 (t, 4H, C=OCH\(_2\)H\(_2\)), 2.35 (t, 4H, C\(_2\)H\(_2\)-C), 1.81 (m, 4H, CH\(_2\)-C\(_2\)H\(_2\)-CH\(_2\)). \(^{13}\)C NMR (CD\(_3\)OD): \(\delta\): 174.3 (C=O), 77.9 (CH\(_2\)-C\(_2\)), 66.0 (C-C\(_2\)), 32.9 (C=O-C\(_2\)H\(_2\)), 23.7 (CH\(_2\)-C\(_2\)H\(_2\)-CH\(_2\)), 18.2 (CH\(_2\)-C\(_2\)). \(^{13}\)C NMR (DMSO): 174.3, 77.9, 66.0, 32.9, 23.7, 18.2.

5,7-Dodecadiynedioic Acid Dichloride (4).\(^{32}\) 5,7-Dodecadiynedioic Acid (3, 0.8 g, 3.6 mmol) was dissolved in an ethanol/tetrahydrofuran (5 ml / 5ml) mixture. To this solution was added an ethanolic NaOH solution (7.2 mmol, 5 ml) at room temperature. After stirring for 5 minutes the solvent was evaporated and the residue dried under vacuum for 5 hr. The residue was dissolved in 10 ml ether and 1 drop of DMF and was cooled to 0\(^\circ\)C. At this temperature oxalyl chloride (2.8 ml, 32 mmol) was added and the solution was stirred for 2 hr. The resulting suspension was filtered, and the filtrate was evaporated to dryness, resulting in 0.85 g of 4, which was used in the next step without purification. \(^{1}\)H NMR (CDCl\(_3\)): \(\delta\): 3.07 (t, 4H, O=C=N-CH\(_2\)), 2.40 (t, 4H, C\(_2\)H\(_2\)-C), 1.94 (m, 4H, CH\(_2\)-C\(_2\)H\(_2\)-CH\(_2\)).

1,10-Diisocyanato-deca-4,6-diyne (5).\(^{33}\) To 5,7-Dodecadiynedioic Acid Dichloride (4, 1.8 g, 6.98 mmol) in dry acetonitrile (25 ml) was added sodium azide (1.0 g; 15.3 mmol) with stirring under an argon atmosphere. The reaction mixture was heated to 65\(^\circ\)C. \(N_2\) started to evolve. After the nitrogen evolution was negligible (1 hour), a white solid was filtered off, and the filtrate was purified by distillation. The diisocyanate was collected as a colorless oil (0.75 g; 50%). \(^{1}\)H NMR (CDCl\(_3\)): \(\delta\): 3.45 (t, 4H, O=C=N-CH\(_2\)), 2.39 (t, 4H, CH\(_2\)-C), 1.80 (m, 4H, CH\(_2\)CH\(_2\)CH\(_2\)). \(^{13}\)C NMR: \(\delta\): 122.4 (O=C=N), 79.4 (CH\(_2\)-C), 65.9 (C-C\(_2\)), 42.2 (N-CH\(_2\)), 31.8 (CH\(_2\)-CH\(_2\)-CH\(_2\)), 13.7 (C-CH\(_2\)). IR \(\nu\): 2249.5 cm\(^{-1}\) (-N=C=O stretch).

3.8 References and Notes

Molecular Recognition in a Thermoplastic Elastomer *

Abstract

Selective incorporation of bisurea guests in thermoplastic elastomers with poly(tetrahydrofuran) soft blocks and bisurea containing hard blocks is observed when the distances between the urea groups of host and guest match. The incorporation leads to significant modulation of mechanical properties. With bisurea functionalized dyes as guests, a strong difference in extractability by detergent solution was shown between dyes differing by just one methylene unit between urea groups. Upon elongation of elastomer films, strong differences in alignability of matching and non-matching dyes was observed.

4.1 Introduction

Molecular recognition in polymers is used extensively to selectively bind small molecules or ions and it provides a powerful tool for the modulation of materials properties.\textsuperscript{1-4} In elastomeric polymers, reversible alignment of e.g. covalently attached azobenzenes molecules\textsuperscript{5} or non-covalently embedded fluorescent dyes\textsuperscript{6} by mechanical deformation of the polymeric matrix has been used to tune the optical properties of the resulting materials. Smith \textit{et al.} studied the orientation of dyes and $\pi$-conjugated polymers that were blended with polyolefins.\textsuperscript{7} Subsequent drawing of the films resulted in highly oriented chromophores, with dichroic ratios exceeding 20 (Figure 4.1).

![Polarized optical microscopy image of a 1% w/w MeO-BPB/UHMW-PE blend before (a) and after (b) orientation ($l/l_0 \approx 25$) (Image adapted from reference 7c).]

Figure 4.1. Polarized optical microscopy image of a 1% w/w MeO-BPB/UHMW-PE blend before (a) and after (b) orientation ($l/l_0 \approx 25$) (Image adapted from reference 7c).

Here, we demonstrate the design of thermoplastic elastomeric hosts bearing uniform bisurea recognition units\textsuperscript{8} and size selective guests that self-assemble into supramolecular ribbons (Figure 4.4) to form functional materials.

Urea groups are known to associate strongly via bifurcated hydrogen bonds\textsuperscript{9}, whose strength exceeds that of amide and urethane hydrogen bonds. Several research groups have utilized the strong association between low molecular weight compounds containing bis-urea groups to obtain gelling agents\textsuperscript{10}. Also thermoplastic elastomers (TPEs) containing urea groups have been synthesized before.\textsuperscript{11} There are however only a few examples of TPEs possessing hard blocks comprising solely urea groups.\textsuperscript{12} Block copoly(ether urea)s 1 and 2 (Scheme 4.1) are a new class of thermoplastic elastomers containing urea groups. They consist of poly(tetrahydrofuran) (pTHF) soft segments ($M_n = 1100$) and uniform bis-ureido-butylene or bis-ureido-pentamethylene hard segments for 1 and 2, respectively. Association of the hard segment domains via hydrogen bonding results in the formation of reversible crosslinks embedded in a soft, rubbery, amorphous pTHF matrix, as was previously demonstrated in Chapter 2.

The design of thermoplastic elastomers 1 and 2 with uniform bisurea hard blocks allows for the incorporation of guests molecules bearing a complementary bisurea moiety via a “perfect-fit”-principle. In this way, modification of the polymer properties, or functionalization of the material can be effectuated in a modular approach, by simply mixing the complementary guests with the polymers (Scheme 4.1). This perfect-fit principle, or molecular recognition within polymers has been studied before in solution. One example from the group of Rotello is shown
in Figure 4.2. Rotello et al. studied guest affinities of polymers featuring a single recognition site in the middle of the polymer chain. The host-guest dyad used in this system is based on diaminopyridine and flavin. Eventually they would like to use their systems for drug-delivery and catalysis.

![Host-guest dyad](image)

**Figure 4.2. Structure of host-guest dyads based on 2,6-diacyldiaminopyridine and flavin and the resulting polymeric host material as studied by Rotello et al.**

In order to establish the suitability of our segmented copoly(ether urea)s for applications such as catalysis, the selectivity of the bisurea recognition unit has been studied in detail. To this end, matching and non-matching bisurea functionalized reinforcement fillers have been incorporated into the elastomeric host-material to see if the properties of the resulting materials can be tuned. Furthermore, selective modulation of the optomechanical properties of the host-guest material by incorporation of matching and non-matching bisurea functionalized dye molecules has been studied in detail.

### 4.2 Design of selective host-guest system

To gain more insight into the way bisurea units associate via hydrogen bonding, crystals were grown from two model compounds (Figure 4.3) containing an ‘even’ bisureido-butylene (3) and an ‘odd’ bisureido-heptylene unit (4). After synthesis, single crystals suitable for X-ray analysis were obtained by slow diffusion of water vapor into a 50 g/l solution of 3 or 4 in DMSO.

From the crystal structures it could be concluded, that the all-trans conformation of the ‘even’ butylene spacer, leads to a transoid arrangement of the two urea groups, whereas the all-cis conformation of the ‘odd’ heptylene spacer leads to a cisoid arrangement of the two urea groups. The urea groups and the spacer are virtually co-planar. The angle between the least-squares planes through the urea group and through the carbon atoms or the spacer are 7.84(10)° for structure 3 and 2.78(7)° for structure 4.

In both crystal structures bifurcated hydrogen bonding between adjacent urea groups gives rise to the formation of infinite stacks of hydrogen bonds, with a spacing between the two hydrogen bonded urea groups of 4.64(8) Å for the 'even' butylene spacer and 4.63(10) Å for the 'odd' heptylene spacer. These values are comparable to the distances in crystal structures of $N, N'$-dialkylureas described in literature. $^{8b,9, 10b,e,f}$

Figure 4.3. Single crystal X-ray structure of 3 (a) and 4 (b).
To see whether block copoly(ether urea)s 1 and 2 with a uniform bisurea hard block would form similar long stacks via hydrogen bonding of the urea groups as described above, the morphology of 1 in a thin film was studied with AFM in the tapping mode. Figure 4.4 shows the resulting AFM images, in which the hard phase appears lighter than the soft phase.

Figure 4.4. AFM images (1µm²) of thermoplastic elastomer 1; height (left) and phase contrast (right).

The AFM images show long fibers with a length of up to 500 nm and an apparent width of 10 nm. Smaller details cannot be discerned since the dimensions of the AFM tip limit the resolution. The fibers most probably consist of stacks of bisurea hard blocks embedded in the soft matrix. The stacks were used to intercalate guest molecules functionalized with a bisurea recognition unit.

4.3 Modification of polymer properties

Polymers 1 and 2, differing from each other by just one methylene group between the two urea groups, are rubber-like materials with a flow point of 140 °C and 105 °C, respectively. The molecular weights Mₙ (as determined with SEC) of 1 and 2 are 45 × 10³ and 50 × 10³ g/mol, respectively. They have an elastic modulus of 95.7 and 82.8 MPa, respectively; plastic deformation sets in at λ = 80% and the elongation at break is approximately 1060%. The relative orientations of the urea groups in the hard blocks of these TPEs are expected to be transoid and cisoid based on the odd-even effect (4 and 5 methylene units, respectively) observed in the crystal structures of model compounds 3 and 4 (4 and 7 methylene units). The effects of 5 and 6 as additives (4 and 5 methylene units between urea groups) on the thermomechanical properties of 1 and 2 are remarkably different. Solution cast films of 1 containing 5, a low molecular weight bisurea compound matching the hard block of 1, were transparent up to 12 wt%. In contrast to this, films of 1 containing 6, which has a non-matching pentamethylene spacer between its two urea groups, were turbid due to phase separation even when small amounts (1 wt%) of the additive were added. The effect of the presence of different amounts of 5 or 6 on the flow temperature of 1 and 2, as determined with optical microscopy, is shown in Figure 4.5. An increase of the flow temperature of 1 from 140 to 175 °C was observed upon addition of 20 wt% of filler 5, whereas the flow temperature only increased to 150 °C upon addition of the same amount of 6, strongly suggesting preferred incorporation of 5 in the hard blocks of 1.
Figure 4.5. Flow temperature of 1 (a) and 2 (b) as a function of the amount of reinforcement filler 5 or 6. Lines are used as guide for the eyes.

To make sure that we are not just looking at differences in the melting points of 5 and 6, similar experiments have also been performed on films of 2 containing different amounts of 5 or 6. A similar trend could be observed for mixtures of 2 and non-matching and matching additives 5 and 6, supporting the preferred incorporation. The flow temperature of 2 increased from 105 °C to 137 °C upon addition of 17 wt% of 6 whereas it only increased to 113 °C upon addition of the same amount of 5.

4.4 Selective extraction of dyes

To further study molecular recognition within block copoly(ether urea)s, extractability of dyes by detergent solution was studied. To this end 0.25 wt% of bisurea functionalized azobenzene dyes 8 or 9, having 4 and 5 methylenes in the spacer between the urea groups, were incorporated in films of thermoplastic elastomers 1 and 2. Combining these compounds gave two matching polymer-guest pairs (1 + 8 and 2 + 9), and two non-matching pairs (1 + 9 and 2 + 8). In none of the films phase separation was observed with optical microscopy. Four similar sized pieces were cut from these films and they were individually stirred in 0.1 M sodium dodecyl sulphate solutions at 60 °C. Extraction of the dyes was followed with UV-Vis spectroscopy of the solutions. The results depicted in Figure 4.6 show that the dyes containing bisurea units that match the hard block of the elastomer are extracted more slowly and to a lesser extent than the non-matching dyes. After 60 hours only 38% of the complementary dyes was extracted from the film compared to approximately 80% of non-complementary dyes, demonstrating the size selectivity of the dye incorporation. The consistently higher extractability of non-matching dyes excludes differences in solubility between the dyes as a possible cause for the effect.
Figure 4.6. (a) Table showing combinations of TPEs and dyes used in extraction experiments. (b) Percentage of dyes 8 and 9 extracted from films of 1 and 2 by aqueous SDS solution as determined with UV-Vis spectroscopy.

Differential dye extraction was also studied in thin fibers of 1 and 2 produced by electrospinning, a technique that produces fibers of nanometer to micrometer size in diameter. Electrospinning of fibers is performed by slowly pumping a polymer solution through a millimeter size nozzle that is connected to a high-voltage supply (12kV). Under the applied electrostatic force, the polymer is ejected from the nozzle as a fiber whose diameter is reduced significantly as it is transported and deposited on a grounded template.\(^{17}\) In this way, materials with a high surface to volume ratio can be obtained, with interesting applications ranging from nano-fiber reinforced composite materials\(^ {18}\) to supports for enzymes\(^ {19}\) and catalysts\(^ {20}\) to sensors.\(^ {21}\)

Fibers of 1 and 2, containing 0.25 wt% dye 9 were spun and analyzed with Scanning Electron Microscopy (SEM), showing very uniform fibers with a diameter of approximately 4 µm (Figure 4.7).

Figure 4.7. SEM image of electrospun sample of 2 containing 0.25wt% of 9. A voltage of 12 kV was applied, a flowrate of 25 µl/min and a height of 20 cm between nozzle and grounded collection plate.

Extraction of the dyes, as described above for films of 1 and 2, was repeated with dye 9 incorporated in electrospin fibers of non-complementary polymer 1 and complementary
polymer 2. The extraction kinetics were much faster in the electrospun fibers due to the increased surface area to volume ratio and slightly more of the dye was extracted. Whereas extraction of films took several hours, extraction reached its final value of 90 % and 50 % respectively after 20 minutes for the electrospun fibers (Figure 4.8).

![Figure 4.8. Percentage of 9 extracted from dyed electrospun fibers of 1 and 2 as determined with UV-Vis spectroscopy.](image)

4.5 Dye orientation

Orientation and alignment of dyes by mechanical deformation is a useful way to modulate optical properties of polymer films.\(^6^,\)\(^7\) The present system offers interesting possibilities to perform mechanical alignment in a guest selective manner. To study guest selective orientation, we first investigated mechanical orientation of urea blocks of host polymers 1 and 2 with infrared linear dichroism spectroscopy,\(^1^4\) a technique that has often been used to study the orientation of functional groups within polymers.\(^2^2\) Using this technique, strain induced orientation of hard segments in polyether urethane ureas has been shown to be perpendicular to the deformation axis at strains beyond the yield point.\(^2^3\) In films of 1, the dichroic ratio of absorption bands due to stretch vibrations was measured with polarized infrared light parallel and perpendicular to the deformation axis. Significant differences were observed between dichroic ratios of bands arising from the hard segment at \(\nu = 3325 \text{ cm}^{-1}\) (N-H stretching vibration) and 1615 cm\(^{-1}\) (C=O stretching vibration) and from the soft segment at \(\nu = 1110 \text{ cm}^{-1}\) (C-O-C stretching vibration). The dichroic ratio of the urea groups in the hard segments reaches values of close to 5 at high strains, indicating that the chain-axis of the hard segment orients parallel to the deformation axis, while the dichroic ratio of the soft pTHF blocks remains below 1.5.

Orientation of dye chromophores was studied by UV spectroscopy in films of 1 and 2 containing small amounts (0.25 wt%) of dye molecules 7, 8 or 9, prepared by dissolving both components in a chloroform/methanol mixture and casting the solution in a Petri-dish. UV-Vis spectra were measured at 0° and 90° polarization angles with respect to the deformation axis and the dichroic ratio was determined at \(\lambda_{\text{max}}\).
Upon elongating films of 1 containing 0.25 wt% of complementary 8, the dichroic ratio increased rapidly, reaching values of 11 for $\lambda = 500\%$ (Figure 4.9a), indicating that the chromophore of the dye is oriented parallel to the deformation axis upon stretching the film. On the other hand, the dichroic ratio for non-complementary dye 9 does not exceed a value of approximately 3 while for mono-urea functionalized dye 7 the dichroic ratio remains below 2, indicating that both 7 and 9 do not orient as strongly as 8. Similar trends were observed for films of 2 to which were added 0.25 wt% of matching dye 9 or non-matching dyes 7 and 8 (Figure 4.7(b)). After relaxation of samples of 1, which were strained to 500%, residual strain was 220%, indicating significant plastic deformation. The dichroic ratio of 8 decreased from 11 to 4.7 after releasing the stress, while for 9 as guest the dichroic ratio decreased from 3 to 1.5.

![Figure 4.9](image1.png)

**Figure 4.9.** Dichroic ratio dye 7, 8 and 9 at $\lambda_{\text{max}}$ (between 405 and 420 nm) in 1 (a) and 2 (b) as function the elongation of dyed films.

The high dichroic ratio observed in elongated films of matching dye and TPE indicates specific incorporation of urea-functionalized dyes in the hard domain of the elastomer resulting in orientation of the transition dipole moment of the dye parallel to the deformation axis. This is schematically depicted in Figure 4.10.

![Figure 4.10](image2.png)

**Figure 4.10.** Schematic representation of dye 8 in the hard block of an elongated film of 1.
The much lower dichroic ratio of non-matching dyes is in line with predominant location in the more weakly oriented amorphous phase.

Further support for the different locations of matching and non-matching dyes comes from the positions of $\lambda_{\text{max}}$ for matching pairs of dye and elastomer ($\lambda_{\text{max}} = 406 \text{ nm}$) and non-matching pairs of dye and elastomer ($\lambda_{\text{max}} = 420 \text{ nm}$). The latter $\lambda_{\text{max}}$ is close to the value of 423 nm found for both dyes in amine-terminated pTHF prepolymer 11, the molecule constituting the soft phase of the TPEs. Upon dissolution of both 8 and 9 in the pTHF prepolymer clear films are obtained, indicating that both 8 and 9 are molecularly dissolved in the prepolymer, which constitutes the soft phase of elastomers 1 and 2. The fact, however that the shape of the absorption band does not change upon going from a matching to a non-matching host is a good indication that the dye molecules are not self-aggregated in either of these host phases.

