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Hydrogen Bonded Polymers

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Hydrogen Bonded Polymers

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Preface

Control of polymeric structure is among the most important endeavours of modern macromolecular science. In particular, tailoring the positioning and strength of intermolecular forces within macromolecules by synthetic methods and thus gaining structural control over the final polymeric materials has become feasible, resulting in the field of supramolecular polymer science. Besides other intermolecular forces, hydrogen bonds are unique intermolecular forces enabling the tuning of material properties via self-assembly processes over a wide range of interaction strength ranging from several kJ mol^{-1} to several tens of kJ mol^{-1}. Central for the formation of these structures are precursor molecules of small molecular weight (usually lower than 10 000), which can assemble in solid or solution to aggregates of defined geometry. Intermolecular hydrogen bonds at defined positions of these building blocks as well as their respective starting geometry and the initial size determine the mode of assembly into supramolecular polymers forming network-, rodlike-, fibrous-, disclike-, helical-, lamellar- and chainlike architectures. In all cases, weak to strong hydrogen-bonding interactions can act as the central structure-directing force for the organization of polymer chains and thus the final materials' properties.

The important contribution of hydrogen bonds to the area of supramolecular polymer chemistry is definitely outstanding, most of all since the potency of hydrogen-bonding systems has been found to be unique in relation to other supramolecular interactions. Thus the high level of structural diversity of many hydrogen-bonding systems as well as their high level of directionality and specificity in recognition-phenomena is unbeaten in supramolecular chemistry. The realization, that their stability can be tuned over a wide range of binding strength is important for tuning the resulting material properties, ranging from elastomeric to thermoplastic and even highly crosslinked duroplastic structures and networks. On the basis of the thermal reversibility, new materials with highly tunable properties can now be prepared, being able to change their mechanical and optoelectronic properties with very small changes of external stimuli. Thus the field of hydrogen-bonded polymers forms the basis for stimuli responsive and adaptable materials of the future. Moreover, the recognition that many aspects of the "bulk"-supramolecular polymer-chemistry can be transferred to binding and recognition events on surfaces is an area still in its infancy. Binding processes of polymers, nanoparticles or other nanosized objects onto (polymeric, quasipolymeric) surfaces by noncovalent interactions already forms a new and strongly expanding area in nanoscience and nanotechnology.

The exploitation of the high specificity of the hydrogen-bonding systems, combined with their dynamic features has opened a new branch in polymer science: dynamic materials with self selection processes. This field, opened up by J. M. Lehn with his "dynamers" is highly prospective for the generation of new materials with properties unachievable with conventional monomers and polymeric materials, relying purely on the covalent bond, instead of the noncovalent, supramolecular interaction.

The present volume on *Hydrogen-Bonded Polymers* provides an overview on these aspects within four main chapters. Different points of view are mirrored, featuring aspects related to (a) classification of hydrogen-bonded polymers according to the nature of the connecting hydrogen bond (by W. H. Binder and R. Zirbs) (b) small-molecule self assembly into hydrogen-bonded polymers (by L. Bouteiller) (c) properties of the resulting materials, with a main focus on the interplay of dynamic properties and polymer-microphases (ten G. Brinke, J. Ruokolainen, O. Ikkala) and (d) nanocomposite materials derived from Hydrogen-bonding elements (H. Xu, S. Srivastava, V. M. Rotello). The varying titles demonstrate that hydrogen-bonded supramolecular polymer chemistry is a highly interdisciplinary research field, where structure, properties and function are closely interrelated to each other.

Still in its infancy, the field of supramolecular polymer chemistry has definitely found its own area and fixed place within the area of macromolecular and polymer chemistry. Although with a certain delay, the recognition of "designed" intermolecular forces as a tool to direct the ordering and function of macromolecules has now been widely acknowledged and respected. The transfer of principles of "organic" supramolecular chemistry is fully accomplished and used with great perfection. Many principles exploited during the past years in this field therefore have already found their application in polymeric material science, and will definitely expand in the near future.

