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Self-assembly of hydrogen-bonded block copolymer complexes

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For several years, the use of block copolymers in nanotechnology has been widely developed. These polymers can be used to obtain a wide range of nanostructured materials in the solid phase (thin films, for example) or in solution (micelles). An interesting method to modulate specific dimensions, morphology and properties of these nanostructures consists in mixing together two copolymers, or one copolymer and one homopolymer. If in addition to being mutually miscible, some sequences interact together through specific non-covalent interactions, an additional degree of control can be obtained. In this work, hydrogen bonds are considered.

When a selective solvent of one of the blocks is used, micelles can be formed. In this work, we have studied micelles formed between PS-*b*-P4VP and PAA or PS-*b*-PAA in organic solvents (THF and DMF) (see Figure 1). Strong hydrogen bonding between the P4VP and PAA blocks induces the formation of complexes which further aggregate into a micellar core surrounded by PS chains. The influence of parameters such as the length of the interacting blocks or the solvents used on the size of the formed micelles has been investigated in order to understand the complexation process.

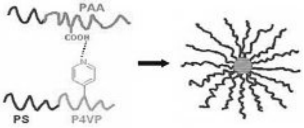

Figure 1. Micelles formed between PS-*b*-P4VP and PAA or PS-*b*-PAA

When a non selective solvent of the different blocks is used, the solutions can be processed into thin films. In this work, the influence of the addition of PAA on the size of the microdomains of a PS-*b*-PEO copolymer has been studied. PAA is miscible with PEO and interact with it by hydrogen bonds. The pure copolymer self-assembled into a cylindrical morphology. When the fraction of PAA is increased, an increase in the interdistance betweencylinders is first observed. Then, when the quantity of PAA reaches a certain level, a change in morphology occurs. A different behaviour is observed according to the PAA length. When the PAA has a smaller or an equal length compared to the PEO, the morphological change takes place for a smaller quantity of added PAA than if the PAA has a larger size than that of the PEO.

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Novel self-assembled polymer therapeutics based on coiled coil peptide sequences

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We have designed a novel class of polymer therapeutics in which a drug is attached to a peptide sequence, which has a strong heterospecific affinity to bind under physiological conditions with its complementary peptide attached to a polymer. As an appropriate non-covalent linker we selected the known E3/K3 coiled coil due to its high stability at pH~7 and partial unfolding at pH ~ 5 [1]. The corresponding polymeric carriers were prepared by copolymerizing K3 peptide sequences bearing an N-terminal methacrylate group with N-(2-hydroxypropyl)methacrylamide (HPMA). The E3 peptide was conjugated with the anticancer drug Methotrexate (MTX) using Fmoc-SPPS synthesis. The self-assembly of the two modified peptides into the heterodimeric coiled coil leads to formation of a conceptually novel class of pH-responsive, functional biomaterials. We have shown by CD, AUC and FRET studies that folding properties of the E3/K3 peptides were not affected by attaching a bulky anticancer drug neither by attaching PHPMA polymeric chain. The self-assembly properties of the E3/K3 coiled coil within the conjugates are evaluated under near physiological conditions, at pH 7 and 5. Moreover, the *in vitro* cytotoxicity, haemolysis, and internalization of the complexes in mice skin melanoma cells (B16F10) were evaluated. The dissociation of the E3/K3 coiled-coil linker upon internalization was verified by the fluorescence resonance energy transfer (FRET) effect, for complexes in which the drug is replaced with a fluorophore.

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Influence of the Molecular Structure on the Properties and Fuel Cell Performance of High Temperature Polymer Electrolyte Membranes

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The research interest for new polymeric materials for energy related applications has been significantly increased in the last years. In the frame of Fuel Cells, high temperature polymer electrolyte membrane Fuel Cells (PEM FCs) are potential candidates for market penetration mainly because of their ability to use directly reformatted hydrogen. Due to the relatively high operation temperature (180°-200°C), there are limited materials reaching the desired conductivity values with the most successful case being the combination of basic polymers with low volatility strong acids.