For the matching pairs of dye and elastomer the perpendicularly polarized $\lambda_{\text{max}}$ shifted from 406 nm to 414 nm upon elongating the films above 300%, whereas no shift was observed for the non-matching pairs. Absorption of light with this polarization is mainly caused by non-oriented dye molecules. This is a strong indication that also the matching dyes are partly present in the pTHF soft block. Thus both dye extraction and dye orientation experiments allow the conclusion that matching dyes are taken up preferentially in the hard blocks, while non-matching dyes are predominantly present in the soft block.

### 4.6 Discussion and Conclusions

We have shown that length-dependent molecular recognition between bisurea units in an elastomeric host results in selective modulation of mechanical properties. Strong discrimination between guests differing in size by a single methylene group was observed. Incorporation of bisurea containing dye molecules in the hard blocks of the polymer is also selective, resulting in different extractabilities of the dyes by detergent solutions. The guest selectivity of the elastomeric material can be used to selectively orient dyes upon elongation of thin films. With the possibility to draw functionalized fibers by electrospinning we introduce a modular approach for thermoplastic meshes with a variety of applications.

The extractability studies clearly showed that even when matching dyes are incorporated in the segmented copoly(ether urea)s, a part of these dyes can still be extracted. UV-studies showed that most probably a part of the matching dyes are dissolved in the pTHF soft segments. This part is most probably extracted from the segmented copoly(ether urea)s similar to the non-matching dyes. It is however not straightforward to determine the amount of the matching dye that is dissolved in the pTHF soft segments.

Orientation studies of pure segmented copoly(ether urea)s showed that at low strains the chain axis in the bisurea hard segments orients perpendicular to the deformation axis. At higher strains the hard segments open up and become oriented along the direction of
elongation. When looking carefully to Figure 4.9, in which the results of the orientation studies of the films containing matching and non-matching dyes are plotted, the dyes follow the deformation behavior of the copolymer at high strains (the transition dipole moment of the dye becomes oriented parallel to the deformation axis as a function of elongation). However, perpendicular orientation of the transition dipole moment of the dye is not observed at low strains. The reason why the orientation mechanism for the dye does not follow the orientation of the segmented copolymer is unknown so far.
4.7 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$_2$O$_5$; dry tetrahydrofuran (THF) was obtained by distillation from Na/K/benzophenone; dimethylformamide was dried over BaO; pyridine was dried by standing over 4Å molsieves and dry toluene was obtained by distillation from Na/K/benzophenone. Di-tert-butyl tricarbonate was synthesized following previously described procedures.$^{24}$ 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). $^1$H-NMR and $^{13}$C-NMR spectra were recorded on a 500 MHz Varian Unity Inova 500, a 400 MHz Varian Mercury Vx and a 300 MHz Varian Gemini-2000. Proton and carbon chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) using the resonance of the deuterated solvent as internal standard. Elemental analysis was performed on a Perkin Elmer 2400 series II CHNS/O Analyser. 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 α-cyano-4-hydroxycinnamic 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. SEM was carried out using a JEOL JSM 840 A microscope using an acceleration voltage of 1 kV and an SE detector.

Atomic Force Microscopy (AFM). Samples for the atomic force microscopy (AFM) study were prepared by dropcasting 1 mg/ml solutions in chloroform/methanol on silicon wafers. AFM experiments were performed using a NanoScope III A instrument operating in the tapping mode, utilizing NanoSensor tapping tips. The amplitude of oscillation at free vibration, $A_0$, was set to 4.0V. The operating setpoint ratio ($A/A_0$) was set to relatively low values ($A/A_0$~0.7).

Preparation of (filled) films. Copoly(ether urea) 1 or 2 (2 g) and the desired amount of 5-9 were dissolved in chloroform (15 ml) and methanol (5 ml). This solution was filtered and cast in a silylated Petri-dish (diameter 9 cm), and the solvent was allowed to evaporate slowly by placing a beaker over the dish. After 15 hours the films were dried in vacuo at 50 °C for 5 hours and peeled off the Petri-dish.

Electrospinning. A 7 wt% solution of 1 or 2 in chloroform containing 0.25 wt% of 9 with respect to 1 or 2 was pumped (25 µl/min) through a nozzle that was subjected to a voltage of 12 kV. Under the applied electrostatic force, the polymer was ejected from the nozzle and was collected on a grounded collection plate 20 cm below the nozzle.

Infrared linear dichroism spectroscopy. Infrared (IR) spectra were recorded by means of a Biorad UMA 500 microscope, coupled to an FTS6000 FT-IR spectrometer. Films with a thickness of 10 µm were cast in a Teflon mould, and tensile bars were punched. Those were clamped and elongated. Infrared spectra were recorded in transmission at 0° ($A_{∥}$) and 90° ($A_{⊥}$) polarization angle with respect to the deformation axis and the dichroic ratio (DR = $A_{⊥}/A_{∥}$) was determined at 3325, 1615 and 1100 cm$^{-1}$.

UV-Vis spectroscopy. UV-Vis spectra were recorded on a Perkin Elmer Lambda 900 spectrometer equipped with a polarizer accessory. Films of 1 and 2 containing 0.25 wt% of 7, 8 or 9 were elongated and clamped, and spectra were recorded at 0° ($A_{∥}$) and 90° ($A_{⊥}$) polarization angle with
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respect to the deformation axis. The Dichroic Ratio (DR = \( \frac{A_{||}}{A_{\perp}} \)) was determined at \( \lambda_{\text{max}} \) (between 405 and 420 nm).

**Single-Crystal X-ray Structure Analysis.** Pertinent data for the structure determinations are given in Table 7.1. Data were collected at 150K on a Nonius KappaCCD diffractometer on rotating anode (graphite monochromated Mo Kalpha radiation, \( \lambda = 0.71073 \) Å). Structures were solved with direct methods using shelxs86\textsuperscript{25} and refined on \( F^2 \) using shelxl-97.\textsuperscript{26} No observance criterion was applied during refinement. All hydrogen atoms were located on difference Fourier maps and their co-ordinates were included as parameters in the refinement. The non-hydrogen atoms of all structures were refined with anisotropic displacement parameters. The hydrogen atoms were refined with a fixed isotropic displacement parameter linked to the value of the equivalent isotropic displacement parameter of their carrier atoms. Neutral atom scattering factors and anomalous dispersion corrections were taken from the International Tables for Crystallography.\textsuperscript{27} Validation, geometrical calculations, and illustrations were performed with PLATON.\textsuperscript{28}

### Table 4.1. Crystallographic Data for Crystal Structure Determinations of 3 and 4.

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</tr>
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</table>

#### Data collection

| X-ray exposure, h | 4.5 | 3.8 |
| \( \theta \)\(_{\text{min}}, \theta \)\(_{\text{max}}\), deg | 1.6, 27.45 | 1.00, 27.50 |
| Data set (hkl) | -46:46, -6:6, -12:12 | -54:54, -5:6, -12:12 |
| Total data | 15525 | 19679 |
| Total unique data | 1849 | 2177 |
| \( R_{\text{int}} \) | 0.0572 | 0.0483 |

#### Refinement

| No. of refined params | 142 | 165 |
| Final R1\(^b\) | 0.0373 {1598 I > 2\( \sigma \)(I)} | 0.0378 {1624 I > 2\( \sigma \)(I)} |
| Final wR2 \( ^b \) | 0.1067 | 0.1082 |
| Goodness of fit | 1.033 | 1.033 |
| \( w^2 \) \( ^c \) | \( \frac{\sigma^2(F^2)}{w} + 0.0642P^2 + 0.70P \) | \( \frac{\sigma^2(F^2)}{w} + (0.0648P)^2 + 0.25P \) |
| Min. and max. residual. density, e Å\(^{-3}\) | -0.23, 0.22 | -0.24, 0.19 |

\(^a\) \( R1 = \sum \left| F_0 \right| - |F_0| \sum |F_0| \)

\(^b\) \( wR2 = \left[ \sum w(F_0^2 - F_c^2)^2 \right] / \left[ \sum w(F_0^2)^2 \right] \right)^{1/2} \)

\(^c\) \( P = \left[ \left( F_0^2 \right) + 2F_c^2 \right] / 3 \)
Synthesis of 3 - 10. The syntheses of compounds 1 and 2 have been reported previously.29

3,3'-Bis-phenyl-(butylene-1,4)-bisurea (3). 1,4-Diaminobutane (2.00 g, 22.7 mmol) was dissolved in chloroform (30 ml), and phenylisocyanate (5.94 g, 50.0 mmol) in chloroform (20 ml) was added dropwise. The suspension was stirred for 1 h, filtered, washed with chloroform, and dried. The product was obtained as a white, microcrystalline powder (7.10 g, 96%). Tm=243°C. 1H-NMR (DMSO-d6): δ 8.39 (s, 2H), 7.38 (dd, 4H, J ortho=8.2 Hz, J meta=0.9 Hz), 7.21 (m, 4H, J=7.7 Hz), 6.87 (t, 2H, J=6.8 Hz), 6.14 (t, 2H, J=5.7 Hz), 3.11 (m, 4H), 1.45 (m, 4H). 13C-NMR (DMSO-d6): δ 155.2, 140.6, 128.6, 120.9, 117.6, 38.8, 27.3. FT-IR (ATR): ν 3320 (N–H stretching), 2940, 2865, 1626 (C=O stretching), 1595, 1556, 1225, 732 cm⁻¹. Anal. Calcd. (%) for C18H22N4O2: C 66.24, H 6.79, N 17.17. Found (%): C 66.24, H 6.22, N 17.07.

3,3'-Bis-phenyl-(heptylene-1,7)-bisurea (4). 1,7-Diaminoheptane (2.00 g, 15.4 mmol) was dissolved in chloroform (30 ml), and phenylisocyanate (4.02 g, 33.8 mmol) in chloroform (20 ml) was added dropwise. The suspension was stirred for 1 h, filtered, washed with chloroform, and dried. The product was obtained as a white, microcrystalline powder (5.56 g, 98%). Tm=229°C. 1H-NMR (DMSO-d6): δ 8.39 (s, 2H), 7.38 (dd, 4H, J ortho=8.2 Hz, J meta=0.9 Hz), 7.22 (m, 4H, J=7.7 Hz), 6.89 (t, 2H, J=6.8 Hz), 6.10 (t, 2H, J=5.7 Hz), 3.07 (m, 4H), 1.42-1.30 (br. m, 10H). 13C-NMR (DMSO-d6): δ 155.6, 141.0, 129.0, 121.3, 117.9, 38.7, 30.15, 29.0, 26.8. FT-IR (ATR): ν 3320, 2940, 2865, 1626, 1595, 1556, 1225, 732 cm⁻¹. Anal. Calcd. (%) for C21H28N4O2: C 68.45, H 7.66, N 15.2. Found (%): C 68.51, H 7.72, N 15.35.

3,3'-Bis-hexyl-(butylene-1,4)-bisurea (5). 1,4-Diaminobutane (0.83 g; 9.36 mmol) was dissolved in chloroform (40 ml), and to this solution was added hexyl isocyanate (2.50 g; 19.66 mmol) in chloroform (20 ml). The solution turned turbid within minutes, and the reaction mixture was stirred for 30 min, and subsequently filtered. The product was washed with chloroform, recrystallized from a 1:1 methanol/chloroform mixture (150 ml) and dried in vacuo. It was obtained as a white powder (2.63 g, 82%). Tm=220°C. 1H-NMR (400 MHz, DMSO-d6 120°C): δ 5.52 (br, 4H), 2.98 (t, 8H), 1.41 (m, 8H), 1.32 (m, 12H), 0.88 (t, 6H). FT-IR (ATR): ν 3321 (N–H stretching), 2931, 2858, 1614 (C=O stretching), 1567, 1476, 1221 cm⁻¹. Elemental analysis calcd (%) for C18H38N4O2: C, 63.12%; H, 11.18%; N, 16.36%. Found: C, 63.02%; H, 11.35%; N, 16.30%.

3,3'-Bis-hexyl-(pentylene-1,5)-bisurea (6). 1,5-Diaminopentane (0.96 g; 9.36 mmol) was dissolved in chloroform (40 ml), and to this solution was added hexyl isocyanate (2.50 g; 19.66 mmol) in chloroform (20 ml). The turbid reaction mixture was stirred for 30 min, and subsequently filtered. The product was washed with chloroform, recrystallized from a 1:1 methanol/chloroform mixture (100 ml) and dried in vacuo. It was obtained as a white powder (2.66 g, 80%). Tm=189°C. 1H-NMR (400 MHz, DMSO-d6 120°C): δ 5.72 (br, 4H), 2.95 (t, 8H), 1.35-1.21 (br.m, 22H), 0.86 (t, 6H). FT-IR (ATR): ν 3326 (N–H stretching), 2932, 2859, 1611 (C=O stretching), 1567, 1476, 1221 cm⁻¹. Elemental analysis calcd (%) for C19H40N4O2: C, 64.00%; H, 11.31%; N, 15.71%. Found: C, 64.19%; H, 11.53%; N, 15.73%.

3(2-Ethyl-hexyl)-1[4(4-nitro-phenylazo)-phenyl]-urea (7). 4-Isocyanato-4'-nitroazobenzene, 10, (0.31 g, 1.00 mmol) was dissolved in THF (15 ml), and 2-ethylhexylamine (0.20 g, 1.5 mmol) in THF (5 ml) was added. The reaction mixture was stirred at room temperature for 30 min, after which it was evaporated to dryness. The product was redissolved in chloroform (20 ml), and extracted with hydrochloric acid solution (10 ml 0.1 M in water), and saturated sodium bicarbonate solution (10 ml). The organic layer was dried with sodium sulfate, filtered and purified by column chromatography using 1% methanol in chloroform as the eluent (Rf = 0.4 ). The product was obtained as an orange solid (0.30 g, 75%). 1H-NMR (400 MHz, DMSO-d6): δ 9.02 (s, 1H), 8.41 (d, 2H, J=9.2 Hz), 8.01 (d, 2H, J=8.8 Hz), 7.91
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(d, 2H, J=8.8 Hz), 7.65 (d, 2H, J=8.8 Hz), 6.35 (t, 1H), 3.08 (q, 2H, J=5.9 Hz), 1.40 (m, 1H), 1.28 (m, 8H), 0.89 (t, 6H, J=6.2 Hz). 13C-NMR (10% methanol-d4 in CDCl3): 156.32, 148.21, 147.62, 144.10, 139.2, 125.04, 124.88, 123.04, 117.37, 41.61, 42.97, 30.43, 28.39, 23.65, 22.51, 13.97, 10.77 FT-IR (ATR): ν 3336 (N–H stretching), 2960, 2928, 1669 (C=O stretching), 1595, 1543, 1515, 1340, 1226, 1140, 1105, 859, 843, 685 cm⁻¹. Elemental analysis calcd (%) for C₂₁H₂₇N₅O₃: C, 63.46%; H, 6.85%; N, 17.62%. Found: C, 63.02%; H, 6.89%; N, 17.10%.

3[(2-Ethyl-hexyl)-3'[4(4-nitro-phenylazo)-phenyl](butylene-1,4)-bisurea (8). 4-Isocyanato-4'-nitroazobenzene, 10, (0.55 g, 2.07 mmol) was dissolved in THF (30 ml), and 4-(Tert-butoxycarbonylamino)-1-butyamine (0.58 g, 3.11 mmol) in THF (4 ml) was added. The reaction mixture was stirred at room temperature for 30 min, after which it was partially concentrated and precipitated in pentane (100 ml). The product was filtered off, and purified by column chromatography using 1% methanol in chloroform as the eluent (Rf=0.3). It was redissolved in dichloromethane (3 ml), and trifluoroacetic acid (2 ml) was added to deprotect the amine group. The reaction mixture was stirred at room temperature overnight, and subsequently evaporated to dryness.

Di-tert-butyl tricarbonate (0.40 1.54 mmol) was dissolved in chloroform (10 ml), and 2-ethylhexyl amine (0.19 g, 1.47 mmol) in chloroform (2 ml) was injected into the former solution. The reaction mixture was stirred for 30 min. The previously deprotected amine was dissolved in pyridine (50 ml), and added to the former solution. The reaction mixture was stirred for 30 min at room temperature, and then evaporated to dryness. The product was purified by column chromatography, first using pure chloroform as the eluent, then chloroform-methanol mixtures with up to 10% methanol (Rf = 0.2). The product was obtained as an orange solid (0.28 g, 27%). 1H-NMR (400 MHz, 10% methanol-d4 in CDCl3): δ 8.37 (d, 2H, J=8.1 Hz), 7.99 (d, 2H, J=8.4 Hz), 7.93 (d, 2H, J=9.2 Hz), 3.26 (t, 2H), 3.15 (t, 2H), 3.07 (t, 2H), 1.54 (m, 4H), 1.4-1.2 (m, 9H), 0.88 (t, 6H). 13C-NMR (10% methanol-d4 in CDCl3): 156.31, 155.75, 154.24, 147.98, 147.34, 144.23, 124.96, 124.95, 123.24, 117.98, 42.95, 39.67, 39.53, 39.11, 30.16, 29.12, 25.83, 23.97, 23.76, 23.01, 13.94, 10.69. FT-IR (ATR): ν 3322 (N–H stretching), 2924, 2859, 1633 + 1623 (C=O stretching), 1584, 1552, 1523, 1343, 1216, 1140, 865, 754 cm⁻¹. UV-Vis (THF): λmax=405 nm. Elemental analysis calcd (%) for C₃₀H₄₃N₇O₅: C, 61.04%; H, 7.29%; N, 19.16%. Found: C, 61.75%; H, 7.50%; N, 18.65%.

3[(2-Ethyl-hexyl)-3'[4(4-nitro-phenylazo)-phenyl](pentylene-1,5)-bisurea (9). 4-Isocyanato-4'-nitroazobenzene, 10, (0.55 g, 2.05 mmol) was dissolved in THF (30 ml), and 4-(Tert-butoxycarbonylamino)-1-pentylamine (0.58 g, 2.86 mmol) in THF (4 ml) was added. The reaction mixture was stirred at room temperature for 30 min, after which it was partially concentrated and precipitated in pentane (100 ml). The product was filtered off, and purified by column chromatography using 3% methanol in chloroform as the eluent (Rf=0.3). It was redissolved in dichloromethane (3 ml), and trifluoroacetic acid (2 ml) was added to deprotect the amine group. The reaction mixture was stirred at room temperature overnight, and subsequently evaporated to dryness.