Vienna, February 2007 Wolfgang H. Binder

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Supramolecular Polymers and Networks with Hydrogen Bonds in the Main- and Side-Chain

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Abstract Control of polymeric structure is among the most important endeavors of modern macromolecular science. In particular, tailoring the positioning and strength of intermolecular forces within macromolecules by synthetic methods and thus gaining structural control over the final polymeric materials has become feasible, resulting in the field of supramolecular polymer science. Besides other intermolecular forces, hydrogen bonds are unique intermolecular forces enabling the tuning of material properties via self-assembly processes over a wide range of interaction strength ranging from several kJ mol^{-1} to several tens of kJ mol^{-1}. The present review provides an overview of hydrogen-bonded polymers, with a focus directed towards the type of hydrogen bond as well as their effect on the final, ordered materials. Thus, the ordering effects of single-, double-, triple-, quadruple and multiple hydrogen bonds are discussed separately. Furthermore, various architectures as well as the use of hydrogen bonds on planar surfaces to assemble quasipolymeric structures are discussed.

Keywords Hydrogen bond · Supramolecular polymer · Surface · Polymeric material · Self assembly

Abbreviations

A	hydrogen-bonding acceptor
AFM	atomic force microscopy
AA-PDMS	diacid telechelic poly(dimethylsiloxane)
A-PDMS	monoacid telechelic poly(dimethylsiloxane)
ATRP	atom transfer radical polymerization
D	hydrogen-bonding donor
DAP	2,6-diamino-pyridine
DBSA	dodecyl benzenesulfonic acid
DMSO	dimethyl sulfoxide
MDI	methylene-4,4′-diisocyanate
NDP	nonadecyl phenol
MMA	methyl methacrylate
NMP	*N*-methyl-morpholine
NMR	nuclear magnetic resonance
PAA	poly(acrylic acid)
PCL	poly(caprolactone)
PDMS	poly(dimethylsiloxane)
PDP	pentadecyl phenol
PEO	poly(ethylene oxide)
PEOx	poly(ethyloxazoline)
PEK	poly(ether ketone)
PI	poly(isoprene)
PIB	poly(isobutylene)
PIPS	polymeric induced phase separation
PMMA	poly(methylmethacrylate)
PPO	poly(propylene oxide)
PS	poly(styrene)
PSSA	poly(styrene-4-sulfonic acid)
PS(OH)	poly(4-hydroxy-phenol)
PVAc	poly(vinylacetate)
PVDAT	poly(vinyldiaminotriazine)
PVP	poly(vinylpyridine)
P4VP	poly(4-vinylpyridine)
ROMP	ring opening metathesis polymerisation
SAM	self assembled monolayer
SAXS	small angle X-ray scattering
SIMS	dynamic secondary ion mass spectrometry
SSL	strong segregation limit
STVPy	styrene-co-4-vinylpyridine
STVPh	styrene-co-4-vinylphenol
STM	scanning tunnelling microscopy
THF	tetrahydrofurane
TDI	toluene-2,4-diisocyanate
WAXS	wide angle X-ray scattering
WSL	weak segregation limit

1
Introduction

Polymeric structure and structure formation has been subjected to strong changes in point-of-view during the past centuries. First, the nineteenth century saw macromolecules viewed as mainly colloids and these were postulated as being aggregates of small organic molecules with the forces involved being "side valence forces or Nebenvalenzen"; however, this view was changed drastically by Herrmann Staudinger [1], who realized that covalent bonds were the building force of macromolecules, which were then identified as the constituent structure of polymers. It was realized that the characteristic properties of polymers were determined by the initial structure of the macromolecules, i.e., the identity of the monomers, the degree of polymerization, the mode of distribution of specific monomers within the chain, the topology of the chains (linear, grafted polymers or dendritic), the stereochemistry (tacticity) and the crosslinking between chains. Furthermore, the ordering of macromolecules was found to be most important in determining the final materials properties by influencing crystallization behavior, phase separation and thus in turn the chemical and mechanical properties of polymers. Most of all, concepts to use weak hydrogen-bonding interactions were found to promote the formation of miscibility and thus the controlled formation of polymer blends [2].