In this presentation, specific emphasis will be given on fully aromatic polymeric membranes doped with strong protic acids. Among these, polymers bearing polar pyridine units across or perpendicular to the main polymeric backbones in combination with other aromatic parts and phosphinoxide or sulfone units, are superior candidates for PEM-FCs operating up to 200 °C. They present excellent conductivity after doping with strong protic acids, even using dry gases, and their properties can be tuned on demand by the strategic choice of co-monomers and their ratios in the polymeric structure. The detailed study of their proton conduction mechanism has revealed that these materials show high proton conductivities at relatively low doping levels and more interestingly that their conductivity strongly depends not only on the membranes' doping level, but also on the detailed chemical structure of the polymeric matrixes. Such materials have been used for membrane-electrode assemblies (MEAs) constraction, which have been successfully tested in single cells operating at 180-200°C showing high performances and reasonable durability.

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Mesoscopic Properties of Amyloid Protein Fibers in Water

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We have studied the liquid crystalline features of two colloidal systems consisting of food protein amyloid fibrils in water, obtained by heat-denaturation and aggregation of β-lactoglobulin, a globular dairy protein. The fibrils had a monodisperse cross section of about 4 nm and two groups of polydisperse contour lengths: (i) fibrils 1-10 μm long, showing semiflexible polyelectrolyte-like behaviour and (ii) rigid rods 100-200 nm long. In both systems, the rod-like particles were highly charged (linear charge density of +5 e/nm) and were stable in water at low pH (pH 2) and no salt.

The phase diagrams of these two systems were investigated, by changing concentration and pH. Both systems were shown to exhibit rich phase behaviours. Interestingly, the experimentally measured isotropic-nematic phase transition was found to occur at 0.4% and at 3% for the long and short fibrils, respectively. For both systems, this phase transition occurred at concentrations more than one order of magnitude lower than what expected based on Onsager [1] and Odjik [2] theories. Moreover, no intermediate biphasic region was observed between the isotropic phase and the nematic phase. The various possible physical reasons responsible for the discrepancies between experimental and theoretical behaviour are considered and discussed within the present work.

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Size is not all: Parameters Affecting the Release of Tertiary Alcohols from the Surface of Dendrimers and Stylomers

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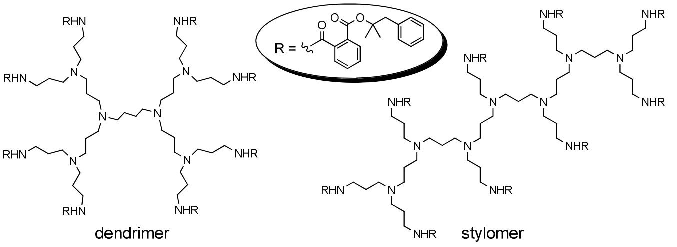
Due to the symmetric structures facilitating their characterisation, dendrimers have often been considered as model compounds for polymers and polymer conjugates. In previous investigations, the influence of the dendrimer structure on the release rates of bioactive compounds from macromolecular conjugates has mainly been described as a function of size (generation), whereas other parameters such as topology, polarity or solubility in different media have so far only been discussed in a few cases.



At the example of 2-carbamoylbenzoates, which have been found to efficiently release secondary or tertiary alcohols by neighbouring group assisted hydrolysis at neutral pH, we now systematically investigated the parameters influencing the release rates of a tertiary fragrance alcohol from "spherical" dendrimers and their corresponding "linear" stylomers [1]. Our data illustrate that the polarity of the conjugates (and thus their solubility) has a stronger influence on the rates of hydrolysis than their size or shape.

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Systematic coarse-graining the non-equilibrium dynamics of polymer melts

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Different multiscale modeling and coarse-graining techniques are currently being developed for polymer dynamics [1]. We present a novel, thermodynamically guided strategy for the dynamic simulation of microscopic models for complex fluids that is able to efficiently bridge the time- and length scale gap between the microscopic level and macroscopic dynamics. The systematic coarse-graining method is exemplified for low-molecular polymeric systems subjected to homogeneous flow fields. We use established concepts of nonequilibrium thermodynamics and an alternating Monte-Carlo-molecular dynamics iteration scheme in order to obtain the model equations for the slow variables [2]. For chosen flow situations of interest, the established model predicts structural as well as material functions beyond the regime of linear response. The results are in quantitative agreement with those obtaind via standard nonequilibrium molecular dynamics simulations. As a by-product, we present the first steady state equibiaxial simulation results for polymer melts. The method is simple to implement and allows for the calculation of time-dependent behavior through quantities readily available from the nonequilibrium steady states. The proposed method is very efficient and particularly powerful for weak up to moderate external forcings, and therefore complements standard nonequilibrium methods which are better suited in the regime of strong external forcings.

