Experimental research activities in recent years:

**Chemomechanical polymers: molecular recognition triggers large motions**

See also movie on drug release model: a chemical corkscrew

We have discovered that polymers bearing specific recognition sites can respond selectively to chemical and biological stimuli through large macroscopic movements. Such chemomechanical polymers are a new type of smart polymer, with the unique feature of combining a sensor and an actuator (a mechanical device for moving or controlling a mechanism or system) within one single unit, without the need of external devices such as a transducer or a power supply. When exposed to chemical or biological stimuli such as nucleotides, aminoacids or peptides in the environment these polymers produce large and reversible expansions or contractions. They can be downsized to thin films or microparticles, with enhanced velocity and sensitivity of response.

Until recently, chemomechanical polymers were essentially known for responding to rather unspecific changes by pH, salts and solvents. In the past few years we applied known principles of supramolecular chemistry to hydrogels bearing suitable recognition sites, which respond to a large variety of external organic stimuli by non-covalent interactions. Different compounds in the aqueous environment trigger quite different macroscopic motions of these gels; not only positional isomers can be distinguished but even optical isomers.

**Enantioselective contraction** induced by \( L \)- or \( D \)-dibenzoyl-tatraric acid in a chitosan hydrogel particle; the \( D \)-enantiomer triggers 94% , the \( L \)-isomer only 20 % contraction.

Recognition elements in a chemomechanical polymer
Logical AND gate: peptides trigger expansion only in presence of $\text{Cu}^{++}$ ions.

The motions moreover depend strongly on the pH of the medium, thus representing the basis of a simple logical AND gate, in which an action depends not only on the presence of one signal – for instance a nucleotide- but also on other conditions, here on a particular pH. A related cooperativity is also observed e.g. between benzoic acid as one component, and aminoacids as second component. A rather spectacular example is the action of aminoacids or peptides with a polymethyl(methyl)acrylate based gel containing also ethylenediamine-type binding sites: here a motion is only triggered if Cu or Zn ions are simultaneously present. It is hoped that these materials will find future uses in systems for controlled drug delivery, or e.g. uptake of toxic compounds, and even for flow control in medical devices or in microfluidic machineries. Also of interest is putting these smart hydrogels into tubes or onto flexible sheets to make unidirectional actuators like artificial muscles.

It is hoped that the implementation of more sophisticated recognition elements into chemomechanical polymers and a better understanding of the underlying mechanisms will lead to even smarter materials in the future.

**Anyone interested in taking up these challenges in his/her own laboratory is invited to contact Hans-Jörg Schneider**

**Possible applications.** (a) expansion as measured with a chitosan gel particle (0.2x 0.2x 0.05 mm); (b) contraction for e.g. drug release (“chemical corkscrew”); (c) expansion for linear movement; (d) expansion or contraction of chemomechanical film coated on flexible support; (e) flow control / microfluidics
Publications of the Saarbrücken group on chemomechanical polymers:

Group members who deserve credit for all this:

Nino Lomadze; Kazuaki Kato, Barabara Palm, Liu Tianjun


2 "Cooperativity in a Chemomechanical Polymer : A Chemically Induced Macroscopic Logical Gate" *Advanced Materials* 2004, 16/7, 613-615

3 "Large macroscopic size changes in chemomechanical polymers with binding sites for metal ions" *Chem. Commun.* 2004, 100-101.

4 "Large macroscopic size changes in chemomechanical polymers with binding sites for metal ions" *Chem. Commun.* 2004, 100-101.

5 “Sensitivity increase in molecular recognition by decrease of the sensing particle size and by increase of the receptor binding site - A case with chemomechanical polymers” *Chem. Commun.* 2004, 2436 to 2437.


7 “A chitosan-based chemomechanical polymer triggered by stacking effects with aromatic effectors including aminoacid derivatives” *Tetrahedron* 2005, 61/36, 8694-8698.


12” Chemomechanical Polymers as Sensors and Actuators for Biological and Medicinal Applications” *Sensors* 2007, 7, 1578-1611 *(with R Strongin et al )*
13 “Cooperativity and Selectivity in Chemomechanical Polyethyleneimine Gels”  
*Langmuir*, 2007, 23 (21); 10741-10745.

14 “Selectively Triggered Dimension Changes of Polyallyamine-Based Hydrogels”  

15 “Molecular recognition in chemomechanical polymers”  

16 “Chitosan-Based Chemomechanical Hydrogels”, *in preparation*

17 H.-J. Schneider, R.M. Strongin:  
“Supramolecular Interactions in Chemomechanical Polymers”  

**Other research activities**

1. Analyses of binding contributions and conformations of supramolecular complexes in solution; mechanisms of molecular recognition: quantification of biologically important interactions.
2. Cyclodextrins, cyclophanes and crown ethers or cryptands as models for the study of molecular recognition and as hosts for selective complexations.
4. Nucleic acid complexes: Binding mechanisms and optimization/ligand design (electrostatic and intercalative); with polyamines, peptides, and their combination with intercalators.
5. Polyamines: interactions with nucleic acids, peptides etc; potential uses as vectors for membrane transport.
6. Supramolecular metal complexes as artificial esterases, nucleases etc.