Lehn et al. [3] first introduced the principle of supramolecular polymer chemistry more as an extension of substituting small organic molecules by telechelic polymers than "real" long chain polymer structures. It was suggested that intermolecular forces can be used to assemble small organic molecules into two- and three-dimensional structures reminiscent of linear or crosslinked polymers. Among other forces (such as dipol-dipol interactions, pi-pi stacking and charge-charge interactions) the hydrogen bonds form a central structural building-force to generate chains with low molecular weights as well as dendritic and weakly crosslinked structures in solution. The idea, however, was revolutionary in that it disrupted the concept of conventional polymer chemistry (in the sense of Staudinger), which regarded polymers as covalently bound monomeric units. Therefore, not only the general influence of hydrogen bonds on the bulk-polymeric structure (as in polyamides, polycarbonates, polyesters) or the solution-structure (as in PMMA, PVAc, PVP, PEOx, polyvinylalcohol) is taken into account, moreover the hydrogen bond as a tuned interaction is used for polymer organization. Thus, polymers became a much larger group of materials, which now included even higher molecular weight aggregates with thermally reversible linkages at room temperature or below. A variety of "highly ordered" structures, in particular those on planar surfaces such as Langmuir–Blodgett films, self-assembled monolayers were given the name "two-dimensional polymer".

More highly organized supramolecular polymers were then introduced by Stadler et al. [4] by transforming a linear, noncrosslinked soft polybutadiene chain into a thermoplastic elastomer. The concept relied on the statistical introduction of hydrogen bonds into the polybutadiene thus creating defined noncovalent crosslinking sites between the polymer chains. It was found that a hydrogen binding donor-acceptor unit for each 50 butadiene-units (i.e.: at approx. 2 mol %) is sufficient to drastically change the thermal and mechanical properties of the material, thus demonstrating that a couple of weak bonds on the side of a polymer chain can be very efficient in determining the final materials properties.

From this the concept of supramolecular polymers has evolved [5, 6]. Central for the formation of these structures are precursor molecules of small molecular weight (usually lower than 10 000), which can assemble in solid or solution to aggregates of defined geometry. Intermolecular hydrogen bonds at defined positions of these building blocks as well as their respective

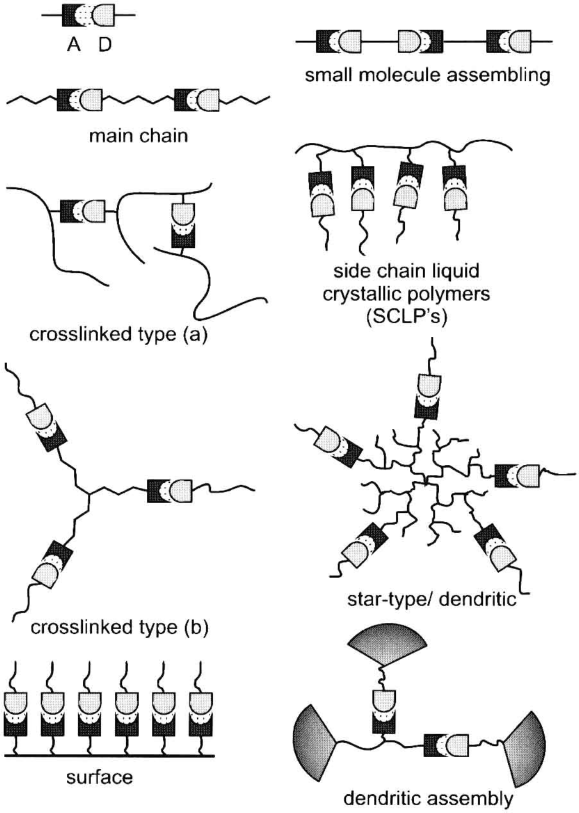

Fig. 1 Architectures of different hydrogen bonded, supramolecular polymers (A = hydrogen-bonding acceptor; D = hydrogen-bonding donor)

starting geometry and the initial size determine the mode of assembly into supramolecular polymers. Ordering can form network-, rodlike-, fibrous-, disclike-, helical-, lamellar- and chainlike structures as depicted in Fig. 1. In all cases, weak-to-strong hydrogen-bonding interactions can act as the central structure-directing force for the organization of polymer chains and thus the final materials properties.

The present review focuses on the formation of macromolecular structure via hydrogen bonds based upon supramolecular concepts, with a focus on the literature published between 2000 and 2006. There are a number of recent reviews relating to the topic of hydrogen-bonded supramolecular polymers, mostly with a focus on specific hydrogen-bonding systems [7–13]. The last review on hydrogen-bonded polymers, related to a broader view on hydrogen-bonding systems by Meijer et al. in 2001 [14] is therefore taken as a starting point for the newer literature. Thus, the focus is directed at designed interactions, deriving from either a functionalized monomer, or a polymeric endgroup, including hydrogen-bonding systems only. The association of molecules with a small molecular weight (below 1000 Dalton) will not be covered, since the work by L. Bouteiller in this series deals with this very aspect. Sect. 2 will give a short overview of hydrogen bonds, a compilation on their strength as well as those used in supramolecular polymer chemistry. Sect. 3 will deal with polymers bearing hydrogen bonds in their main chain, ordered according to the number of hydrogen bonds involved. Sect. 4 deals with polymers bearing hydrogen bonds in their side-chain. Sect. 5 focuses on the use of hydrogen bonds on surfaces, to bind polymers or generate quasipolymeric structures.