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Post-modification of Poly(glycidyl methacrylate) Brushes

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Polymer brushes are thin layers consisting of polymer chains tethered by one chain end to a surface. These polymer coatings, which are commonly generated *via* surface-initiated polymerization (SIP) techniques, represent a powerful strategy to adjust the chemical and physical surface properties of materials. Depending of the chemical composition of the polymer brush, the coated surfaces will exhibit specific responses towards biointeractions.

Polymer brushes composed of poly(poly(ethylene glycol) methacrylate) (PPEGMA) or poly(2-hydroxyethyl methacrylate) (PHEMA) are well known to suppress non-specific adhesion of proteins and cells, but they also contain hydroxyl groups that can be further derivatized to react with specific biomolecules [1][2]. However, polymer brushes natively containing functional groups in their side chains, such as epoxide, active ester or aldehyde groups, can be exploited without further derivatization to bind (bio)molecules. Poly(glycidyl methacrylate) (PGMA) brushes, bearing epoxide moieties, are excellent candidates for bioanalytical applications as they promote covalent and non-specific binding of a wide variety of (bio)molecules [3].

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Opposites attract?! Hierarchical co-assemblies of block copolymers in aqueous solution

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Electrostatically driven co-assembly of two oppositely charged double hydrophilic block copolymers in aqueous solutions results in core-shell micelles with a mixed core, consisting of polyelectrolyte blocks, and a mixed corona, consisting of neutral solvent-swollen blocks. The miscibility of the shell-forming blocks, and thereby the extent of chain mixing / segregation in the micellar corona, can be tuned by, for example, segment chemistry and solvent quality. A mixed shell is observed for PGMA / PAAm, and PNIPAAm / PEO, while a de-mixed shell (Janus-type) is observed for PAAm / PEO.[12] Such 'complex coacervate core micelles'; i.e. C3Ms, form spontaneously and can be equilibrium structures. Hence, C3Ms possess the unique ability to combine a compartmentalized internal structure with full responsiveness to external stimuli, such as pH, ionic strength, and mixing fraction. Furthermore, temperature sensitivity can be achieved through incorporation of a LCST block in the micellar corona, such as PNIPAAm or PDEAAm. Micellar stability can be enhanced by selection of polyelectrolyte blocks with a rather hydrophobic backbone, such as a modified poly(butadiene) block.

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PAMAM dendrimer mediated siRNA delivery to target Hsp27 and induce potent gene silencing and anticancer activity in prostate cancer

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RNAi holds great promise provided safe and efficient siRNA delivery systems are available. We have recently demonstrated that structurally flexible triethanolamine-core PAMAM dendrimers [1-2] are effective vectors for siRNA delivery in a luciferase-model system.[3] Presently, we have demonstrated that this family of dendrimers are effective nanovectors for delivering Hsp27 siRNA into androgen-independent prostate cancer PC-3 cells and produced specific gene silencing, resulting in a pronounced apoptosis-induced anticancer effect.[4] Altogether, our dendrimers should represent promising siRNA delivery systems and hold great potential for further *in vivo* therapeutic applications.

