Mechanically linked oligorotaxanes
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Summary

Rotaxanes represent a group of compounds in which a dumbbell-shaped molecule is encircled by a macrocycle. These relatively new and exciting supramolecular architectures might find their applications in molecular devices (e.g. data storage). For such application, the shuttling motion of the ring over the linear chain in the dumbbell must be controlled to obtain a molecular switch. An important issue to achieve this, is the understanding of the interactions that operate between the two moieties of the rotaxane structure.

To apply rotaxanes in the construction of new materials, these interlocked compounds can be incorporated into polymers to give mechanically linked polymers. The driving force for chemists to prepare such polymers is the anticipated deviation in mechanical and elastic properties, compared to covalently linked polymers. Until now, the synthesis of mechanically linked polyrotaxanes has not been realized.

In this thesis, a new approach to the synthesis of these mechanically linked polymers by a stepwise procedure is presented. The shuttling dynamics in solution are studied, as well as the possibility to have control over the motion by introducing a topological constraint in the rotaxane structure. Attempts are made to determine the movement of rotaxane oligomers under the influence of an electrical field by means of scanning force microscopy (SFM). Finally, the interactions in dibenzylammonium ion–crownether complexes are investigated with SFM.

In chapter 1, an overview is given of the different types of interactions which can be present in rotaxanes and examples are given for each case. For the cyclophane–polyether (C–P) rotaxanes, the synthesis and variations in the structure are discussed. From an application point of view, the principle of molecular shuttles and switches and possible structures of polyrotaxanes are given.

The ‘stepwise’ polymerization procedure, which will be applied by us in the synthesis of mechanically linked oligorotaxanes, is presented in chapter 2. As a starting material, a rotaxane monomer with one protected functionality in the cyclic unit and one in the dumbbell is needed. Via selective deprotection of the functional groups in separate batches and subsequent coupling, the number of repeating units in the oligomer can be doubled after each sequence to obtain a dimer, tetramer, etc. The advantage of this method is that monodisperse oligomers are obtained. Based on several requirements that the monomer has to fulfill, a C–P rotaxane with diphenylmethane blocking groups has been selected, bearing one phenol in the dumbbell and one carboxylic acid in the cyclophane. The coupling (esterification) can proceed fast, in high yield and under mild conditions, a few of the requirements for the coupling reaction. As the protective group for the phenol, tert-butyldiphenylsilane (TBDPS) is chosen because of its chemical stability and ease and selectivity of cleavage. To determine which
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The protective group is best suited for the acid group, model reactions are performed. From these it is concluded that both tetrahydropyranyl (THP) and allyl can be used.

Chapter 3 concerns the synthesis and characterization of two rotaxane monomers. In the first one, bearing the TBDPS-protected phenol and THP-protected carboxylic acid, we found that the THP-ester is very labile and is removed quantitatively during the synthesis of the rotaxane. In addition, the carboxylic acid is not very reactive towards esterification. Both problems are attributed to a combination of the strong electron-withdrawing effect of the pyridinium groups in the cyclophane and steric hindrance. To reduce these two effects, we have introduced a spacer group between the cyclophane and the carboxylic acid functionality. Moreover, the THP protective group was replaced by the allyl group, which is more stable. The second rotaxane, bearing the TBDPS–allyl protective group combination and the additional spacer is found to satisfy all requirements for the ‘stepwise’ polymerization. Selective deprotection of the two functional groups in the rotaxane monomer in two separate batches and subsequent esterification yields the dimer, as was confirmed by $^1$H-NMR spectroscopy and MALDI-TOF mass spectrometry. Unfortunately, we found evidence for the slow degradation of this type of rotaxane due to cleavage of the etheric bond between the linear part and the blocking group of the dumbbell, resulting in a low yield in the rotaxane synthesis and a small amount of unreacted dumbbell recovered after the reaction.