Di-tert-butyl tricarbonate (0.43 1.65 mmol) was dissolved in chloroform (10 ml), and 2-ethylhexyl amine (0.20 g, 1.55 mmol) in chloroform (2 ml) was injected into the former solution. The reaction mixture was stirred for 30 min. The previously deprotected amine was dissolved in pyridine (50 ml), and added to the former solution. The reaction mixture was stirred for 30 min at room temperature, and then evaporated to dryness. The product was purified by column chromatography, first using 5% methanol in chloroform as the eluent, then chloroform-methanol mixtures with up to 10% methanol (Rf = 0.2). The product was obtained as an orange solid (0.26 g, 24%). 1H-NMR (400 MHz, 10% methanol-d4 in CDCl3): δ 8.34 (d, 2H, J=9.1 Hz), 7.96 (d, 2H, J=8.8 Hz), 7.89 (d, 2H, J=8.8 Hz), 7.57 (d, 2H, J=8.8 Hz), 3.23 (t, 2H), 3.13 (t, 2H), 3.05 (t, 2H), 1.54 (m, 4H), 1.4-1.2 (m, 11H), 0.88 (t, 6H). 13C-NMR (10% methanol-d4 in CDCl3): 156.12, 155.98, 154.20, 148.07, 147.31, 144.39, 124.95, 124.65, 123.04, 117.98, 42.97, 39.71, 39.55, 39.37, 30.84, 29.62, 29.05, 28.83, 23.97, 23.72, 22.96, 13.92, 10.69. FT-IR (ATR): ν 3322 (N–H stretching),
2924, 2859, 1633 + 1623 (C=O stretching), 1584, 1552, 1523, 1343, 1226, 1140, 1106, 865, 754 cm⁻¹. UV-Vis (THF): λ_max=405 nm. Elemental analysis calcd (%) for C₂₇H₃₉N₇O₄: C, 61.69; H, 7.48%; N, 18.65%. Found: C, 61.84%; H, 7.21%; N, 18.54.

4-Isocyanato-4’-nitroazobenzene (10). Disperse Orange (4-(4-Nitro-phenylazo)-aniline) (0.50 g, 2.07 mmol) was dissolved in THF (40 ml), and phosgene (2.2 ml 20% in toluene, 4.1 mmol) was added. The reaction mixture was heated to reflux temperature and stirred for 1 h, while argon was bubbled through the solution. It was evaporated to dryness, and the product was obtained as a red solid. FT-IR (ATR): ν 2257 (NCO), 1734 (NHCOCl) cm⁻¹.

4.8 References and Notes


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G.M. Sheldrick, SHELXS86, Program for crystal structure determination; University of Göttingen, Germany, 1986.

G.M. Sheldrick, SHELXL-97, Program for crystal structure refinement; University of Göttingen, Germany, 1996.


Abstract

Electrospun segmented block copoly(ether urea)s, containing supramolecularly bound rhodium phosphine complexes, have been shown to be efficient catalysts for the hydroformylation of 1-octene. The ligands used in this study are mono- and diphosphine ligands 1 – 3 based on triphenylphosphine, equipped with a bisurea recognition unit, required for hydrogen bond formation to the segmented block copoly(ether urea)s. The activity and selectivity observed for supported and unsupported rhodium-phosphine complexes of 2 are comparable. The solvent used for the hydroformylations appeared to have a large impact on the observed activity. The activity was the highest in toluene, which causes the solid support to swell. The immobilization conditions also appeared to have a large influence on the outcome of the hydroformylation reactions. Fibers drawn from solution, in which the metal-ligand complex is prepared prior to association to the elastomer in chloroform, show a higher selectivity than fibers prepared from solutions, in which the ligand was associated to the elastomer prior to addition of the metal precursor. The ability to recycle the supported catalyst system based on ligand 2 was studied by performing a series of consecutive hydroformylation runs. These recycling studies show unchanged selectivity and even increased activity during the first 3 runs. After that the catalyst performance starts degrading, probably due to the formation of rhodium nano particles, rhodium leaching or catalyst decomposition.
5.1 Introduction

The development of well-defined catalyst systems that allow rapid and selective chemical transformations and at the same time can be completely recovered from the product is a well-studied research area in basic and applied chemistry.

Biphasic catalysis is a well-studies approach to facilitate catalyst recovery. The aqueous biphasic system developed by Ruhrchemie/Rhône-Poulenc is a good example of such a process.\(^1\) It involves water-soluble ligands in combination with a rhodium precursor, providing an active catalyst for hydroformylations that can be easily separated from the organic phase and recycled. Its main drawback however is the fact that it can only be applied to substrates that are slightly water-soluble, such as propene and 1-butene. In the industrial hydroformylations of higher olefins, which are not soluble in water, the catalyst has to be separated by extractions or distillation, which causes partial decomposition. Solid supports might offer an alternative in this respect.

![Figure 5.1. Schematic representation of biphasic catalysis: A homogeneous catalyst is tailored to dissolve in water, while the reactant is dissolved in an organic solvent (Left). At the reaction temperature, catalyst, reactant, and solvents form a single phase in which the reaction takes place (Middle). After the reaction is completed, the system is cooled down, resulting in phase separation. The catalyst and product are in separate phases, facilitating separation (Right) (Image adapted from reference 2).](image)

More recently Horvath, Gladysz and co-workers published a new example of biphasic catalysis called "fluorous catalysis" in which fluorocarbons are used to support a homogenous catalyst with highly fluorinated ligands.\(^3\) Teflon-like "ponytails" are chemically attached to phosphine ligands bound to a metal center. The perfluoroalkyl group imparts high solubility in fluorocarbon solvents, and the methylene spacers insulate the phosphorus center from the electron-withdrawing fluoro-substituents. Heating hydrocarbon/fluorocarbon mixed solutions of these catalysts and substrates results in a single phase and effective catalysis for several reactions. After the reaction is complete, the system can be cooled for phase separation (Figure 5.1).

An intensively studied and promising approach to facilitate catalyst-product separation is the attachment of homogeneous catalysts to polymeric organic, inorganic, or hybrid
supports⁴, and more recently to dendritic supports⁵,⁶. Key problems for many of these approaches, however, involve catalyst instability and leaching of catalytic material in the product phase during the recycling procedure.⁷

Also silica appeared particularly suited as heterogeneous catalyst support, because of its high physical strength and chemical inertness. The covalent anchoring of hydroformylation catalysts onto inorganic silica surfaces was studied as early as the late seventies.⁸ The field of organo-functionalized silanes and polysiloxanes was pioneered by Pantser and coworkers, who used the very mild sol-gel process to obtain novel functional materials that allowed transition metal complexation.⁹ Sandee et al. recently reported the development of a polysilicate immobilized homogeneous catalyst system based on diphosphine ligands with large natural bite angles, based on the Xanthene backbone that can act both as a hydrogenation and a regioselective hydroformylation catalyst. The system affords a quantitative and straightforward separation of the catalyst from the products, it is reusable in numerous catalytic cycles without any deterioration of catalytic activity, and it enables clean and selective reactions for different important catalytic processes using only one catalyst system.¹⁰,¹¹

Polymers like polystyrene have also been studied widely for catalyst immobilization. The advantage of these supports is the relative ease of functionalization and furthermore the wide range of physical properties, which can be tuned by the degree of cross-linking. The drawbacks of these supports however, are their poor heat transfer properties and poor mechanical properties (they are pulverized in the reactor). Nozaki et al. recently reported the immobilization of a hydroformylation catalyst immobilized on a highly crosslinked polystyrene support. By using different ligands the degree of freedom of the ligand in the polymer matrix was varied. The influence of the degree of cross-linking and the polymer/catalyst preparation method was investigated.¹²

In all the systems mentioned above, the catalyst was covalently linked to the support. An interesting alternative approach would be the non-covalent anchoring of the catalysts to the support using well-defined binding sites. In this way the supports could in principle be easily de- and re-functionalized which enables the easy reuse of the support. Furthermore, multicomponent assemblies could be easily prepared, which is interesting for tandem reactions and combinatorial techniques. A comprehensive overview of supramolecular transition metal catalysis was recently written by Wilkinson et al.¹³

The group of Bianchini investigated utilization of hydrogen bonding for the non-covalent immobilization of Ru- and Rh-complexes on silica gel.¹⁴ The loading of the support was done on unmodified silica gel. The investigated supported complexes were used for hydrogenations of alkenes, nitriles and α,β-unsaturated ketones as well as for hydroformylation reactions. De Groot et al. described a very nice example of non-covalent anchoring of ligands to a soluble support. The efficient reversible functionalization of the periphery of urea adamantly poly(propylene imine) dendrimers with catalytic sites, using non covalent interactions was described. Phosphine ligands equipped with complementary urea acetic acid groups were prepared and assembled to the dendrimer support. The resulting supramolecular complex was used as a multidentate ligand system in the palladium catalyzed allylic amination.
The activity and selectivity of the dendritic complex was found to be similar to that of the monomer complex, indicating that the catalytic centers act as independent sites.\(^{15}\)

Very recently, Chen et al. described the efficient reversible functionalization of silica with catalytic sites using non-covalent interactions based on hydrogen bonds or metal-ligand interactions. Silica was prepared with well-defined binding sites that selectively bind guest molecules equipped with complementary binding sites. The immobilized complexes were used as a ligand system in the Pd-catalyzed allylic substitution and Rh-catalyzed hydroformylation of 1-octene.\(^{16}\) The supramolecular interaction between the transition metal catalyst and the binding site of the silica support was sufficiently strong to enable efficient catalyst recycling.

### 5.2 Hydroformylation

Hydroformylation of olefins to give aldehydes as predominant products was discovered by Roelen in 1938, and is an intriguing and well-studied reaction (Scheme 5.1).\(^{17,18}\) Today, this method has developed into an extremely important industrial process with worldwide capacity over seven million tons per year. The most important applications of the hydroformylation products are as plasticizers in polymers and as starting materials for detergents. Since mostly linear aldehydes are being used for these applications, control over regioselectivity is an important goal of research. Surprisingly, the product range of technical hydroformylation has remained nearly unchanged in the past five decades, although between 1965 and 1980 a remarkable diversification of products, refinement of methods and further development of the Co-based processes took place as did the initial application of Rh-based catalysts and its substitution of the Co-based process.\(^{19}\)

\[
R=CH=CHR' \xrightarrow{\text{[Rh]}} H_2, CO \xrightarrow{} R=CH-CHO + R-CHO + R'=CHR
\]

**Scheme 5.1. The Rhodium-Catalyzed Hydroformylation of Alkenes.**

Early studies found that alkene hydroformylation usually suffers from low selectivity and/or low yield. Fortunately, during the latest two decades, several effective catalysts such as the catalyst system of \([\text{Rh(CO)}_2(\text{acac})]\) and sophisticated bisphosphite ligands were developed. The discovery of rhodium as an active metal center has been one of the major breakthroughs in homogenous catalysis. They proved to be three orders of magnitude faster than their cobalt-analognes. Furthermore, selectivity for the linear product rose up to 90\%, while hydrogenation side-reactions were strongly suppressed. Heck et al. published the mechanism for the cobalt-catalysed hydroformylation in 1961\(^{20}\). Even though more detailed studies have now been performed, the general cycle has remained the same (Figure 5.2).
Figure 5.2. Simplified catalytic cycle for the rhodium-catalysed hydroformylation. For clarity reasons only the formation of the branched aldehydes is shown (Image reprinted from reference 21. For a more detailed mechanism, see 18).

In the first step of the catalytic cycle, a carbon monoxide molecule of the HRh(CO)$_2$PP resting state is substituted by an alkene, which coordinates in an equatorial position. In the next step, this species is converted into the alkyl-rhodium intermediate through insertion of the alkene into the Rh-H bond. Migratory insertion of the alkyl moiety to a CO molecule coordinated to the metal center provides the acyl-rhodium species, which, at the end of the catalytic cycle, interacts with hydrogen via an oxidative addition, giving rise to the aldehyde products and regenerates the rhodium-hydride species.

The ligand used greatly affects the regioselectivity and activity of the hydroformylation. Monodentate ligands were the first ligands to be reported to increase regioselectivity towards linear aldehydes. Monodentate triphenylphosphine ligands have been used in the hydroformylations of olefins in order to increase the selectivity towards linear aldehydes.

For bidentate ligands one property that can be defined is the bite angle, first described by Casey et al.\textsuperscript{22} The same group performed a study on the influence of this bite angle on the regioselectivity in the hydroformylation.\textsuperscript{23} They found that angles of around 120 ° increased the selectivity to linear products. In the case of a trigonal bipyramidal complex, such as Rh(H)(CO)$_2$(P)$_2$, which is the catalytic resting state in the hydroformylation, both donor atoms can be coordinated in an equatorial position (ee) or one in an equatorial and the other in an apical position (ea) (Figure 5.3). The ee coordination seems to be highly favorable for a good regioselectivity to the linear product and is mostly achieved by ligands having a large bite angle.

However, apart from steric factors, electronic factors should also be considered. Studies by Van der Veen et al. on the electronic effects of ligands showed that electron rich systems have a low ee to ea ratio and that electron deficient systems have much higher ee to ea ratio.\textsuperscript{24}
Apart from this preference for the ee position by electron deficient systems, studies by Casey et al. showed that electron deficient ligands on an equatorial position have a positive effect on linearity and that electron deficient groups on an apical position have a negative effect.\textsuperscript{25}

![Equatorial-equatorial and equatorial-apical coordination of a ligand to rhodium.](image)

**Figure 5.3.** Equatorial-equatorial and equatorial-apical coordination of a ligand to rhodium.

### 5.3 Ligand design

In Chapter 4 the specificity of molecular recognition of bisurea groups between host and guest molecules was shown. The modular approach provided us with a handle to supramolecularly and selectively incorporate all kinds of functional groups in our thermoplastic host material via the well-defined bisureum recognition unit. With the possibility to draw functionalized fibers by electrospinning, a modular approach to thermoplastic meshes was introduced with a variety of applications e.g. catalysis, drug-delivery etc. As a first attempt our thermoplastic elastomers will be used for supramolecular anchoring of catalysts as schematically depicted in Scheme 5.2. We believe that the key strength of our system might be its modular nature, which allows us for rapid structural variations and optimization of catalysts by just mixing together different components. It should be noted, that de- and re-functionalization of the support as shown by e.g. De Groot\textsuperscript{15} and Chen\textsuperscript{16} is not possible for our system (the support would simply be dissolved). Simple functionalization of our system with different ligands by just mixing the support and the ligands together, however, gives our system an advantage over covalently anchored systems. Therefore, our system could be placed in between the covalently bound systems of e.g. Nozaki\textsuperscript{12} and the non-covalently anchored systems of e.g. Chen\textsuperscript{16}.

![Scheme 5.2. The concept of supramolecular anchoring of catalysts to a polymeric support having complementary well-defined recognition units.](image)
Electrospinning of solutions of the copoly(ether urea)s, the ligands and the transition metal in chloroform provides us with a possibility to obtain meshes with a high specific area. As an indication: assuming a density of the copoly(ether urea)s of 1 g/cm$^3$ (the density of the prepolymer), 1 g of these elastomers would give rise to approximately 80 km of electrospun fibers with a diameter of 4 µm, resulting in a surface area of the fiber of approximately 1 m$^2$. This is important, since in supported catalysis the reaction mainly takes place at the interface between substrate and support. The resulting immobilized complexes will be used for hydroformylation reactions in apolar solvents using [Rh(acac)(CO)$_2$] as metal source. Since triphenylphosphines (TPPs) are well-studied ligands for hydroformylations, we decided to use TPP based mono- and diphosphines as ligands, which have been functionalized with a bisurea recognition unit (Scheme 5.3). The activity and selectivity of the immobilized complexes will be investigated, as well as the recyclability of the system by performing a series of consecutive runs.

Scheme 5.3. Mono- and bidentate triphenylphosphine ligands 1 – 3 equipped with a complementary bisurea recognition unit.

5.4 Synthesis of ligands 2 and 3

Diphosphine ligand 1, appeared to be difficult to dissolve in concentrated solutions of the segmented block copoly(ether urea)s in chloroform (6 w%). Dissolving 10 mol% of 1 relative to the copoly(ether urea) in these viscous solutions took over a week. Since these viscous solutions are needed to electrospin meshes of the elastomer, a more soluble analogue of 1 was synthesized (2). One way to increase the solubility of 1 is to incorporate a spacer between the ureum group and TPP. For synthetic reasons a methylene spacer was added according to Scheme 5.4. Furthermore monophosphine ligand 3 was synthesized. In this way comparison of the activity and regioselectivity of the hydroformylation with mono- and diphosphine ligands is made possible.

For the synthesis of 2 and 3 (Scheme 5.4), $p$-cyanodiphenylphospane was required. A nucleophilic phosphorylation of 4-chlorobenzonitrile was used to synthesize $p$-cyanodiphenylphospane$^{26}$ The phosphanylbenzylamine was readily accessible in a straightforward manner using LiAlH$_4$. In the final step the phosphanylbenzylamine was coupled to hexanediisocyanate in chloroform, leading to 2, which was characterized with $^1$H-NMR, $^{13}$C-NMR, $^{31}$P-NMR, Maldi-TOF MS and elemental analysis. The overall yield was approximately 58%.

To obtain 3, diaminohexane was mono-Boc protected with di-tert-butyldicarbonate. Subsequently it was converted to the isocyanate with di-tert-butyl tricarbonate and reacted with
phosphanylbenzylamine. It was then deprotected with trifluoro acetic acid and coupled with ethylhexylisocyanate, which was obtained from the corresponding amine after reaction with di-tert-butyl tricarbonate. The product was purified by means of column chromatography (1: 100% CHCl₃, 2: 4% MeOH/CHCl₃). Due to difficulties during the purification steps the overall yield was only 23%. 3 was characterized with ¹H-NMR, ¹³C-NMR, ³¹P-NMR, Maldi-TOF MS and elemental analysis.

5.5 Mesh preparation

Meshes of pTHF₁₁₀₀µ₆µ containing 10 mol% of ligands 1, 2 or 3 relative to bisurea groups of the elastomer and 10 mol% of [Rh(acac)(CO)₂] relative to TPP were prepared via electrospinning. All 3 meshes were analyzed with SEM and the results are shown in Figure 5.4. All meshes contain 2 µm thin fibers, showing no signs of crystallites of the ligands or [Rh(acac)(CO)₂]. This is a good indication that they have been incorporated into the fibers.
Figure 5.4. SEM images of electrospun fibers of pTHF₁₁₀U₆U containing 10 mol% 1 (a), 2 (b) or 3 (c) relative to bisurea groups of the elastomers, and 10 mol% [Rh(acac)(CO)₂] relative to TPP. The following electrospinning conditions were applied: A voltage of 12 kV, a flow rate of 15 µl/min and a height of 20 cm between the nozzle and collection plate.