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Dynamics of the self-assembly of polymer-coated ceramic nanoparticles at liquid-liquid interfaces

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Self-assembly is found in uncountable natural phenomena and at all length scales [1]. In recent times men have started to harness Nature's self-organization to direct the assembly of materials and composites. Trapping at the interface, combined with lateral mobility and the presence of specific interactions, makes self-assembly of colloidal particles at liquid-liquid interfaces a process with huge potential for the creation of controlled structures and patterns [2], including novel ultrathin materials such as membranes and capsules [3]. We propose here to self-assemble core-shell, ultra-stable, ceramic nanoparticles into ultrathin membranes. The nanoparticles are stabilized by dispersants with anchor groups showing irreversible binding to the oxide cores [4]. Moreover a large range of dispersants can be used, allowing for the tailoring of the particle surface properties. Understanding the dynamics of particle adsorption at the interface and the mechanical properties of these assemblies is a prerequisite to direct the design of the nanoparticle constituents and for further processing into membranes and capsules. We have performed detailed pendant drop tensiometry experiments which show indeed an extremely rich and unexplored dynamical behaviour. Such experiments will be integrated by a microscopic characterization of the mechanical properties of the assembly via quantitative confocal microscopy by of fluorescent tracers at the interface.

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Liquid-Crystalline Rod-Coil Di-, Tri- and Tetra-Block Copolymers

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Self-organized polypeptide block copolymers are of great interest due to their potential uses as materials for nano-devices and bio-engineering. In order to explore the effect of block copolymer topologies on their structures, a series of di-, tri- and tetra-block copolymers has been synthesized (Figure 1). A coil-like soft block based on poly(propylene oxide) chemistry was chosen due to its low glass transition temperature, amorphous nature and immiscibility with biological systems. On the other hand, rod-like block polypeptide based on poly(*L*-glutamic acid γ-benzyl ester) was selected and grown from the coil soft macroinitiator by ring opening polymerization. Because of the mono-, bi-, or tri-functionality of the coiled blocks, linear di-block, tri-block and star-like tetra-block copolymers could be successfully synthesized. The resulting materials show microphase separated liquid-crystalline morphologies, in which the architecture or connectivity of the blocks, the molecular weight of the coil segment, the volume fraction and the secondary structure of the polypeptide blocks all contribute to their microphase separated features. These materials can be seen as model reference systems towards the design of biocompatible scaffolds and artificial muscles.

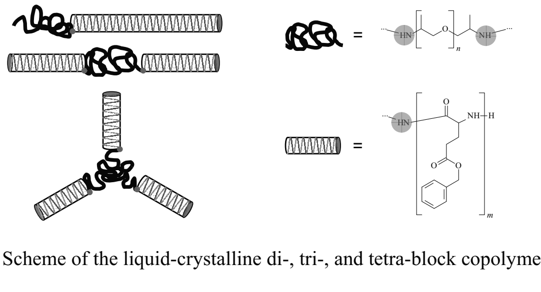

Figure 1. Scheme of the liquid-crystalline di-, tri-, and tetra-block copolymers

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Nanocomposites: Tuning morphology, concentration and orientation of particles integrated within a Polymethylmethacrylate matrix

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Combining nanoparticles and a polymer matrix in order to obtain nanocomposite systems in a controlled way remains a challenge. Any attempt to create nanocomposites with novel tailored properties thus requires a sound understanding of the relevant parameters that allow a control of the size, anisotropy, volume fraction, orientation, dispersion and distribution of the nanoparticles in the hybrid systems. Here we present successful ways to incorporate silica [1], silica-coated core-shell particles [2] and anisotropic iron oxide nanoparticles [3] into a polymethylmethacrylate matrix (PMMA). We also show some effects of tuning morphology, concentration and orientation of particles in order to create adaptive polymer colloid nanomaterials. Our approaches are based on a controlled synthesis, a subsequent in-situ surface functionalization using 3-(trimethoxysilyl)-propyl-methacrylate (TPM, 98%) silane agent, followed by a transfer to the methylmethacrylate (MMA) monomer solvent, and finally an in-situ co-polymerization of the surface-modified particles dispersed in the MMA monomer [4]. Another pathway towards nanocomposites is the use of a solvent approach where particles are first dispersed in organic solvents such as THF or chloroform which are good solvents for PMMA. After mixing with dissolved PMMA in the same solvent, the so-obtained nanocomposite can be recovered either by coprecipitation or solvent evaporation. We demonstrate and compare the results obtained with these different fabrication methods.