A new, more stable rotaxane, bearing tetraphenylmethane instead of diphenylmethane blocking groups is discussed in chapter 4. The rotaxane monomer, bearing again the two protected functional groups, can be synthesized in a better yield of up to 6.6 %, while the unreacted dumbbell can be recovered almost quantitatively, indicating that the tetraphenylmethane blocking group is indeed more stable. Via the ‘stepwise’ polymerization procedure, the dimer and tetramer have been synthesized. To ascertain a high yield for the esterification reaction with dicyclohexylcarbodiimide, the rearrangement of the $O$-acylurea into the $N$-acylurea must be prevented. As model reactions show, a mixture of dimethylaminopyridine (DMAP) and $p$-toluenesulfonic acid (TosH) is needed as the catalyst, where the former is present in a slight excess. In this way, a polyrotaxane is also prepared from the dimer, in which both functional groups have been deprotected. This ‘uncontrolled’ polycondensation yielded a polymer with, on average, 150 rotaxane molecules in each polymer chain.

In chapter 5, the dynamic properties of rotaxane molecules in solution, determined by NMR spectroscopy, are presented. Temperature-dependent measurements of ‘symmetric’ rotaxanes without the functional groups, with either diphenylmethane or tetraphenylmethane blocking groups show a coalescence of peaks on raising the temperature from 223 K to 298 K. From the coalescence temperature, the shuttling energy barrier is determined to be ca. 13.5 kcal.mol$^{-1}$ for both rotaxanes, which is in close agreement with literature values, corresponding to a shuttling rate of ca. 300 Hz at room temperature. The spectra of the
tetraphenylethane-based rotaxane monomer are very complex and no isolated peaks can be observed to calculate the shuttling energy barrier. Two-dimensional NOESY build-up experiments were conducted to determine a shuttling energy barrier of 12.8 kcal.mol\(^{-1}\), comparable to the values found for the ‘symmetric’ rotaxanes. By the intramolecular coupling of the two functional groups in the rotaxane monomer, we have synthesized a ‘molecular lasso’. From NOESY build-up experiments it is concluded that there is no shuttling motion at 233 K, due to the introduced topological constraint, while the rotaxane without constraint shuttles at ca. 5 Hz at the same temperature. In the ‘lasso’, the motion is inhibited by a chemical linkage.

The reversible control of the shuttling in rotaxanes is described in chapter 6. Monolayers of the monomer and dimer rotaxane are prepared on gold substrates. By changing the direction of an electrical field applied over these monolayers, it should be possible to either collapse the molecules, or extend them away from the surface, due to the positive charges in the cyclophane units. The measurements were performed in a SFM in an organic salt solution. Attempts to monitor the changes in the monolayer thickness, however, did not reveal the expected effect. We related this to the mechanical deformation of the monolayer by the tip during the measurements and to the limited sensitivity of the SFM. Nonetheless, apparent changes in height were observed in all monolayers and on bare gold substrates, due to optical effects. The applied electrical field creates a local high concentration of either positive or negative ions around the cantilever, which influences the refractive index of the solution. This causes a deflection of the laser beam used for the detection of the cantilever movement, and hence an apparent change in cantilever deflection is observed.

In chapter 7, SFM is employed to study the complexation behavior between dibenzylammonium (DBA) ions and crownethers. The adhesion forces between a tip, chemically modified with a DBA monolayer, and a substrate covered with either ‘open’ or ‘closed’ crownethers are determined. From the corresponding interfacial free energies, it is concluded that the DBA ions form a stronger complex with the ‘closed’ crownether due to its preorganized shape, the so-called ‘macrocyclic effect’. Furthermore, the DBA–‘closed’ crownether system shows a solvent dependency which agrees with previous observations in literature. for the DBA ion, a good correlation is found between the adhesion force and the Gibbs free energy of transfer from water to the given solvent, i.e. the solvation of the ion. Analysis of the force–distance curves shows the presence of a combination of hydrogen bonding and Van der Waals interactions between the two moieties. Similar results were previously found from X-ray studies.