All hydroformylation reactions presented in the remainder of this chapter have been performed on meshes containing bifunctional ligand 2 and [Rh(acac)(CO)₂]. In all reactions the molar ratio between 2 and [Rh(acac)(CO)₂] was kept at approximately 10:1. The ratio between substrate and rhodium was 4000:1. The solutions from which these meshes were electrospun were prepared in two ways. Method 1): A solution of [Rh(acac)(CO)₂] and ligand 2 in chloroform was added to a viscous chloroform solution of the elastomer. Method 2): first ligand 2 was dissolved in a viscous chloroform solution of the elastomer, followed by the addition of [Rh(acac)(CO)₂] prior to using these solutions for electrospinning. It is expected that meshes obtained from solutions prepared via both methods behave differently in the rhodium-catalyzed hydroformylation reaction. In method 1, coordination of [Rh(acac)(CO)₂] to TPP of the ligand, might lead to the formation of oligomeric or cyclic species. These species will then aggregate to the elastomer, via the bisurea recognition unit of the ligand. In method 2, the ligands will be randomly incorporated into the hard domains of the elastomer. Addition of [Rh(acac)(CO)₂] will then lead preferably to mono-coordination to TPP (Scheme 5.5).

Scheme 5.5. Schematic representation of the proposed coordination of ligand and metal to the elastomer after preparing meshes from solution obtained via method 1 (a) or method 2 (b).
Before performing hydroformylation reactions of 1-octene, the swelling behavior of the meshes in different solvents was visually investigated. Water didn’t seem to influence the fibers at all. In hexane and cyclohexane, however, the fibers did swell slightly. In toluene this swelling is increased even more. The swelling behavior of the fibers didn't have an effect on the physical properties: No degradation of the meshes was observed upon vigorous stirring in cyclohexane or toluene. Since 1-octene is not soluble in water, and since the swelling of the meshes in cyclohexane and toluene might lead to better accessibility of the substrate to the active rhodium species, the hydroformylation reactions were carried out in cyclohexane and toluene at 80 °C under 20 bar syn-gas (H₂/CO 1/1). Hydroformylation experiments in cyclohexane, however, showed a very low activity towards the aldehyde (7% after 24 hrs). Therefore toluene was used as solvent for the hydroformylation reactions carried out in the remainder of this chapter.

### 5.6 Hydroformylation of 1-octene

Hydroformylation experiments carried out in toluene under 20 bar syngas at 80 °C for 24 hours using a mesh prepared via method 1 showed a much higher activity and selectivity for the aldehyde than hydroformylation experiments performed in cyclohexane (Table 5.1, entry supported 2). Whereas in cyclohexane the conversion to the aldehyde was only 7%, in toluene, under the same experimental conditions, the conversion increased to 63.4 %. The l/b ratio observed was approximately 3. This relatively low regioselectivity towards linear aldehydes is typical for rhodium-catalyzed hydroformylations using TPP as ligand and most probably the bis (PPh₃) –Rh is the dominant species under these conditions.¹⁸

These results were compared to unsupported rhodium-phosphine complexes of 2. In this experiment similar amounts of 2 and [Rh(acac)(CO)₂] compared to the supported system were used in the autoclave, while keeping all experimental conditions the same. The results (Table 5.1, entry unsupported 2) show that the unsupported system is slightly less active than the supported system. The regioselectivity however is slightly higher (l/b = 3.9 vs l/b = 2.8 for the unsupported system).

The recyclability of the supported catalyst was studied by performing a series of consecutive runs (Table 5.2, entries recycle 1 - 4). Between runs, the autoclave was cooled down and the pressure released before the autoclave was filled with argon to limit catalyst decomposition while the product phase was removed with a syringe and the system washed with a further 6 ml of solvent. The autoclave was then recharged with solvent, substrates and syngas before stirring at 80 °C for the next run. Using this procedure, 5 consecutive experiments were performed. During the first 2 cycles no deterioration of the catalytic performance could be observed: The l/b ratio remained the same, whereas the activity increased slightly. During the last 2 runs however, a decrease in activity and regioselectivity was observed. This might indicate the presence of free Rh, or the formation of Rh nanoparticles, as a result of rhodium leaching during recycling. Rhodium analysis on the product phase by means of Atomic Adsorption Spectroscopy (AAS) should confirm this and these
experiments are currently being performed. Another explanation for the decrease in activity and selectivity might be ligand leaching. This seems highly unlikely, since the ligand only dissolves in toluene at elevated temperatures and precipitates at room temperature. Even after 4 recycling runs, however, no precipitate of the ligand could be observed in the product phase at room temperature.

Table 5.1. Hydroformylation of 1-octene in toluene on electrospun meshes of pTHF$_{1100}$U$_6$U containing 10 mol% 2 relative to bisurea groups of the elastomer and 10 mol% [Rh(acac)(CO)$_2$] relative to TPP prepared via method 1.

<table>
<thead>
<tr>
<th></th>
<th>TOF $^a$</th>
<th>% octene</th>
<th>% isomer</th>
<th>% linear aldehyde</th>
<th>% branched aldehyde</th>
<th>l/b $^b$</th>
<th>% conv. aldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsupported 2</td>
<td>93</td>
<td>47.3</td>
<td>9.4</td>
<td>34.3</td>
<td>8.9</td>
<td>3.9</td>
<td>43.2</td>
</tr>
<tr>
<td>Supported 2</td>
<td>105.7</td>
<td>29.7</td>
<td>6.8</td>
<td>46.9</td>
<td>16.5</td>
<td>2.8</td>
<td>63.4</td>
</tr>
<tr>
<td>Recycle 1</td>
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<td>8.0</td>
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<td>54.7</td>
<td>20.6</td>
<td>2.7</td>
<td>75.3</td>
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<tr>
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<td>144.2</td>
<td>8.3</td>
<td>8.8</td>
<td>60.0</td>
<td>22.9</td>
<td>2.6</td>
<td>82.9</td>
</tr>
<tr>
<td>Recycle 3</td>
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<td>8.8</td>
<td>34.0</td>
<td>35.1</td>
<td>22.2</td>
<td>1.6</td>
<td>55.6</td>
</tr>
<tr>
<td>Recycle 4</td>
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<td>8.8</td>
<td>48.4</td>
<td>27.9</td>
<td>14.8</td>
<td>1.9</td>
<td>42.8</td>
</tr>
</tbody>
</table>

$^a$ TOF = average turnover frequency = (mol of aldehyde)/(mol of Rh) $^{-1}$ h $^{-1}$; the reaction was stopped after 24 hours. $^b$ l/b = linear/branched ratio. $^c$ product distribution: percent isomerizations to 2-, 3- and 4-octene and percent aldehydes (% aldehydes = %linear aldehyde + % branched aldehyde).

The mesh was analyzed with SEM after the use in the experiments described above. The SEM pictures after the hydroformylation reactions are depicted in Figure 5.5. The fibrillar structure of the mesh was still intact. The fibers are still swollen and seem to have fused together at some places. Furthermore some particles are present, which were not observed before. These might be rhodium particles, however, discriminating between different materials by SEM and especially when using an SE detector as in this case is difficult.

Figure 5.5. SEM images of electrospun fibers of a mesh of pTHF$_{1100}$U$_6$U containing 10 mol% 1 relative to bisureas of the elastomers, and 10 mol% [Rh(acac)(CO)$_2$] relative to TPP after hydroformylation reactions in toluene magnified 400 (a) and 3200 (b) times.
Hydroformylation experiments carried out in toluene under 20 bar syngas at 80 °C for 24 hours using a mesh prepared via method 2 (addition of [Rh(acac)(CO)₂] after incorporation of the ligand into the hard blocks of the elastomer) showed different behavior than meshes prepared via method 1 (Table 5.2). The supported ligand system prepared via method 2 is slightly more active than the supported ligand system prepared via method 1. The regioselectivity to linear aldehydes, however, decreased significantly. Whereas the supported system prepared via method 1 has an l/b ratio of approximately 3, the supported system prepared via method 2 only has an l/b ratio of 1. The higher activity and lower selectivity observed in this experiment indicate that monophosphorous ligand Rh complexes are the dominant species under these conditions.

Table 5.2. Hydroformylation of 1-octene in toluene on electrospun meshes of pTHF₁₁₀U₆U containing 10 mol% 2 relative to bisurea groups of the elastomer and 10 mol% [Rh(acac)(CO)₂] relative to TPP prepared via method 2.

<table>
<thead>
<tr>
<th></th>
<th>TOF</th>
<th>% octene</th>
<th>% isomer</th>
<th>% linear aldehyde</th>
<th>% branched aldehyde</th>
<th>l:b</th>
<th>% conv. aldehyde</th>
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<tbody>
<tr>
<td>Unsupported 2</td>
<td>93</td>
<td>47.3</td>
<td>9.4</td>
<td>34.3</td>
<td>8.9</td>
<td>3.9</td>
<td>43.2</td>
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<tr>
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<td>152</td>
<td>16.5</td>
<td>14.6</td>
<td>36.3</td>
<td>32.6</td>
<td>1.1</td>
<td>68.9</td>
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<td>Recycle 2</td>
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<td>22.7</td>
<td>1.4</td>
<td>54.7</td>
</tr>
<tr>
<td>Recycle 3</td>
<td>82</td>
<td>19.8</td>
<td>46.7</td>
<td>22.8</td>
<td>10.6</td>
<td>2.2</td>
<td>33.4</td>
</tr>
</tbody>
</table>

*a TOF = average turnover frequency = (mol of aldehyde)(mol of Rh)⁻¹ h⁻¹; the reaction was stopped after 24 hours. **l/b = linear/branched ratio. c product distribution: percent isomerizations to 2-, 3- and 4-octene and percent aldehydes (% aldehydes = %linear aldehyde + % branched aldehyde).

The recyclability of the supported catalyst prepared via method 2 was also studied by performing a series of consecutive runs (Table 5.2, entries recycle 1 - 3). No deterioration of the catalytic performance was observed after 1 recycling run. Upon further recycling, a decrease in activity was observed from approximately 157 mol/mol/h to 82 mol/mol/h for recycle run 3. The regioselectivity, however, increased from 1.0 for recycle run 1 to 2.2 for recycle run 3. It appears that upon recycling, the catalyst behavior becomes more ‘homogenous’-like, which suggests degradation of the mesh into looser fibers. Degradation is most probably caused by the fact that a smaller and thus less stable mesh was used for these experiments compared to the experiments performed on meshes prepared via method 1.

Because of the degradation of the mesh, Rh may be able to move and bind to 2 ligand centers and thus effectively neutralizing the differences between the 2 methods to some extent (it should be borne in mind that their is bound to be more than one active catalyst species in these systems as both mono- and bis coordinated Rh are possible). This effect, however, is probably negated somewhat by the formation of RH particles.
5.7 Discussion and Conclusions

Rhodium complexes of bisurea functionalized triphenylphosphine ligands 1 - 3 were supramolecularly anchored to segmented block copoly(ether urea)s. Functionalized meshes were drawn from these mixtures by electrospinning and were used as supports for the rhodium-catalyzed hydroformylation of 1-octene. It was found that these systems do work as efficient supports for catalysis. The activity and regioselectivity observed for supported rhodium-phosphine complexes of 2 are comparable to unsupported rhodium-phosphine complexes of 2, which is in contrast to the general observation for catalysts immobilized on insoluble supports. Similar reaction rates and selectivities relative to the unbound analogue, however, were also observed for the non-covalently anchored TPP ligands to dendritic supports studied by De Groot et al.

The solvent used for the hydroformylations appeared to have a large impact on the observed activity. In cyclohexane, a 7 % conversion to the aldehyde was observed after 24 hours. In toluene, which causes swelling of the mesh, a conversion up to 80% was observed after 24 hours.

The immobilization conditions also appeared to have a large influence on the supported catalyst formation and consequently on the performance. When the metal-ligand complex is prepared prior to association to the elastomer in chloroform, and when meshes were drawn from these solutions, the l/b ratio was approximately 3. Meshes that were prepared from solutions, in which the ligand was associated to the elastomer prior to addition of the metal, resulted in a lower regioselectivity (l/b = 1). The higher regioselectivity in the first case probably originates from the presence of bis (PPh₃)-Rh as the active species under these conditions. In the second case monodentate Rh coordination might result in lower regioselectivity.

The ability to recycle the supported catalyst was studied by performing a series of consecutive hydroformylation reactions. These recyclability studies show unchanged selectivity and even increased activity during the first 3 runs. In later runs the catalyst performance starts degrading, probably due to rhodium leaching or the formation of supported rhodium particles. As a comparison, the rhodium catalyst based on a functionalized Xantphos ligand, which was non-covalently anchored to a silica support, could be used in the hydroformylation of 1-octene in 11 consecutive reactions without showing catalyst deterioration or metal leaching, as shown by Chen et al.¹⁶ The use of the bidentate Xantphos ligand clearly suppresses rhodium leaching.

Besides repeating hydroformylation reactions in toluene with monophosphine ligand 3 to compare the activity and regioselectivity with that of diphosphine ligand 2, the versatility of this supported system will be examined further by performing palladium catalyzed allylic aminations. Furthermore, it should be possible to increase the selectivity of the hydroformylation reaction by using a ligand with a large natural bite-angle. The comparable outcomes of the supported and unsupported hydroformylation reaction suggests that the support does not influence the regioselectivity, rather the pre-organisation of the ligands into bis-ligand systems (method 1) rather than mono-ligand systems (method 2) before
incorporation into the support does have a large effect. Bisurea functionalized Xantphos ligands could be good alternatives in this regard (Figure 5.6), since they have proven to be highly selective in rhodium catalyzed hydroformylations due to their large natural P-M-P bite-angle.

**Figure 5.6.** Proposed bisurea functionalized Xantphos ligands for potential use as immobilized ligands in rhodium catalyzed hydroformylations.
5.8 Experimental section

**General Methods.** All starting materials were obtained from commercial suppliers and used as received. Ligand 1 was provided by Dr. J. N. H. Reek. All moisture-sensitive reactions were performed under an atmosphere of dry argon. Dry and ethanol-free dichloromethane was obtained by distillation from P₂O₅; dry tetrahydrofuran (THF) was obtained by distillation from Na/K/benzophenone; 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. 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). ¹H-NMR and ¹³C-NMR spectra were recorded on a 500 MHz Varian Unity Inova 500, a 400 MHz Varian Mercury Vx and a 300 MHz Varian Gemini-2000. Proton and carbon chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) using the resonance of the deuterated solvent as internal standard. Elemental analysis was performed on a Perkin Elmer 2400 series II CHNS/O Analyser. Matrix assisted laser desorption/ionization mass-time of flight spectra (MALDI-TOF) were obtained using α-cyano-4-hydroxycinnamic 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. SEM was carried out using a JEOL JSM 840 A microscope using a 2.0 kV acceleration voltage and an SE detector. GC analysis were carried out on a Shimadzu GC-17A with a DB-1 column.

**Hydroformylation reactions.** All hydroformylation reactions were carried out in the laboratories of Reek / Van Leeuwen at the University of Amsterdam by Dr. M. J. Wilkinson. A 25 ml stainless steel autoclave, equipped with a Teflon stirring bar, was charged with a mesh of the electrospun fibers containing 30.8 µmol of the ligand and 3.3 µmol Rh(acac)(CO)₂. The autoclave was placed under vacuum before filling with argon and the addition of solvent (6 ml). The mixture was then incubated overnight at 80 °C under 18 bar CO/H₂, before the addition of 4000 equivalents of 1-octene relative to [Rh(acac)(CO)₂] and 1 g of decane (as internal standard). The CO/H₂ pressure was then adjusted to 20 bar and kept constant by a Bronckhorst Mass Flow Controller. The mixture was stirred for 24 hours at 80 °C while the gas uptake was measured. The autoclave was then cooled down and the pressure released before the autoclave was filled with argon to limit catalyst decomposition while the product phase was removed with a syringe and the system washed with a further 6ml of solvent. The autoclave was then recharged with solvent, substrates and syngas before stirring at 80 °C for a further 24 hours. This recharging procedure was continued until a drop in the catalyst activity was observed. The conversion was determined by GC measurements of the crude products.

**Synthesis of 2 – 7.**

3,3’-Bis-(4-Diphenylphosphanyl-benzyl)-(hexylene-1,6)-bisurea (2). 4-(diphenylphosphino)phenylmethylamine (5, 0.6g, 2.07 mmol) was dissolved in 40 ml dry CHCl₃. Slowly hexanediisocyanate (0.18g, 1.04 mmol) in 10 ml dry CHCl₃ was added dropwise. A white precipitate forms as the reaction continues. The reaction was monitored with IR: as soon as an isocyanate peak at 2269 cm⁻¹ became visible, the addition of the hexanediisocyanate was stopped. The white precipitate was filtrated, washed with CHCl₃ and dried in vacuo. Finally 2 was recrystallized from CHCl₃/hexane (0.45 g, 58 %).¹H NMR (CDCl₃/MeOD): δ 7.39-7.20 (m, 28H), 5.85 (t, 2H), 5.56 (t, 2H), 4.35 (s, 4H), 3.17 (t, 4H), 1.50 (m, 4H), 1.34 (m, 4H). ¹³C NMR (CDCl₃/MeOD): 159.5, 140.7, 137.2 (d, J=10.3 Hz), 135.8 (d, J=10.1 Hz), 134.1 (d, J=20.0 Hz), 133.8 (d, J=19.5 Hz), 128.9, 128.7 (d, J=6.9 Hz), 127.4 (d, J=6.9 Hz), 43.8, 39.7, 29.8,

3[(2-Ethyl-hexyl)-3'[(4-Diphenylphosphanyl-benzyl](hexylene-1,6)-bisurea (3). To a solution of 4-((Tert-butoxycarbonylamino)-1-hexylisocyanate (7, 0.90g, 3.7 mmol) in 5 ml dichloromethane was added 4-(diphenylphosphino)phenylmethylanime (5, 1.16g, 4 mmol). A white precipitate forms as the reaction continues. The white precipitate was filtrated, washed with CHCl3 and dried in vacuo. It was redissolved in 16 ml dichloromethane and trifluoroacetic acid (2 ml) was added to deprotect the amine group. The reaction mixture was stirred at room temperature overnight, and subsequently evaporated to dryness.