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Influence of Macromolecular Architecture on the Frustration of Supramolecular Liquid Crystalline Polymers

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Supramolecular chemistry is a very useful tool to create self-assembling materials based on non-covalent bonds. It is a biologically-inspired process that has been widely used for more than twenty years to easily tune macromolecules by attaching side chains onto the periphery of a macromolecular template via intermolecular forces such as hydrogen bonding, ionic interactions or metal coordination [1]. The widespread interest in these systems comes from the fact that the induced architectures may be reversible by playing with some stimuli such as the light, or the pH or ionic strength of the solution.

In our group we have extensively studied the supramolecular assembly of specific dendrons, dendronized polymers and dendrimers with flexible chains via ionic bonding. These systems have been shown to exhibit a wide variety of structures [2].

In this poster we discuss the consequences of increasingly high frustration and reduced degrees of freedom, on the self-assembly behaviour of supramolecular liquid crystals based on macromolecular dendridic templates. These results are benchmarked to previous finding on dendrimer and dendron supramolecular systems.

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Synthesis of silver nanoparticles in polyelectrolyte matrix

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Nowadays, a wide variety of composite materials consisting of polymers containing metal nanoparticles have been extensively investigated to realize their potential applications ranging from optoelectronics to biomaterials. Nanostructured materials consisting of silver nanoparticles (Ag-NPs) embedded in polymeric matrices show physico-chemical, optical and antibacterial properties [1, 2]. A simple method to prepare a AgNP/polyelectrolyte composite was successfully used. Thus, Ag-NPs were obtained through spontaneous formation of nanostructured silver from an Ag_2O/polystyrene sulfonate (PSS) solution. The kinetics of Ag-NP-formation was investigated by dynamic light scattering and UV/vis spectroscopy, and related morphology was investigated by X-ray diffraction techniques. The synthesis of the Ag-NP/polystyrene sulfonate composite was performed by mixing a PSS solution in water with a Ag_2O solution in diluted ammonia during 48 hours. The nanoparticle size was determined by TEM and SEM.

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Electrostatic Patch-Charge Attraction induced by Adsorbed Polyelectrolytes

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Forces between positively charged colloidal latex particles are directly measured in the presence of adsorbed anionic linear polyelectrolytes with the atomic force microscope (AFM). Electrophoretic measurements reveal that with increasing polyelectrolyte dose, the particles undergo a charge reversal at the isoelectric point (IEP). Away from the IEP, one finds strongly repulsive inter-particle forces dominated by electrostatic double layer overlap. Electrostatic surface potentials determined from these forces show good agreement with those obtained from electrophoresis. At the IEP, strongly attractive forces are observed. These forces exceed van der Waals forces, and clearly show exponential distance dependence. The decay length is consistent with electrostatic interactions due to patch-charge heterogeneities, whose existence can be rationalized through the laterally heterogeneous structure of adsorbed polyelectrolyte layers. The measured retraction forces further demonstrate that very few polyelectrolyte chains are bridging both surfaces. Based on these two observations we conclude that these attractions originate from electrostatic interactions between patch-charge heterogeneities.

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Comparison of two cationic polymeric flocculant architectures on the destabilization of negatively charged latex suspensions.

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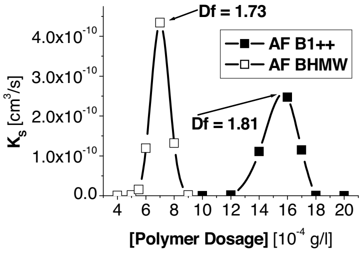
Flocculation studies between cationic polymers and oppositely charged latex colloidal particles are reported in which both flocculation kinetics and floc structures are systematically investigated. The flocculation rate constant, stability ratio and kinetics laws have been experimentally determined using particle counting for two polymer architectures; a cationic linear polymer and a two-branched polymer. The results suggest that the polymer architecture plays important roles on the polymer dosage for the rapid destabilization of the colloidal suspension.



The linear polymer at optimal dosage exhibits the highest flocculation rate constant, whereas on the other hand, the branched polymer concentration range of flocculation is larger. Branched polymers yield to the formation of compact flocs in comparison to those obtained with linear polymers indicating that the polymer architecture also plays a role on the flocculation mechanisms and floc structures. Floc structures were characterized calculating the floc fractal dimension Df.