2
Hydrogen Bonds

Hydrogen bonds as intermolecular forces have been reviewed intensely in books [15] and reviews [16]. In principle three different classes of hydrogen-bonding systems are discriminated (Fig. 2) (a) strong hydrogen bonds, (b) medium or weak hydrogen bonds, and (c) nonclassical hydrogen bonds. Jeffrey and Sanger classify strong hydrogen bonds as those where two center bonds (such as $F-H\cdots F^-$; $O-H\cdots O^-$; $O^+-H\cdots O$ bonds) are involved, which display short distances, a strongly directional nature and association energies higher than $\sim 40\,\mathrm{kJ\,mol^{-1}}$. Medium and weak hydrogen bonds are classified by a $D-H\cdots A$ structure, where directionality is partially lost, and the bond energies are between 20–40 $\mathrm{kJ\,mol^{-1}}$. Usually, the residue A is strongly electronegative, whereas the residue D may be electronegative or even a carbon atom. Nonclassical (also termed unconventional) hydrogen bonds [17] involve the interaction of $D-H$ with $A = \pi$-systems as well as transition metals (interaction directly with the metal or via the metal hydride) or boron hy-

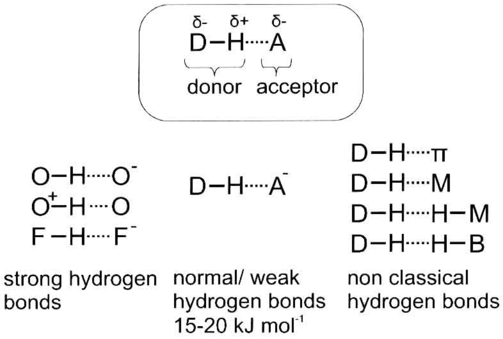

Fig. 2 Overview on various hydrogen bonds ranging from strong to nonclassical hydrogen bonds (D = hydrogen-bonding donor; A = hydrogen-bonding acceptor; M = metal; B = boron)

drides. In general, the strength of each individual hydrogen bond is strongly dependent on solvent effects, most of all polar and protic solvents. It has been demonstrated quite often, that the addition of a polar solvent significantly lowers the hydrogen bond over many orders of magnitude. Therefore, the supramolecular chemistry of hydrogen-bonded polymers is mostly done in aprotic and nonpolar solvents such as linear and cyclic alkanes, toluene, dichloromethane and chloroform.

The main parameter determining the strength of a hydrogen-bonding system is the number of individual bonds involved. Thus, as a rule of the thumb, more hydrogen bonds imply a stronger binding interaction, with the ideal value of about 7.4 kJ mol^{-1}/hydrogen bond. Figures 3–5 list the most prominent hydrogen-bonding systems used in supramolecular chemistry of polymers. Starting from those with only one hydrogen-bonding interaction (Fig. 3), two-centered hydrogen bonds (Fig. 4), three- (Fig. 5), four- and multiple hydrogen-bonding interactions (Fig. 6) are listed. In contrast to other

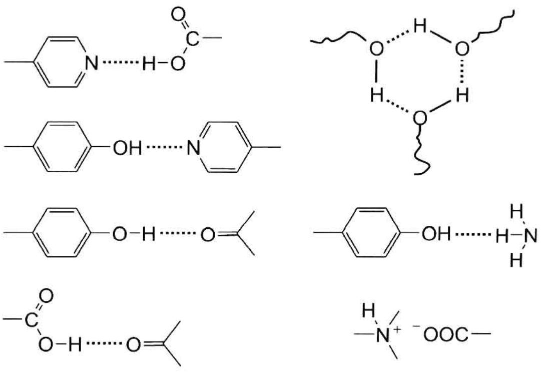

Fig. 3 Molecular structures of single hydrogen bonds