Di-tert-butyl tricarbonate (1.02g 3.9 mmol) was dissolved in chloroform (10 ml), and 2-ethylhexyl amine (0.48 g, 3.7 mmol) in chloroform (2 ml) was injected into the former solution. The reaction mixture was stirred for 30 min. The previously deprotected amine was dissolved in pyridine (50 ml), and added to the former solution. The reaction mixture was stirred overnight at room temperature, and then evaporated to dryness. The product was purified by column chromatography, first using pure chloroform as the eluent, then chloroform-methanol mixtures with up to 4% methanol. The product was obtained as a white solid (0.50 g, 23% ).

1H NMR (CDCl3): δ 7.39-7.20 (m, 14H), 6.12 (s, 1H), 5.77 (s, 1H), 5.50 (s, 1H), 5.41 (s, 1H), 4.27 (s, 2H), 3.06 (m, 6H), 1.47-1.07 (m, 17H), 0.83 (s, 3H), 0.79 (s, 3H). 13C NMR (CDCl3): δ 159.5, 159.2, 140.8, 137.1 (d, J = 10.7 Hz), 135.1 (d, J = 10.6 Hz), 133.9 (d, J = 19.9 Hz), 133.6 (d, J = 19.6 Hz), 128.7, 128.4 (d, J = 6.9 Hz), 127.2, (d, J = 7.2 Hz). 31P NMR (CDCl3): δ -6.2. Elemental analysis calcd (%) for C35H49N4O2P: C, 71.40%; H, 8.39%; N, 9.52%. Found: C, 71.21%; H, 8.13%; N, 9.32%. MALDI-TOF [M+H+] = Calcd. 589.78 Da. Obsd. 589.36.

4-(Diphenylphosphino)benzonitrile (4). A red colored 0.5 M solution of potassium diphenylphosphine in THF (21.97 ml; 10.99 mmol) was cooled to –78 °C. A stoichiometric amount of 4-chlorobenzonitrile (1.51 g; 10.99 mmol) was added at this temperature. The reaction mixture was stirred overnight under argon. After removal of the solvent in vacuo, the oily residue was washed with water and recrystallized from methanol, resulting in large colorless crystals (2.1 g; 67%).

1H-NMR (CDCl3): δ 7.56 (d, J = 8.4 Hz, 2H), 7.39-7.30 (m, 12H). 13C NMR (CDCl3): δ 145.3 (d, J = 16.8 Hz), 135.8 (d, J = 10.7 Hz), 134.3 (d, J = 19.8 Hz), 133.9 (d, J = 18.3 Hz), 131.8 (d, J = 6.1 Hz), 129.7, 129.0 (d, J = 7.6 Hz), 119.0, 112.1. 31P NMR (CDCl3): -3.2. FT-IR (ATR): ν 2200 cm⁻¹. Elemental analysis calcd (%) for C19H14NP: C, 79.04%; H, 4.91%; N, 4.88%. Found: C, 79.41%; H, 4.80%; N, 4.88%. MALDI-TOF [M+H+] = Calcd. 288.30 Da. Obsd. 288.25.

4-(Diphenylphosphino)phenylmethylanime (5). A solution of 4-(diphenylphosphino)benzonitrile (4, 0.89g, 3.09 mmol) was added to a 1.0 M solution of LiAlH4 in THF (3.55 ml, 3.55 mmol). 3 ml of THF was added. The resulting mixture was refluxed for 1 hr. Water (0.14 ml), 20% NaOH (100 µl), and water (0.5 ml) were added successively at 0°C to precipitate orange solid of the aluminium residue. The organic layer was separated by filtration through a celite pad and the solid was repeatedly washed with ether. Chromatography over silica gel with benzene/Meh (8/1) gave a white solid (0.75 g, 83.3%).

1H NMR (CDCl3): δ 7.28-7.20 (m, 14H), 1.91 (s, 2H), 1.44 (s, 2H). 13C NMR(CDCl3), 144.1, 137.5 (d, J = 10.9 Hz), 135.6(d, J = 19.9 Hz), 134.3 (d, J = 20.0 Hz), 133.8 (d, J = 20.0 Hz), 129.0, 128.7 (d, J = 7.3 Hz), 127.4(d, J = 7.3 Hz), 46.3.

4-((Tert-butoxycarbonylamino)-1-hexylamine (6). Di-tert-butyl dicarbonate (7.04 g; 32.2 mmol) was dissolved in chloroform (100 ml), and added dropwise to a solution of 1,6-diaminohexane (15.0 g; 129 mmol) in chloroform (150 ml) at 0 °C. The reaction
mixture was washed 3 times with water (100 ml) and the product was extracted by hydrochloric acid solution (100 ml 1 M in water). The aqueous layer was isolated, basified by addition of sodium hydroxide solution (15 ml 10 M in water), and subsequently extracted 3 times with dichloromethane (3 times 80 ml). The combined organic layers were dried with sodium sulphate, filtered and the dichloromethane was removed under reduced pressure, resulting in a colorless oil. 1H NMR (6.01 g; 86.8 %). 1H NMR (CDCl3): δ 4.85 (s, 1H), 3.12 (q, 2H), 2.67 (t, 2H), 1.50-1.40 (m, 8H), 1.44 (s, 9H), 1.25 (s, 2H). 13C NMR (CDCl3): δ 155.8, 80.2, 41.8, 40.2, 31.5, 28.5, 26.9, 25.8. FT-IR (ATR): ν 3360, 1689, 1521, 1166.

4-((Tert-butoxycarbonylamino)-1-hexylisocyanate (7). 4-((Tert-butoxycarbonylamino)-1-hexylamine (5, 0.80g, 3.7 mmol) was dissolved in 15 ml dry dichloromethane. To this solution di-tert-butyl tricarbonate (1.02g, 3.9 mmol) was added. The reaction mixture was stirred for 30 minutes, and the solvent was partly evaporated under reduced pressure. 4-((Tert-butoxycarbonylamino)-1-hexylisocyanate (6) was used in the next step without further purification. FT-IR (ATR): ν 2269 cm⁻¹.

5.9 References and Notes

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21 New diphosphonite ligands applied in asymmetric hydroformylation, graduation report of J.M.J. Paulusse, 2002
Helical Supramolecular Aggregates Based on Ureidopyrimidinone Quadruple Hydrogen Bonding*

Abstract

A series of mono- and bifunctional compounds 2-7 based on the ureido pyrimidinone quadruple hydrogen bonding unit were prepared to study their mode of aggregation in the bulk and in solution. In chloroform, the bifunctional compounds form cyclic dimers at millimolar concentrations, which are in equilibrium with linear species above a critical concentration of 6 mM to larger than 260 mM, depending on the structure of the spacer. Circular Dichroism measurements in chloroform did not show a Cotton effect. Dodecane solutions of compounds 3, 4b, and 7b display a Cotton effect at the absorption band of the phenyl-pyrimidinone unit. Amplification of chirality was observed in mixtures of 7a and 7b, but not in mixtures of 4a and 4b, indicating that 7a and 7b form mixed polymeric aggregates with a helical architecture in dodecane solution, whereas 4a and 4b do not. The Cotton effect is lost upon increasing the temperature. Half of the helicity is lost at 25 °C for 3 and 60 °C for 4b suggesting that 3, bearing the shorter spacer, forms less stable columns than 4b. Compound 7b loses half of its helicity at 45 °C. Compounds 2b, 5 and 6 do not exhibit a helical organization as evidenced by the absence of a Cotton effect.

6.1 Introduction

Supramolecular polymers\textsuperscript{1,2} are a fascinating class of materials, formed by the association of monomers via reversible, non-covalent interactions, such as hydrogen bonding, metal-coordination or $\pi$-$\pi$ stacking. Lehn and coworkers described linear hydrogen bonded supramolecular polymers, based on triple hydrogen bonds between monomers.\textsuperscript{3,4} Monomers with tartaric acid backbones were shown to form liquid-crystalline materials in which the molecules are packed in helical columns, which form helically twisted fibers. Stronger interactions have been obtained with single hydrogen bonds between carboxylic acids and pyridines or by use of arrays of more than three hydrogen bonds. We have employed the high strength of quadruple hydrogen bonding units ureidotiazines\textsuperscript{5} and ureidopyrimidinones (Figure 6.1),\textsuperscript{6} to obtain linear supramolecular polymers with high degrees of polymerization in bulk as well as in solution from monomers containing two of these units.\textsuperscript{7}

![Figure 6.1. Triazine and pyrimidine derivatives that dimerize through quadruple hydrogen bonds. (a) Ureidotriazine, featuring a self-complementary DADA array or donor (D) and acceptor (A) sites. (b) Ureidopyrimidinone, featuring a DDAA array.](image)

The directionality and the selectivity of multiple hydrogen bonds allow 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 addition of trifunctional compounds. Additional non-covalent interactions between monomeric units in supramolecular polymers may cause the chain to take up a well-defined conformation. This phenomenon, which is responsible for the secondary and tertiary structure of biomacromolecules like DNA, has recently become a fruitful area of research in synthetic polymers, where oligomers with well-defined secondary structures are known as “foldamers”.\textsuperscript{8-11} 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. Hirschberg and Brunsveld developed supramolecular foldamers based on strong quadruple hydrogen bonding interactions between complementary ureidotiazines, in combination with solvophobic interactions between aromatic chromophores to bring about a specific secondary structure with additional, weaker non-covalent interactions\textsuperscript{12,13}. Ureido-s-triazine (UTr) units were connected by a spacer and provided with solubilizing trialkoxyphenyl groups to obtain supramolecular polymers with a helical columnar architecture in dodecane (Figure 6.2). The structure of the columns was shown to be biased towards a single helicity by the use of homochiral side chains. 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 ($K_{\text{dim}} = 2 \times 10^4 \text{ M}^{-1}$).\textsuperscript{5} This approach was extended to defined architectures in water, by using chiral pentamethylene glycol derivatives.

Ureidopyrimidinones (UPy) have a much higher dimerization constant\textsuperscript{14} ($K_{\text{dim}} = 6 \times 10^7 \text{ M}^{-1}$ in CHCl$_3$) and bifunctional compounds containing this unit would in principle allow the construction of polymers with a higher degree of polymerization in either dodecane or chloroform.

**Figure 6.2.** Ureido-s-triazine derivative C$_6$-(Utr)$_2$, and schematic representation of helical supramolecular polymers (observed in dodecane) and random coil polymers (observed in chloroform).

**Figure 6.3.** a) structural formula of bifunctional Upy derivative 1. b) Three isomeric cyclic dimers observed for this compound. c) Crystal structure of the syn dimer (Image reprinted from reference 15).
Previously, we have shown that bifunctional UPy derivative 1, which is strongly preorganized by its $\alpha, \alpha'$-tetramethyl xylylene spacer, exclusively forms cyclic dimers in CHCl$_3$ and in the crystal (Figure 6.3). In solution, the cyclic dimers of 1 exist as a slowly interconverting mixture of syn and anti isomers, with UPy units present in either the keto or the enol tautomeric form.$^{15}$

![Scheme 6.1. Mono- and bifunctional molecules 2-7.](image-url)

In order to achieve highly preorganized supramolecular polymers with a columnar architecture, we studied the mode of aggregation (cyclic vs. polymeric) of bifunctional ureidopyrimidinones, with less preorganized spacer units than 1, and we provided these molecules with trialkoxyphenyl groups to promote a columnar architecture. In this chapter the results of a study of compounds 2-7 (Scheme 6.1) in solution, using $^1$H-NMR and circular dichroism spectroscopy are presented. The thermotropic liquid crystalline properties of 2-7 in combination with a detailed X-ray investigation of 2a will be discussed in chapter 7.

### 6.2 Synthesis and characterization

Monofunctional ureidopyrimidinone 2a and 2b and bifunctional derivatives 3-7 were synthesized by acylation of isocytosines 11a or 11b with butylisocyanate or the appropriate disiocyanate, which are commercially available, or were prepared by the action of di-tert-butyl tricarbonate on the corresponding diamine (Scheme 6.2).

In the reported synthesis of isocytosine 2a,$^{16}$ ethyl 3,4,5-trialkoxybenzoyleacetate 9a was obtained from the corresponding benzyol chloride by reaction with ethyl acetoacetate 8, followed by decarboxylation.$^{17}$ In the present work a more efficient method was used for the
synthesis of 9b, in which the acid chloride reacts with potassium ethyl malonate 10 under the action of anhydrous magnesium chloride/ triethylamine as a base system. Using this method,

\[
\begin{align*}
\text{N-N} & \quad \text{NCO} \\
\text{RO} & \quad \text{O} \\
\text{RO} & \quad \text{H} \\
\text{N} & \quad \text{RCN} \\
\text{N-CO} & \quad \text{O} \\
\text{NCOOCN} & \quad \text{CH}_2 \text{OCN} \\
\text{NCO} & \quad \text{n} \\
\text{7a-b} & \quad \text{11a,b} \\
\end{align*}
\]


β-keto ester 9b was obtained in 86% yield. Condensation of the β-keto esters (used without further purification) with guanidinium carbonate in ethanol afforded isocytosines 11a and 11b in 39% and 45% yield, respectively (Scheme 6.2). 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.

6.3 Aggregation in solution

6.3.1 Aggregation in chloroform

Ureidopyrimidinones have been shown$^5$ to exist in solution as a mixture of strongly dimerizing tautomers, a 4[H]-pyrimidinone (keto) tautomer and a pyrimidin-4-ol (enol) tautomer (Figure 6.4, inset).

\[
\begin{align*}
\text{Hd} & \quad \text{O} \\
\text{R} & \quad \text{N} \\
\text{NC} & \quad \text{N} \\
\text{H} & \quad \text{H} \\
\text{Ha} & \quad \text{RC} \\
\text{Hd} & \quad \text{O} \\
\text{H} & \quad \text{O} \\
\text{Ha} & \quad \text{H} \\
\text{enol} & \quad \text{O} \\
\text{keto} & \quad \text{O} \\
\end{align*}
\]

Figure 6.4. $^1$H NMR spectrum of compound 2b recorded in CDCl$_3$. 
The position of the keto-enol equilibrium has been studied by $^1$H-NMR, and is substituent and solvent dependent. Equilibration between dimeric keto- and enol forms was also observed in the present study. The $^1$H-NMR spectrum of monofunctional compound $2b$ in CDCl$_3$ is shown in Figure 6.4 and shows signals of the keto and the enol tautomer in a 87:13 ratio. From the position of the NH protons (between 10 and 14 ppm for both tautomers) it can be concluded that the molecules are present as hydrogen bonded dimers.

$^1$H-NMR spectra of dilute solutions of bifunctional compounds $3$-$7$ in CDCl$_3$ are much more complex. As an example spectra of solutions of $3$ and $4b$ are shown in Figure 6.5 (a-c and e-g, respectively). Upon addition of a small amount of trifluoroacetic acid, which disrupts the hydrogen bonds between ureidopyrimidinone units, the spectrum simplifies dramatically (Figure 6.5d and 6.5h).

![Figure 6.5. $^1$H NMR spectra of bifunctional compound $3$ and $4b$ in CDCl$_3$ at different concentrations (spectra a-c and e-g, respectively), and spectra after addition of small amounts of TFA (d and h).](image_url)

Similarly complex spectra have been observed for bifunctional compound $1$, which exists in solution as a mixture of isomeric cyclic dimers I, II, and III, which interconvert slowly on the NMR timescale, and give rise to a set of 4 signals for each proton in the molecule. Concentration dependent $^1$H NMR studies were performed on compounds $3$, $4b$, $5$, $6$ and $7b$ to study the presence of cycles in chloroform. Spectra of solutions of $3$ show four sets of signals. To establish the relative size of the aggregates giving rise to the different sets of signals, Diffusion-ordered 2D NMR (DOSY) experiments were performed on a 100 mM chloroform solution of $3$. DOSY NMR experiments yield conventional chemical shift spectra in one dimension and spectra of diffusion constants D in the second dimension. The diffusion constants relative to solvent molecules are similar for all sets of signals (Table 6.1) and are relatively high, indicating that at this concentration $3$ is present in small, cyclic aggregates.
Based on the similarity of the spectrum with that of 1, we conclude that these cycles are a mixture of isomeric dimers with UPy groups in keto and enol tautomeric forms. Upon increasing the concentration to 260 mM, no signals originating from additional, larger aggregates were observed.

Compound 4b, however, displays different behavior. In the $^1$H-NMR spectrum of this compound, multiple sets of signals are observed at low concentrations, with similar diffusion constants as for the cyclic dimers of 3, while above 10 mM, an additional set of peaks from polymeric aggregates is observed which shows a much lower diffusion constant (Table 6.1).

Table 6.1. Diffusion constants relative to solvent molecule of compound 3 and 4b.

<table>
<thead>
<tr>
<th></th>
<th>3</th>
<th>4b</th>
</tr>
</thead>
<tbody>
<tr>
<td>D/D$_{CHCl_3}$ cyclic aggregates</td>
<td>0.095 (± 0.006)</td>
<td>0.129 (± 0.013)</td>
</tr>
<tr>
<td>D/D$_{CHCl_3}$ polymeric aggregates</td>
<td>--</td>
<td>0.0312 (± 0.003)</td>
</tr>
</tbody>
</table>

Equilibria between cyclic and linear species consisting of strongly associating bifunctional monomers have been predicted to display a critical concentration, a concentration below which virtually no linear aggregates are present, and above which the concentration of cycles remains constant.$^{19,20}$ Such behaviour has indeed been observed by us in bifunctional UPy derivatives.$^{21}$ The lowest concentration at which polymeric species could be observed in the $^1$H-NMR spectrum was determined for compounds 3, 4b, 5, and 6. The critical concentrations are summarized in Table 6.2. The results show that there is a large influence of spacer structure on the critical concentration. Unfortunately, due to the extremely complex spectrum of 7b, it was not possible to establish a critical concentration for this most strongly preorganized compound in the series of molecules we have studied.

The chiroptical properties of the chiral bifunctional compounds 3, 4b, 5, 6 and 7b were investigated with Circular Dichroism (CD) spectroscopy in chloroform, at a concentration of 1mM, where polymeric aggregates were shown to be absent with NMR. None of the compounds showed a Cotton effect, indicating that the cyclic dimers are not highly ordered in this solvent.

Table 6.2. Critical polymerisation concentration of compounds 3, 4b, 5 and 6.

<table>
<thead>
<tr>
<th></th>
<th>3</th>
<th>4b</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;260 mM</td>
<td>10 mM</td>
<td>7 mM</td>
<td>30 mM</td>
<td></td>
</tr>
</tbody>
</table>

6.3.2 Aggregation in dodecane

$^1$H-NMR spectra of 2 and of bifunctional compounds 3-7 in deuterated dodecane showed broad unresolved signals for the alkyl chains and broad signals for the phenylpyrimidinone core of the molecules, indicating the formation of large aggregates in this solvent.
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.

CD spectra of chiral compounds 2b, 3, 4b, 5, 6 and 7b were recorded in dodecane in order to probe the degree of order in aggregates of these compounds. In dodecane a 1 mM solution of monofunctional compound 2b gave no Cotton effect. In the series of bifunctional compounds, Cotton effects at the $\pi-\pi^*$ transition of the phenyl-pyrimidinone moiety were observed in dodecane for compounds 3, 4b and 7b (with more or less similar intensities), while compounds 5 and 6, with C-7 and C-8 spacers, respectively, showed no signal in CD. Although the CD effects observed are relatively small (see Figure 6.6a) they are reproducible. The cooperativity of the CD effect in mixed solutions of chiral and achiral bifunctional compounds 4a,b and 7a,b was studied in a “Sergeants and Soldiers” type of experiment by varying the relative amounts of chiral and achiral molecules at a constant total concentration of chromophores. The results of these measurements are plotted in Figure 6.6b as the Cotton effect normalized to the concentration of chiral chromophores. In this way chirality induced in achiral molecules shows up as an amplification larger than 1.

For mixtures of compounds 4, no amplification of chirality was observed, even when the samples were annealed at 80 °C, or when the mixtures were prepared in CHCl3, followed by removal of this solvent and redissolution in dodecane. Therefore, only the chiral molecules 4b contribute to the CD effect in dodecane solution. For compounds 7, however, strong amplification of chirality is observed. At a fraction of 0.1 of chiral compound 7b, the CD effect is amplified by a factor of 6. Since a simple model suggests that in cyclic dimers the amplification should not exceed 2, this suggests that polymeric aggregates with helical order are present.

Temperature dependent CD measurements were performed on 1 mM dodecane solutions of 3, 4b and 7b in order to establish the thermal stability of the aggregates (Figure 6.7). A plot of the molar ellipticities at $\lambda = 325$ nm (normalized against the values at –6 °C)
versus temperature shows that the chiral order gradually disappears for all three compounds. The temperature at which half of the CD effect has been lost, is different for these compounds, and varies from 25 °C for 3 to 60 °C for 4b.

![Figure 6.7.](image)

Figure 6.7. Temperature dependence of the CD effect in spectra of 1 mM solutions of compound 3 (□), 4b (○) and 7b (●) in dodecane. The fraction of the maximum ellipticity remaining is plotted against temperature.

### 6.4 Discussion and Conclusions

The mode of aggregation (cyclic vs. linear) of mono- and bifunctional ureidopyrimidinones 2-7 provided with trialkoxyphenyl groups to promote a columnar architecture was studied in solution using 1H-NMR and circular dichroism spectroscopy. Due to keto-enol tautomerism, 1H-NMR spectra of the UPy derivatives in CDCl₃ are much more complex than those of the corresponding triazine derivatives. Study of the concentration dependence of the spectra show that compounds 2-7 are present as small cyclic aggregates in the millimolar concentration range. A more detailed study of compounds 3 and 4b, including measurement of the diffusion constants of the different species, shows that 3 is present as cyclic dimer even at 260 mM, while for 4b, a critical concentration of approximately 10 mM is observed, above which linear aggregates are formed.

It is of interest to compare the aggregation behavior of the UPy derivatives with that of triazine derivative (C₆-Utr)₂. The latter compound forms columnar aggregates by stacking of dimerized units induced by solvophobic interactions. Preorganization by spacer moieties is required for a helical stacked arrangement of dimerized UTr units, as no CD effect is observed for the monofunctional triazine. In the chiral monofunctional UPy derivative 2b, the absence of a Cotton effect in chloroform as well as in dodecane shows that the same requirements hold for ureidopyrimidinones. The absence of a Cotton effect in cyclic dimers of bifunctional UPy derivatives 3-7 in chloroform shows that even when the spacers connecting the two layers enforce a stacked arrangement, there is no bias in the supramolecular chirality. In dodecane cotton effects are absent for compound 5 and 6, which have longer spacers and are therefore
less preorganized to form ordered helical polymers. The Cotton effects that are observed for compounds 3, 4b, and 7b, however, show that highly ordered aggregates with supramolecular chirality are formed. The observed strength of the “sergeants and soldiers” effect in mixtures of 7a and 7b demonstrates that in this solvent, chirality may be transferred from 7b to a large number of achiral molecules 7a. This makes it improbable that 7 forms stacks of cyclic dimers in dodecane, and we conclude that helical polymeric aggregates are formed instead. A sergeants and soldiers effect is completely absent in dodecane solutions of compounds 4. As even transfer of chirality in a cyclic dimer would lead to amplification by a factor 2 \(^2\), it is probable that the formation of mixed aggregates of 4a and 4b is thermodynamically unfavorable. Melting experiments, analogous to thermal denaturation experiments performed on double-helical DNA show that the stability of the helical arrangement of 4b and its direct ureidotriazine analog are quite similar (60 vs. 70 °C).

The reason why 7 forms polymers in dodecane, whereas it forms cyclic dimers in chloroform, is not fully understood by us at the moment. A possible explanation would need to take into account entropic effects, which strongly disfavor polymerization in chloroform, whereas in dodecane, the entropic cost of polymerization would be much smaller, because cyclic dimers would already be aggregated into columns by solvophobic interactions. Further study of the structure of the aggregates of 7 in dodecane would be of high interest, because a transition from a stack of cyclic dimers to a helical polymer is analogous to the transition between a stack of disks and a polymeric helix in the self-assembly of tobacco mosaic virus (TMV)\(^{24}\), which is brought about by subtle changes in conditions such as ionic strength or pH.
6.5 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 P2O5; 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, methyl 3,4,5-tri((S)-3,7-dimethyloctyloxybenzoyl chloride, 3,4,5-tri((S)-3,7-dimethyloctyloxybenzoyl chloride and ethyl 3,4,5-tri(dodecyloxy)benzoylacetate 9a were synthesized following previously described procedures. 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). 1H-NMR and 13C-NMR spectra were recorded on a 500 MHz Varian Unity Inova 500, a 400 MHz Varian Mercury VX and a 300 MHz Varian Gemini-2000. Proton and carbon chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) using the resonance of the deuterated solvent as internal standard. Elemental analysis was performed on a Perkin Elmer 2400 series II CHNS/O Analyser. 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 α-cyano-4-hydroxycinnamic 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.

Synthesis of 2 – 11.

N-Butylaminocarbonyl-6-[3,4,5-tri(dodecyloxy)phenyl]-isocytosine (2a). 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 2a (0.85 g, 75%). IR(UATR): ν = 3226, 1694, 1120 cm–1. 1H-NMR (CDCl3): 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-CH2), 3.29 (m, 2H, NH-C6H4), 1.86 (m, 6H, O-CH2-C6H4), 1.77 (m, 2H, NH-CH2-CH2), 1.65 (m, 2H, NH-CH2-CH2-CH2), 1.50 (m, 6H, O-CH2-CH2), 1.29 (br, 48H, CH2), 0.890 (t, 12H, CH3). 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. 13C-NMR (CDCl3): δ = 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, 29.8-29.4, 26.2, 22.8, 20.3, 14.2, 13.8. Anal Calcd. (%) for C51H90N4O5 (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 (2b). The title compound was synthesized via the same procedure as used for compound 2a (Y = 43%). IR: ν = 3226, 1694, 1120 cm–1. 1H-NMR (CDCl3): 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-CH2), 3.30 (m, 2H, NH-CH2), 1.88-0.95 (m, CH2), 0.890 (t, 12H, CH3). 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. 13C-NMR (CDCl3): δ = 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 C45H78N4O5 (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 (3). 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 (CDCl3 + TFA): δ = 6.87 (s, 4H, Ar-H), 6.64 (s, 2H, alkylidene H), 4.19 (m, 4H, O-CH2), 4.09 (m, 8H, O-CH2), 3.37 (m, 4H, NH-C2H2), 1.87 (m, 12H, O-CH2-C2H2), 1.67 (m, 4H, NH-CH2-C2H2), 1.66-0.86 (multiple peaks, 104 H, CH2, CH3). 13C NMR (CDCl3): δ = 173.2, 156.3, 155.3, 153.8, 148.6, 140.9, 132.1, 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 C87H148N8O10 (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 (4a). 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 disiocyanate (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. The crude product was purified by column chromatography (eluent: 2% tetrahydrofuran in chloroform, then 1/1 hexane/chloroform) and precipitation in methanol, ethanol and ethyl acetate. Further purification by column chromatography (eluent: 6% tetrahydrofuran in chloroform) and precipitation in methanol, resulted in pure 4a (2.11 g, 59%). IR(UATR): ν = 3226, 1693, 1117 cm –1. 1H NMR (CDCl3 + TFA): δ = 6.91 (s, 4H, Ar-H), 6.37 (s, 2H, alkylidene H), 4.04 (m, 12H, O-CH2), 3.32 (m, 4H, NH-C2H2), 3.17, 1.81 (m, 12H, O-CH2-C2H2), 1.75 (m, 4H, NH-CH2-CH2), 1.60 (m, 4H, NH-CH2-CH2), 1.47 (m, 12H, O-CH2-CH2), 1.26 (br, 96H, CH2), 0.88 (t, 18H, CH3). 13C-NMR (CDCl3): δ = 173.3, 156.9, 155.3, 153.8, 149.5, 140.9, 126.0, 104.5, 103.8, 73.4, 69.3, 40.1, 31.2, 31.6, 30.5, 30.0, 29.9-29.4, 26.4, 22.5, 20.4, 14.2, 13.8. Anal. Calc. (%) for C100H174N8O10 (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 (4b). 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 off to remove traces of water. After cooling, 1,6-hexane disiocyanate (0.05 mL, 0.3 mmol) was added via a syringe and 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 4b (0.12 g, 27%). IR(UATR): ν = 3226, 1692, 1115 cm –1. 1H NMR (CDCl3 + TFA): δ = 6.91 (s, 4H, Ar-H), 6.48 (s, 2H, alkylidene H), 4.09 (m, 12H, O-CH2), 3.33 (m, 4H, NH-CH2), 1.87 (m, 12H, O-CH2-CH2), 1.71 (m, 4H, NH-CH2-CH2), 1.66-0.86 (multiple peaks, 104 H, CH2, CH3). 13C NMR (CDCl3): δ = 173.1, 157.0, 155.2,
Helical Supramolecular Aggregates Based on Ureidopyrimidinones

N,N'-(1,7-Heptamethylene)-bis-(2-ureido-6-[3,4,5-tri((-S))-3,7-dimethyloctyloxy)phenyl]-4-pyrimidinone (5). The title compound was synthesized from 1,7-diisocyanatoheptane in the same way as compound 4. Purification was performed by column chromatography (eluent: 2% tetrahydrofuran in chloroform) and precipitation in methanol, resulting in pure 5 (Y = 29%). IR(UATR): δ = 3222, 1694, 1114 cm⁻¹. ¹H NMR (CDCl₃ + TFA): δ = 6.88 (s, 4H, Ar-H), 6.62 (s, 2H, alkylidene H), 4.19 (m, 4H, O-CH₂), 4.09 (m, 8H, O-CH₂), 3.33 (m, 4H, NH-C₃H₂), 1.87 (m, 12H, O-CH₂-C₃H₂), 1.68 (m, 4H, NH-CH₂-C₃H₂), 1.66-0.86 (multiple peaks, 108 H, CH₂, CH₃). Anal. Calcd. (%) for C₈₉H₁₅₀N₈O₁₀ (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'-(1,8-Octamethylene)-bis-(2-ureido-6-[3,4,5-tri((-S))-3,7-dimethyloctyloxy)phenyl]-4-pyrimidinone (6). The desired compound was synthesized from 1,8-diisocyanatooctane following the procedure of compound 3. Purification was carried out with column chromatography (eluent: 2% tetrahydrofuran in chloroform) and precipitation in methanol, resulting in pure 6 (Y = 28%). IR(UATR): δ = 3226, 1692, 1115 cm⁻¹. ¹H NMR (CDCl₃ + TFA): δ = 6.88 (s, 4H, Ar-H), 6.57 (s, 2H, alkylidene H), 4.08 (m, 12H, O-CH₂), 3.32 (m, 4H, NH-C₃H₂), 1.87 (m, 12H, O-CH₂-C₃H₂), 1.69 (m, 4H, NH-CH₂-C₃H₂), 1.66-0.86 (multiple peaks, 110 H, CH₂, CH₃). ¹³C NMR (CDCl₃): 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 C₉₀H₁₅₄N₈O₁₀ (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,N'-m-Xylylene-bis-(2-ureido-6-[3,4,5-tri((-S))-3,7-dimethyloctyloxy)phenyl]-4-pyrimidinone (7a). The title compound was obtained from m-xylylenediisocyanate in the same way as 3. Column chromatography (flash silica, 2/4/94 methanol/tetrahydrofuran/chloroform) gave pure 7a (Y = 36 %). IR(UATR): ν = 3226, 1692, 1115 cm⁻¹. ¹H NMR (CDCl₃ + 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-C₃H₂), 4.15 (t, 4H, OCH₂), 4.06 (t, 8H, OCH₂), 1.81 (m, 12H, OCH₂-C₃H₂), 1.49 (m, 12H, OCH₂-CH₂-C₃H₂), 1.29 (br, 96H, CH₂, CH₃), 0.90 (t, 18H, CH₃). Anal. Calcd. (%) for C₁₀₂H₁₇₀N₈O₁₀ (1668.51): C 73.43; H 10.27; N 6.72. Found (%): C 72.54; H 9.87; N 6.71. MALDI-TOF-MS: (MW = 1507.18) m/z 1508.18 [M]+, 1530.16 [M+Na]+.

N,N'-m-Xylylene-bis-(2-ureido-6-[3,4,5-tri((-S))-3,7-dimethyloctyloxy)phenyl]-4-pyrimidinone (7b). For the synthesis of the title compound see the procedure for compound 3. 2% Tetrahydrofuran in chloroform was used as an eluent for column chromatography, and precipitation in methanol gave pure 7b (Y = 14%). IR(UATR): ν = 3226, 1692, 1115 cm⁻¹. ¹H NMR (CDCl₃ + TFA): δ = 7.34 (s, 2H, m-Ph-H), 7.10, 6.87 (s, 4H, Ar-H), 6.61 (s, 2H, alkylidene H), 4.52 (d, 4H, NH-C₃H₂), 4.15 (t, 4H, OCH₂), 4.06 (t, 8H, OCH₂), 1.81 (m, 12H, OCH₂-C₃H₂), 1.49 (m, 12H, OCH₂-CH₂-C₃H₂), 1.29 (br, 96H, CH₂, CH₃), 0.90 (t, 18H, CH₃). Anal. Calcd. (%) for C₉₀H₁₄₆N₈O₁₀ (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]+.

Ethyl 3,4,5-tri((-S))-3,7-dimethyloctyloxy)benzoylacetae (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 Et₃N (2.56 g, 3.5 mL) followed by dry MgCl₂ (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 H2O (2x10 mL) and a 5% NaHCO3 solution (20 mL) and then concentrated under vacuum to give the product as a solid (3.9 g, 86%), which was used in the following step without further purification. 1H NMR (CDCl3): δ = 7.21 (s, 2H, Ar-H), 4.24 (q, 2H, O-C(H2)CH3), 4.06 (m, 6H, O-CH2), 1.75-1.93 (m, 6H, O-CH2-C(H2)), 1.75-0.9 (multiple peaks, 54H, CH, CH2, CH3).

Potassium mono ethyl malonate (10). Diethyl malonate (50 g, 0.312 mol) was dissolved in ethanol (200 mL). A solution of potassium hydroxide (17.5 g, 0.312 mol) in ethanol (200 mL) was added dropwise over one hour. 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%). 1H NMR (CDCl3): δ = 4.06 (q, 2H, OCH2), 3.15 (s, 2H, CH2C=O), 1.12 (t, 3H, CH3).

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 guanidinium 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. 1H-NMR (CDCl3): δ = 12.35 (br, 1H, NH), 7.13 (s, 2H, Ar-H), 6.19 (s, 1H, alkylidene H), 5.84 (br, 2H, NH2) 4.02 (m, 6H, O-CH2), 1.7-1.9 (m, 6H, O-CH2-C(H2)), 1.49 (m, 6H, O-CH2-CH2-C(H2), 1.28 (br, 48H, CH2), 0.89 (t, 9H, CH3). 13C-NMR (CDCl3): 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 C46H81N3O4 (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 guanidinium 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. 1H NMR (CDCl3) δ = 12.35 (br, 1H, C=C-NH-C=N), 7.13 (s, 2H, Ph-H), 6.18 (s, 1H, H-C=C-N), 5.82 (br, 2H, N=C-NH2) 4.07 (m, 6H, O-CH2), 1.7-1.9 (m, 6H, O-CH2-CH2), 1.7-0.8 (multiple peaks, 51H). 13C NMR (CDCl3) 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. Anal. Calcd (%) for C40H69O4N3 (656.01): C 73.7; H 10.6; N 6.41. Found (%): C 73.02; H 10.30; N 6.09.
6.6 References and Notes

23. Model for chiral amplification in n-mers (sergeants and soldiers effects)
   (cyclic) dimers:
   Assumptions: two kinds of monomers , achiral (a) and chiral (c)
   CD effect (ellipticity): $\varepsilon(a) = 0$; $\varepsilon(c) = 1$
   concentrations of a, c: $[a]$, $[c]$
   fraction of a: $f(a) = [a]/([a] + [c])$
   fraction of c: $f(c) = [c]/([a] + [c])$
fraction of aa dimers $f(aa) = [aa]/ ([aa] + [ac] + [cc])$
Statistical distribution of aa, ac and cc dimers:
$f(aa) = f(a)^2$; $f(cc) = f(c)^2$; $f(ac) = 1- f(a)^2 - f(c)^2$.
Assume that cc dimers and ac dimers have the same CD effect:
total ellipticity: $\Delta \varepsilon(tot) = \Delta \varepsilon(c) \times [f(ac) + f(cc)]$
$\Delta \varepsilon(tot) = \Delta \varepsilon(c) \times (1- f(a)^2)$
Chiral amplification: $A = \Delta \varepsilon(tot)/(\Delta \varepsilon(c) \times f(c)) = \Delta \varepsilon(tot)/(1- f(a))$
A = $(1-f(a)2)/(1-f(a))$.
Plotting gives a straight line with values of 1 when $f(a)=0$ and 2 when $f(a)$ approaches 1.

Monodispersed solution of n-mers:
Assumptions: $a_n$ does not contribute to the CD effect. All other n-mers containing at least 1 chiral monomer equally contribute to the CD effect.
Statistical distribution of chiral monomers among n-mers:
$f(a_n) = f(a)^n$
Chiral amplification $A = (1-f(a)^n)/(1-f(a))$
Plotting gives a curved line with a maximum value of $n$ when $f(a)$ approaches 1.

Tautomerism in Columnar Mesophases of Quadruple Hydrogen Bonded Dimers of a Liquid Crystalline Ureidopyrimidinone*

Abstract

A study of the thermotropic behavior of quadruple hydrogen bonded dimers based on ureidopyrimidinone 1-6 is presented. 1-6 exhibit thermotropic liquid crystalline properties as evidenced by DSC and optical microscopy. Compound 1a, showing liquid crystallinity between 40 and 140 °C, as evidenced by differential scanning calorimetry and optical polarization microscopy, was studied in more detail with temperature dependent X-ray diffraction in order to study effects of tautomerism in the thermotropic mesophase. One disordered hexagonal columnar phase and two more highly ordered phases were observed. The presence of both keto and enol tautomeric forms of dimerized 1a in separate columns of the C_{ho} phase was established with temperature dependent IR, solid state NMR, and X-ray diffraction.

* Part of this work will be published: Rolf A. Koevoets, Rint P. Sijbesma, Lianbin Li, Pieter C. M. M. Magusin, Wim H. de Jeu and E. W. Meijer, J. Mater. Chem, in prep.
7.1 Introduction

Self-assembly is a useful way to generate highly organized supramolecular structures. Reversible non-covalent interactions are used to selectively favor the formation of desired structures at the expense of other aggregates. Multiple hydrogen bonding and metal-ion complexation are very useful interactions in this respect, and their use in the construction of well defined aggregates of discrete size in solution has been amply demonstrated in rosettes, capsules, boxes and many other structures.

Figure 7.1. (a) Calix[4]arene based capped assembled through hydrogen bonding (Image adopted from reference 3). (b) Gridlike structure via complexation of the 3,6-bis(2-pyridyl)pyridazine ligand with copper(I) ions (Image adapted from reference 4).

Hydrogen bonding has also been used extensively to induce calamitic mesophases in low molecular weight molecules, as well as in polymers. Hydrogen bonding between complementary molecules has also been used to form dimeric or oligomeric discs, which assemble in columnar mesophases. This concept was used by Malthête et al. in columnar mesophase in which the discs consist of two carboxylic acid dimers. Lattermann and Lilly have reported on self-complementary amides, which form columnar mesophases. In these discotic mesophases, the discs are formed by one single dimer. Lattermann has also described the formation of discotic phases with six tri(decyloxy)phenyl benzoate molecules in one disc. Further examples of hydrogen bonded assemblies which form columnar phases include the biologically significant tetramers of deoxyguanosine derivatives and folates, trimers of dihydrophthalazine-1,4-diones, and complexes of triazines with alkoxybenzoic acids. We have shown that ureidotriazines dimerize through a self-complementary DADA array of 4 hydrogen bonds with an association constant of $2 \times 10^4$ M$^{-1}$ in CDCl$_3$, and we have reported that dimers of mono- and bifunctional ureidotriazines substituted with trialkoxyphenyl groups form helical columnar structures in dodecane solution. The same arrangement was observed for monofunctional ureidotriazine derivatives substituted with a conjugated oligo(p-phenylene vinylene) group, while the bistriazine derivative forms less ordered aggregates in dodecane. Helical columnar phases have also been observed for bis-ureidopyrimidinones. Ureidopyrimidinones (UPy’s) have been shown to exist as a mixture of dimers of the 4[1H]-
pyrimidinone (keto) tautomer and pyrimidin-4-ol (enol) tautomer (Figure 6.4, inset). Dimerization in solution through the self-complementary DDAA and ADAD arrays\textsuperscript{18} of 4 hydrogen bonding sites is very strong (association constant $K_a = 6 \times 10^7 \text{ M}^{-1}$ in CHCl$_3$).\textsuperscript{19} The keto-enol equilibrium of UPy's in solution has been reported to be solvent and substituent dependent.\textsuperscript{20} However, the effects of tautomerism in thermotropic UPy's has not been studied so far. In this chapter the thermotropic liquid crystalline properties of 1-6 (Scheme 7.1) are presented. Furthermore we report dimerization and tautomerism in the thermotropic mesophases of N-butylaminocarbonyl-6-[3,4,5-tridodecyloxy)phenyl]-isocytosine 1a, using FTIR, solid state NMR, DSC, polarization microscopy and X-ray diffraction.

### 7.2 Thermotropic liquid crystallinity

UPy derivatives 1-6 dimerize in chloroform, as is shown by the position of the NH signals between 10 and 14 ppm in the $^1$H-NMR spectrum in CDCl$_3$ (See Figure 6.4 and 6.5, chapter 6). Assignment of the peaks for 1 shows that the keto and the enol tautomer are present in a 87:13 ratio.

![Chemical structure](image)

**Scheme 7.1. Mono- and bifunctional molecules 1-6.**

UPy derivatives 1a and 1b form disc shaped dimers upon dimerization, with a rigid, planar core, surrounded by flexible alkyl groups. This architecture is conducive to the formation of a columnar discotic mesophase in bulk.\textsuperscript{21} In bifunctional derivatives 2-6, similar columns of UPy dimers may be formed when each spacer moiety connects two stacked discs. Depending on the arrangement of the spacers, the columns are either polymeric, or they consist of stacks of cyclic dimers of the bifunctional molecules (Figure 7.2).
Dimerization in the bulk at elevated temperature was investigated for 1-6 by ATR, using the distinct peak at 3140 cm\(^{-1}\) characteristic for the ureido N-H hydrogen bonded to the central pyrimidine ring nitrogen. This band persists upon heating a thin film of this compound from room temperature to 150 °C, while bands of free NH stretch vibrations remain absent, indicating that 1-6 remain dimerized in the isotropic melt.

<table>
<thead>
<tr>
<th>Table 7.1. Thermotropic properties of compounds 2-7b determined with DSC.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound &amp; K &amp; (T_m) &amp; (\Delta H_m) &amp; M &amp; (T_{iso}) &amp; (\Delta H_{iso}) &amp; I</td>
</tr>
<tr>
<td>1a &amp; &amp; 40 &amp; 38.5 &amp; &amp; 131 &amp; 1.8 &amp;</td>
</tr>
<tr>
<td>1b &amp; &amp; 98 &amp; 1.5 &amp; &amp;</td>
</tr>
<tr>
<td>2 &amp; &amp; 173 &amp; 2.2 &amp; &amp;</td>
</tr>
<tr>
<td>3a &amp; &amp; -11 &amp; 14 &amp; &amp; 164 &amp; 3.7 &amp;</td>
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<tr>
<td>3b &amp; &amp; -11 &amp; 14 &amp; &amp; 160(^{b}) &amp;</td>
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<tr>
<td>4 &amp; &amp; 147 &amp; 2.2 &amp; &amp;</td>
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<tr>
<td>5 &amp; &amp; 207 &amp; 12.3 &amp; &amp;</td>
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<tr>
<td>6a &amp; &amp; -17 &amp; 18 &amp; &amp; 242 &amp; 7.1 &amp;</td>
</tr>
<tr>
<td>6b &amp; &amp; 239 &amp; 7.5 &amp; &amp;</td>
</tr>
</tbody>
</table>

\(^{a}\) The phase is observed; \(K\) = crystalline phase; \(M\) = mesophase; \(I\) = isotropic phase. \(^{b}\) Only observed after precipitation in methanol.

In order to investigate the presence of (columnar discotic) mesophases, the thermal behavior of compounds 1-6 was studied with polarization microscopy and DSC. All compounds feature strong birefringent textures, which are liquid-like at room temperature. Monofunctional compound 1a and bifunctional compound 2 feature flower or fan-like textures upon slowly cooling from the isotropic phase (Figure 7.3). These focal conic textures are typical for discotic hexagonal phases. For compounds 1b and 3-6 only tiny homeotropic monodomains were present in the liquid crystalline state, probably due to the highly viscous isotropic melt. Upon heating, the DSC traces of the compounds show a transition from the mesophase to the
isotropic state at temperatures between 98 and 242 °C. The transition was also observed upon cooling, except for chiral compound 2. Sharp melting points were observed for achiral compounds 1a (Figure 7.4), 3a, and 6a, while the chiral compounds only showed broad transitions, below –50 °C, presumably due to a glass transition. The phase transition temperatures are summarized in Table 7.1.

Figure 7.3. Optical microscopy photos of compound 2 (left) and compound 1a (right). Textures were grown by slowly cooling from the isotropic melt (5 K min⁻¹).

7.3  Dimerization and tautomerism in thermotropic mesophases of 1a

The effect of tautomerism in thermotropic UPy’s has not been studied so far. In the remaining part of this chapter, focus will be on dimerization and tautomerism in the thermotropic mesophases of N-butylaminocarbonyl-6-[3,4,5-tridodecyloxy)phenyl]-isocytosine 1a, using FTIR, solid state NMR, DSC, polarization microscopy and X-ray diffraction.

7.3.1  Aggregation in bulk

As described above, the thermal behavior of 1a was studied with DSC and optical microscopy to investigate the presence of mesophases. Compound 1a is liquid-like, yet strongly birefringent above 40 °C. Furthermore it displays fan-like textures upon slowly cooling from the isotropic phase. These focal conic textures are characteristic for columnar hexagonal phases.

The DSC thermogram of microcrystalline 1a features a large endotherm (ΔH = 38.5 J/g) at 40 °C (Figure 7.4). This endotherm is ascribed to melting of the crystalline phase to a liquid crystalline mesophase. A second endotherm, with a much smaller enthalpy (ΔH = 1.8 J/g) is observed at 131 °C, which corresponds to the isotropisation temperature observed with polarization microscopy. Compound 1a crystallized at 20 °C upon cooling at a rate of 10 °C/min.
7.3.2 X-Ray diffraction of 1a

To elucidate the identity of the mesophase, compound 1a was studied with X-ray diffraction at 35, 50, 55, 60 and 70 °C on samples that were first heated to up to 70 °C for 5 min, and then cooled down to measuring temperature.\textsuperscript{22} The observed reflections in the circularly integrated diffraction patterns (Figure 7.5) are summarized in Table 7.2.

The reflections indicate that three different phases can be discerned. A liquid crystalline phase is present from the highest temperature down to the melting point of 40 °C, below which it is replaced by a highly ordered crystalline phase. The phase behavior of the system is complicated by the presence of a third phase, which coexists with either of the two other phases at temperatures below 60 °C.
The mesophase present at 70 °C features a first order reflection with a diffraction spacing of 27.8 Å. Higher order reflections with scattering vectors $\sqrt{3}$ and $\sqrt{4}$ times the 100 reflection are observed, indicative for a columnar hexagonal phase. In the wide-angle region (measured at 65 °C, Figure 7.6) only diffuse scattering is observed, attributed to a liquid-like arrangement of the flexible alkyl chains. The absence of a disc-disc reflection indicates that the columnar hexagonal phase is disordered and consequently it is assigned as Col$_{hd}$.

In the scattering diagram at 35 °C, below the melting point of 1a, the disordered hexagonal mesophase (Col$_{hd}$) has disappeared and is replaced by a phase with a first order reflection at 30.4 Å and higher order reflections with relative distances of $\sqrt{2}$, $\sqrt{4}$ and $\sqrt{8}$ to the 100 reflection. From the relative distances it can be concluded that this phase has a rectangular lattice. In the wide-angle region a set of peaks appears at 4.11 and 3.96 Å. Based on the large enthalpy associated with the transition at 40 °C (Figure 7.4) the low temperature phase has been assigned crystalline, K. The number of molecules per unit cell for this phase was determined using the following relationship between the density, $\rho$, of the complexes in the mesophase and the number of molecules in the unit cell, $Z$: $\rho = (M/N) / (V/Z)$, where $M$ is the molar mass of the pure compound, $N$ the Avogadro number, and $V$ the unit cell volume (cm$^3$): $V = (\sqrt{3}/2)a^2c \cdot 10^{-24}$. Assuming that the density of the dimers should not differ significantly from 1 g/cm$^3$, it is clear that there is 1 supramolecular dimer present per unit cell.

Table 7.2. Diffraction spacings in Å for the three different mesophases of compounds 1a.

<table>
<thead>
<tr>
<th>Phase Identity</th>
<th>K</th>
<th>Col$_{ho}$</th>
<th>Col$_{hd}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>30.4</td>
<td>30.4</td>
<td>-</td>
</tr>
<tr>
<td>010</td>
<td>21.6</td>
<td>21.5</td>
<td>-</td>
</tr>
<tr>
<td>110</td>
<td>-</td>
<td>-</td>
<td>47.0</td>
</tr>
<tr>
<td>200</td>
<td>15.1</td>
<td>15.2</td>
<td>40.7</td>
</tr>
<tr>
<td>020</td>
<td>10.8</td>
<td>10.7</td>
<td>-</td>
</tr>
<tr>
<td>420</td>
<td>-</td>
<td>-</td>
<td>15.1</td>
</tr>
<tr>
<td>600</td>
<td>-</td>
<td>-</td>
<td>13.7</td>
</tr>
<tr>
<td>610</td>
<td>-</td>
<td>12.5</td>
<td>12.4</td>
</tr>
<tr>
<td>620</td>
<td>11.4</td>
<td>11.3</td>
<td>-</td>
</tr>
<tr>
<td>?</td>
<td>11.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>001 (disc-disc)</td>
<td>4.11</td>
<td>4.49 ; 4.17</td>
<td>-</td>
</tr>
<tr>
<td>hk1</td>
<td>3.96</td>
<td>4.35 ; 4.05</td>
<td>-</td>
</tr>
<tr>
<td>Density</td>
<td>1.08</td>
<td>1.04</td>
<td>-</td>
</tr>
<tr>
<td>Molecules per unit cell</td>
<td>2</td>
<td>12</td>
<td>-</td>
</tr>
<tr>
<td>Temperature range</td>
<td>&lt;40 °C</td>
<td>&lt;60 °C</td>
<td>&gt;40 °C</td>
</tr>
</tbody>
</table>
Figure 7.6. Circularly integrated WAXS diffraction pattern of 1a at different temperatures as indicated.

The melting point of 1a corresponds to a transition (K → Col$_{hd}$) of columns with rectangular packing into hexagonal packing. A decrease of the intercolumnar spacing upon melting (when going from K → Col$_{hd}$) is a well-known phenomenon, which is attributed to stiffening of side chains into the extended all-trans configuration in the K phase.

Figure 7.7. Presence of the different phases and tautomeric forms (keto and enol) of 1a as a function of temperature.

The third phase is formed when the sample is cooled below 60 °C, where it coexists with the Col$_{hd}$ phase; it persists below the melting point of 1a. This phase is characterized by reflections at 47.0, 40.8, 15.1, 13.7, 12.5 and 11.4 Å which coincides with spacings calculated for higher order reflections of a columnar hexagonal phase with a first order spacing of 80.2 Å. Unfortunately, this first order reflection is not observed in the SANS pattern. Comparison with the unit cell of the Col$_{hd}$ and K phases shows that the third phase contains 6 columns of dimers per unit cell. In the wide-angle region, 4 peaks with similar intensities appear at 4.49, 4.35, 4.17, and 4.05 Å. We tentatively assign these peaks to 001 and hk1 reflections in an ordered columnar hexagonal phase designated as Col$_{ho}$, with different intercolumnar distances in non-equivalent columns. The presence of the three phases as a function of temperature is depicted in figure 7.7.
7.3.3 Keto-enol tautomerism of 1a

The complex phase behavior and the presence of a phase with several columns in the unit cell may well be related to the coexistence of the keto and enol tautomeric forms of 1a. Therefore, temperature dependent tautomerism was studied in detail using solid-state NMR and FTIR. CP-MAS spectra were recorded for compound 1a in a 4 mm spinner with a spinning rate of 10 kHz, $d_1 = 5$ s and $p_1 = 5$ ms at 4 different temperatures: $20^\circ$C, $35^\circ$C, $55^\circ$C and $75^\circ$C. CP-MAS measurements are not amenable to quantitative analysis because nuclei may have different rates of cross polarization. For qualitative interpretation the spectra were compared to $^{13}$C NMR spectra of 1a in solution, in which the keto-form has a characteristic peak at 148.7 ppm while the enol-form has a distinguishing signal at 164.9 ppm.

Up to $55^\circ$C all peaks in the CP-MAS spectra can be accounted for and indicative peaks for both keto and enol tautomeric forms are present (Figure 7.8), indicating that up to this temperature the keto and enol tautomers coexist. At $75^\circ$C the peaks in the spectrum become very broad due to the liquid-like nature of the sample and no further conclusions about the composition of 1a at and above this temperature can be drawn.

Figure 7.8. CP MAS spectrum of 1a recorded at $35^\circ$C.

Since IR spectra of dimers in the solid state in the 4[H]-pyrimidinone and the pyrimidin-4-ol tautomer show pronounced differences (the keto from has characteristic peaks at 1692 cm$^{-1}$, whereas the enol form has characteristic peaks at 1557 and 1311 cm$^{-1}$),24 temperature dependent FT-IR was used as an additional technique to determine the presence of tautomeric forms at different temperatures.

Figure 7.9 shows that at $75^\circ$C, 1a is entirely in its keto-dimeric form, since the characteristic bands of the enol form are absent. When the temperature is lowered to $50^\circ$C, where Col$^{hd}$ and Col$^{ho}$ coexist, peaks of the enol tautomer appear, showing that at this temperature both tautomeric forms are present. Upon cooling to $35^\circ$C, no further changes occur in the FT-IR spectrum. The results of the X-ray, IR and solid-state NMR measurements are summarized in Figure 7.7, in which the presence of the different phases and two tautomeric forms is shown as a function of temperature.

With these data, it is possible to establish the presence or absence of keto and enol tautomeric forms in each of the three phases. Firstly, from FTIR it is clear that Col$^{hd}$ consists purely of keto-dimers. Since the $K \rightarrow$ Col$^{hd}$ transition is attributed to a reorganization of the...
columns from a rectangular to a hexagonal packing, it is very likely that the crystalline phase also consists of pure keto dimers. The presence of enol tautomers in the FTIR spectra recorded at the temperature range where these phases coexist with Col_{ho} shows that Col_{ho} consists at least partly of enol-dimers. The unit cell of Col_{ho} therefore contains dimers of each tautomeric form. The cell parameters indicate that the columns of this phase are ordered, but that the 6 columns are not all equivalent, because two different repeat distances (4.5 and 4.2 Å) along the c-axis are observed. This implies that keto and enol dimers each form separate columns in a shared lattice.

![Figure 7.9](image)

**Figure 7.9.** Temperature dependent IR measurements at 35 (---) and 75 °C (—) performed on 1a. For clarity, the spectrum recorded at 50 °C is omitted.

### 7.4 Discussion and Conclusions

Ureidopyrimidinone derivatives 1-6 form liquid crystalline mesophases in which dimeric units are stacked in columns with hexagonal order. Quadruple hydrogen bonding in 1a leads to stable keto and enol dimers in solution and bulk. 1a predictably forms a discotic mesophase over a broad temperature range, as confirmed by X-ray analysis. Temperature dependent X-ray analysis showed the presence of three different phases. The complicated phase behavior is related to the existence of the two different tautomeric forms of 1. A crystalline phase with rectangular symmetry (K) is present up to the melting point and can be attributed to columns of keto dimers. This phase melts at 40 °C to form a disordered hexagonal mesophase (Col_{ho}), also consisting of dimers of the keto form. Finally, an ordered mesophase (Col_{ho}) coexists with the other phases and is present up to 60 °C. This phase contains separate columns of keto and enol dimers, constituting a lattice of 6 columns per unit cell. The incommensurability of the disc-to-disc distances in the columns frustrates crystallization of the Col_{ho} phase.
7.5 Experimental section

General methods. The synthesis of compounds 1-6 is described in detail in chapter 6. Unless otherwise stated, all reactions were carried out under an atmosphere of dry nitrogen and technical grade solvents were used. Anhydrous THF was obtained by distillation from sodium/potassium/benzophenone.

NMR-spectra were recorded on a Varian Gemini 300 or a Bruker AM400. Chemical shifts are given in ppm relative to TMS for proton spectra and carbon spectra. IR-spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. Melting points and liquid crystalline mesophase ranges were determined on a Jenaval THMS 600 polarizing microscope, and are uncorrected. DSCs were taken on a Perkin-Elmer DSC-7 under a nitrogen atmosphere, with heating and cooling rates of 10 °C min⁻¹. Solid state NMR measurements were performed on a Bruker AVANCE DMX-500 spectrometer (magnetic field 11.7 T) equipped with a 4mm MAS probe. WAXS and SAXS measurements were performed by Dr. Liangbin Li of AMOLF Amsterdam, using an in-house setup (AMOLF Amsterdam) with a rotating anode X-ray generator (Rigaku RU-300H, 18 kW) equipped with two parabolic multi-layer mirrors (Bruker, Karlsruhe), giving a highly parallel beam of monochromatic CuKα radiation (λ = 0.154 nm) with a divergence of about 0.012°. The X-ray flux of this arrangement is an order of magnitude larger than for conventional pinhole collimation in combination with a nickel filter. The beam size was defined by two sets of slit-pinholes while a guard slit-pinhole was placed in front of the sample to cut parasitic scattering from the beam-defining slits and the mirrors. The SAXS intensity was collected with a two-dimensional gas-filled wire detector (Bruker Hi-star) at a distance of 34.25 cm from the sample position. A semi-transparent beamstop in front of the area detector allowed us to monitor the intensity of the direct beam. The WAXS intensity was recorded by a linear position sensitive detector (PSD-50M, M. Braun, Germany), which could be rotated around the beam path to measure in either the meridional or the equatorial direction. The SAXS and WAXS intensities were normalized to the intensity of the direct beam attenuated by the semi-transparent beam stop.

Experimental procedure. A Linkam CSS450 system was used as a temperature controlled sample stage. Samples were kept in a brass sample holder with Kapton windows replacing the original glass windows of the system. SAXS and WAXS were employed to track the step heating and cooling scan. Each step was equilibrium for 5 min, and then SAXS and WAXS measurements were taken for 30 min for each frame. The two-dimensional SAXS intensity was first integrated azimuthally to obtain the scattering pattern as a function of q = 4πsinθ/λ, the modulus of the momentum transfer vector q, λ being the x-ray wavelength and 2θ the scattering angle.

X-ray data.

Reflections for columnar phases:
d-spacing: h, k, l; Miller indices, a, b, c

Reflections for hexagonal phases:
\[
\frac{1}{d_{100}^2} = \frac{4}{3}\left(h^2 + h^2 + k^2\right)/a^2
\]
\[
d_{100} : d_{110} : d_{200} : d_{210} : d_{300} : d_{220} : \ldots = 1 : 1/\sqrt{3} : 1/\sqrt{7} : 1/3 : 1/\sqrt{12} : \ldots
\]

Reflections for rectangular phases:
\[
\frac{1}{d_{hk}^2} = h^2/a^2 + k^2/b^2
\]
7.6 References and Notes


X-ray diffraction patterns appeared to be highly dependent on the way the sample was prepared. Upon annealing at 50 °C from the isotropic melt, a completely different diffraction pattern was observed, indicative for another hexagonal phase: 31.1 (100), 17.95 (110), 11.73 (210), 10.4 (300).


Summary

Functional materials based on multiple hydrogen bonding motifs are described in this thesis. In the first part, the strongly aggregating bisurea hydrogen-bonding motif is used to obtain well-defined thermoplastic elastomers (TPEs). TPEs constitute a commercially relevant and fundamentally interesting class of polymeric materials. They combine the properties of irreversibly crosslinked elastomers, such as impact resistance and low-temperature flexibility, with the characteristics of thermoplastic materials, e.g. the ease of processing. In general, TPEs are phase-separated systems consisting of a hard phase, providing physical crosslinks, and a soft phase, contributing to the elastomeric properties. In the second part of this thesis, the self-complementary quadruple hydrogen bonding ureidopyrimidinone (UPy) unit is employed to obtain highly ordered supramolecular polymers (Chapter 6 - 7) that fold into well-defined aggregates due to π-interactions.

A general introduction on the strongly aggregating bisurea groups is given in Chapter 1. Supramolecular aggregation of low-molecular weight bisurea compounds and a scanning tunnelling microscopy study of the multilevel order of these low molecular weight bisurea compounds on solid substrates are described. Finally, TPEs with bisurea hard blocks are introduced.

In Chapter 2 of this thesis, an overview is given of the synthesis, mechanical and thermal properties as well as the morphology of segmented block copoly(ether urea)s with poly(tetrahydrofuran) (pTHF) soft blocks of various lengths (350 g/mol – 4000 g/mol) and uniform hard blocks consisting of two urea groups that are separated by a methylene spacer varying from butylene to heptylene. These materials show very interesting tensile properties. The co-continuous hard phase of these materials, as observed with AFM, however, resulted in large plastic deformation. Attempts to improve the mechanical properties of these TPEs by changing the co-continuous hard phase to a dispersed hard phase by incorporation of association inhibitors are discussed in bulk and solution. Finally a new way of processing these TPEs via electrospinning is presented.

In Chapter 3, a diacetylene group was incorporated within the hard segment domain of the TPEs. The diacetylene groups provide a means to topochemically crosslink our TPE in the solid state using UV radiation. With the development of this diacetylene segmented copoly(ether urea), the behaviour of thermoplastic elastomers has been expanded to include mechano-optic and chromic properties, characteristic of polydiacetylenes. In this way, the mechanical properties of the copoly(ether urea)s could be altered, without altering its original morphology. The mechanochromic as well as thermochromic behavior of the resulting materials are studied using infrared linear dichroism spectroscopy in combination with polarized UV spectroscopy. Below the yield point (80 % strain), the hard domains tilt in a direction parallel to the deformation axis. Above the yield point however, fragmentation and irreversible reorganization of the hard domains occur, resulting in perpendicular orientation. As a result of this reorganization process, an irreversible mechanochromic transition was observed at strains larger than 80%. The optical properties of the diacetylene-segmented copolymer were further
modified by temperature. An irreversible shift of the absorption band to higher energies was observed during temperature cycling.

In Chapter 4, we showed that length-dependent molecular recognition between bisurea units in an elastomeric host results in selective modulation of mechanical properties. Strong discrimination between guests differing in size by a single methylene group was observed. Incorporation of bisurea containing dye molecules in the hard blocks of the polymer is also selective, resulting in different extractabilities of the dyes by detergent solutions. The guest selectivity of the elastomeric material can be used to selectively orient dyes upon elongation of thin films. With the possibility to draw functionalized fibers by electrospinning we introduce a modular approach for thermoplastic meshes with a variety of applications, like catalysis.

In Chapter 5 the segmented block copoly(ether urea)s have been used as solid supports for hydroformylation catalysts with the aim to facilitate catalyst recovery. We showed that electrospun meshes of segmented copoly(ether urea)s, containing supramolecularly bound rhodium phosphine complexes, are efficient catalysts for the hydroformylation of 1-octene. The ligands used are mono- and diphosphine ligands based on triphenylphosphine, equipped with a bisurea recognition unit. The activity and selectivity observed for supported and unsupported rhodium-phosphine complexes are comparable. The solvent used for the hydroformylations and the immobilization conditions appeared to have a large impact on the observed activity. Recycling studies showed unchanged selectivity and even increased activity during the first 3 runs. After that, the catalyst starts degrading. These very promising preliminary results are a reason to continue studying this system in more detail.

In Chapter 6 highly ordered structures were obtained by combining the concept of linear supramolecular polymers formed by bifunctional molecules, with the columnar organization of tri-(alkoxy)phenyl-ureido-pyrimidinone. The effects of length and preorganisation of the spacer on the aggregation behavior is investigated. In chloroform, the bifunctional compounds form cyclic dimers at millimolar concentrations, which are in equilibrium with linear species above a critical concentration. No Cotton-effect was observed for any of the compounds. In dodecane, however, a CD-effect was observed for the bifunctional compounds with a pentylene, hexylene and m-xylylene spacer, indicating the presence of highly ordered helical superstructures.

In Chapter 7 the thermotropic behavior of a monofunctional tri-(alkoxy)phenyl-ureido-pyrimidinone is studied in detail. It showed liquid crystalline behavior between 40 and 140 °C as evidenced with DSC and optical polarization microscopy. Temperature dependent X-ray analysis showed the presence of three different phases. The complicated phase behavior was found to be related to the existence of two different tautomeric forms. The presence of the tautomeric forms in the three different phases was studied with temperature dependent IR and solid state NMR.
Samenvatting

In dit proefschrift worden functionele materialen beschreven die gebaseerd zijn op meervoudige waterstofbruggen. In het eerste deel van dit proefschrift wordt de sterk aggregerende waterstofbrug-vormende bisureum eenheid gebruikt om goed gedefinieerde thermoplastische elastomeren (TPE) te verkrijgen. TPE’s zijn vanuit commercieel oogpunt een relevante en fundamenteel interessante verzameling van polymeren. Ze combineren de eigenschappen van irreversibel vernette elastomeren, zoals weerstand tegen inslag en flexibiliteit bij lage temperaturen, met de kenmerken van thermoplastische materialen, zoals verwerkbaarheid. TPE’s zijn fasegescheiden systemen bestaande uit een harde fase die zorgt voor fysische vernetting, en een zachte fase, die zorgt voor de elastische eigenschappen van het materiaal. In het tweede deel van dit proefschrift, worden de zelfcomplementaire viervoudige waterstofbrug-vormende 2-ureido-4[1H]-pyrimidinone (UPy) eenheden gecombineerd met π-interacties om goed georganiseerde supramoleculaire polymeren te verkrijgen, die zich kunnen opvouwen tot helische superstructuren.

Hoofdstuk 1 introduceert de sterk aggregerende bisureum groepen. De supramoleculaire aggregatie van laag moleculaire bisureum verbindingen en de ordening van deze verbindingen op vaste substraten is beschreven. Tenslotte worden TPE’s gebaseerd op bisureum groepen geïntroduceerd.

In hoofdstuk 2 van dit proefschrift wordt een overzicht gegeven van de synthese, de morfologie, en de mechanische en thermische eigenschappen van gesegmenteerde blok copoly(ether urea)s met zachte blokkken bestaande uit poly(tetrahydrofuran) (pTHF) van variërend molekuulgewicht (350 g/mol tot 4000 g/mol) en goed gedefinieerde harde blokken waarin de twee ureum groepen gescheiden zijn door een verbindingstuk variërend van butyleen tot heptyleen. Deze materialen vertonen interessante rek-eigenschappen. De co-continue harde fase, zoals die waargenomen werd met atomic force microscopie (AFM), leidt echter tot grote plastische vervorming. Om deze plastische vervorming tegen te gaan, is geprobeerd de co-continue harde fase om te zetten in een disperse harde fase met behulp van associatie remmers in zowel de vaste fase als in oplossing. Ten slotte wordt elektrospinnen als een nieuwe manier beschreven om deze TPE’s te verwerk.

Een diacetylen groep werd ingebouwd tussen de twee ureum groepen van het harde blok. Door middel van UV licht werden de diacetylen groepen topochemisch vernet in de vaste fase. Op deze manier werden de mechanische eigenschappen van de blok copoly(ether urea)s veranderd, zonder de morfologie te beïnvloeden. De ontwikkeling van dergelijke diacetylen gesegmenteerde blok copoly(ether urea)s, welke beschreven staan in Hoofdstuk 3, stelde ons in staat om de mecano-optische en chromische eigenschappen, die karakteristiek zijn voor polydiacetylenen, in detail te bestuderen. De mechanochrome en thermochrome eigenschappen van deze vernette TPE’s zijn uitvoerig bestudeerd met behulp van infrarood lineair dichroïsme en gepolariseerde UV spectroscoopie. Met deze technieken werd zowel een irreversibele mechanochrome als thermochrome overgang waargenomen.
Moleculaire herkenning op basis van verschillende afstanden tussen de twee ureum groepen van gastmoleculen in de gesegmenteerde blok copoly(ether urea)s leidt tot selectieve modulatie van de mechanische eigenschappen, zoals aangetoond in Hoofdstuk 4. Een sterk verschil werd waargenomen voor een aantal gastmoleculen, die slechts verschillen in het aantal methyleen groepen tussen de ureas. Vermenging van kleurstof moleculen, die gefunctionaliseerd zijn met een bisureum groep van verschillende lengtes, is ook selectief, resulterend in verschillen in uitwasbaarheid uit de elastomeren matrix. De mogelijkheid om selectief gast moleculen in de polymeren matrix in te bouwen kan benut worden om op modulaire wijze functionele materialen te verkrijgen met toepassingen in bijvoorbeeld katalyse.

In Hoofdstuk 5 zijn de TPE’s gebruikt als drager materiaal voor hydroformylerings-katalysatoren, met als doel de terugwinning van de katalysator uit de productfase te vergemakkelijken. Gaasjes, die verkregen zijn door electrospinnen, en de daarin supramoleculair gebonden rhodium-phosphine complexen, bleken efficiënte katalysatoren voor de hydroformylering van 1-octeen. Hiervoor werden mono- en diphosphine liganden gebruikt gebaseerd op triphenylphosphine, welke gefunctionaliseerd zijn met een complementaire bisureum-groep. Zowel de activiteit als de selectiviteit van aan drager materiaal gebonden rhodium-phosphine complexen en homogene rhodium-phosphine complexen zijn vergelijkbaar. Het oplosmiddel dat werd gebruikt voor de hydroformylering, alsmede de manier waarop de gaasjes werden verkregen, bleken echter een grote invloed te hebben op de waargenomen activiteit. Uit recycling experimenten bleek een onveranderde selectiviteit en zelfs een licht toegenomen activiteit gedurende de eerste drie cycli. Hierna begon de prestatie van de katalysator echter af te nemen.

Door het concept van supramoleculaire polymeren, opgebouwd uit bifunctionele moleculen, te combineren met columnaire ordening van tri(alkoxy)phenyl-ureidopyrimidinone, werden zeer geordende secundaire structuren verkregen in apolaire oplosmiddelen. Het effect van de lengte en de pre-organisatie van het verbindingsstuk tussen de twee UPy-groepen op de aggregatie is bestudeerd. In chloroform vormen de bifunctionele verbindingen dimeren bij lage concentraties, terwijl bij hogere concentraties lineaire structuren werden waargenomen. Voor geen van de verbindingen werd echter een CD-effect waargenomen. In dodecaan werd echter een CD-effect waargenomen voor de bifunctionele verbindingen die met elkaar verbonden zijn via een pentylen, hexyleen en m-xylylene verbindingsstuk, duidend op een goed georganiseerde helische superstructuur.

In Hoofdstuk 7 werd het thermotrope gedrag van een monofunctioneel tri-(alkoxy)phenyl-ureido-pyrimidinone in detail bestudeerd. Een vloeibaar kristallijne fase werd waargenomen tussen 40 en 140 °C met behulp van DSC en optische polarisatie microscopie. Met temperatuurafhankelijke Röntgen-verstrooiing werden 3 verschillende fases aangetoond. Dit gecompliceerde fasegedrag bleek gerelateerd te zijn aan de aanwezigheid van twee verschillende tautomere vormen. De aanwezigheid van de tautomere vormen in de drie verschillende fases is bestudeerd met temperatuurafhankelijke infrarood spectroscopie alsmede met vaste stof NMR.
Curriculum Vitae

Rolf Koevoets was born in Rucphen, the Netherlands on July 12th, 1977. He obtained his VWO (pre-university) degree at the Gertrudis Lyceum in Roosendaal. In 1995 he started the study of Chemical Engineering at the Eindhoven University of Technology. From 1998 to 1999 he participated in an exchange program at the University of Osaka in Japan. In May 2001 he obtained his Master of Science degree with a graduation project at the Laboratory of Macromolecular and Organic Chemistry. In July 2001 he started as a Ph.D. student in the same group under the supervision of prof.dr. E.W. Meijer and dr. R.P. Sijbesma. The most important results of the research, part of which is performed in cooperation with dr. J.N.H. Reek and dr. M.J. Wilkinson at the University of Amsterdam and prof. dr. W.H. de Jeu and dr. L. Li at Amolf Amsterdam, are described in this thesis.
Dankwoord

Na een aantal maanden zwoegen, is nu de tijd aangeroepen voor leukere dingen: terugkijken op 4 prachtige jaren binnen SMO. Jaren die zo mooi zijn geweest door de geweldige sfeer binnen SMO en de bereidheid van mensen elkaar te helpen waar mogelijk. Vandaar dat het niet meer dan normaal is, dit proefschrift te beëindigen met het bedanken van al die mensen die hebben bijgedragen aan dit proefschrift. Een aantal van hen wil ik hierbij nog specifiek noemen.

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