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Optimization of Ni-NTA-functionalized vesicles for molecular recognition in solution

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Various copolymer membranes were modified for molecular recognition by attaching specific sites such as biotin or integral membrane protein receptors.[1][2] We introduced a new approach by metal-nitrilotriacetic acid functionalized amphiphilic diblock copolymers, which self-assemble in vesicles and expose the metal at their surface for molecular recognition.[3] Here we present our strategy to optimize the system for a high protein-binding affinity by increasing the NTA-metal concentration on the vesicle surface or by changing the environmental conditions such as solvents or pH.

To test the molecular recognition of our system, we used as model proteins His_6-tagged Enhanced Green Fluorescent Protein (EGFP), and His_6-tagged Red Fluorescent Protein (RFP), depending on the media in which the vesicles were formed. Protein binding in solution was visualized by fluorescence microscopy and characterized with Small Angle X-ray scattering (SAXS) and Fluorescence correlation spectroscopy. The value of the dissociation constant K_D determined for His_6-RFP in optimized hybrid system containing 15% Ni ions exposed at the surface of vesicles indicates a high binding affinity of protein which make our system to be very sensitive for further applications in molecular recognition.

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AGGREGATION AND GELATION BEHAVIOR OF POLYMER-MAGNETIC COLLOIDS UNDER THE INFLUENCE OF AN EXTERNAL MAGNETIC FIELD

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For this work, magnetic nanoparticles, composed of magnetite nanocrystals dispersed into a polymer matrix, have been prepared via miniemulsion polymerization. Due to the superparamagnetic behavior of the nanocrystals embedded in the polymer matrix, these nanoparticles, which have an average size below 100nm, develop strong and reversible dipolar interactions only in the presence of an external magnetic field.

We have then studied the aggregation and gelation behavior of dispersions of these nanoparticles in presence and absence of an external magnetic field. The magnetic nanoparticles, stabilized by means of electrostatic interactions, are partially destabilized by adding controlled amount of electrolytes. In the absence of magnetic fields, the particles self-assemble into random fractal clusters, which eventually percolated to form a gel, if the volume fraction of the particles is sufficiently high. Instead, when an external magnetic field is applied, the particles align themselves in columnar structure. If the external magnetic field is applied when the gelation process has already begun, both particles and clusters are aligned in the direction of the magnetic field. By tuning the time at which the field is applied, different structures and characteristic pore sizes in the gel are obtained.

To be able to study the final structure of the obtained materials, their structure is fixed by reactive gelation where the polymer particles are swollen with a small amount of monomer and crosslinker. After post polymeriztion the weak physical bonds keeping the particles together in a gel are transformed in much stronger covalent bonds.

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Synthesis and self-assembly behaviour of poly(florenyl styrene)-*block*-poly(2-vinyl pyridine) block copolymers and their blends with single wall carbon nanotubes (SWCNTs)

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A series of poly[4-(9,9-dihexylfloren-2-yl)styrene]-*block*-poly(2-vinyl pyridine) and poly[4-di(9,9-dihexylfloren-2-yl)styrene]-*block*- poly(2-vinyl pyridine) (P(St-$F1_n$)-*b*-P2VP, n=1 and 2)comb-like block copolymers were synthesized and their self-assembly behaviour were investigated. Depending on the number of pendant fluorene units, the block volume ratio, the solvent used to cast the samples and thermal annealing history, spherical, hexagonally packed cylinders, lamellar, gyroidal and hexagonally perforated lamellae were found. Though side chains composed by up to two fluorene units were not sufficient to induce any liquid crystalline structure, the resulted conformational asymmetry of block copolymers gave much more asymmetrical phase diagram compared to the reference PS-*b*-P2VP system.

The capability of P(St-$F1_n$)-*b*-P2VP to host COOH-modified single wall carbon nanotubes (SWCNTs) was also investigated. It was found that hydrogen bonding between COOH and P2VP favors miscibility of SWCNT within P2VP domains and the blending of these two components was reflected both on the final morphologies of the block copolymers as well as on the electron conductivity of the SWCNT-block copolymer blends.

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Towards 2D Polymers: Monomer Design, Synthesis & Preorganization

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One monomer unit thick covalent networks with a translational periodicity are referred to as 2D polymers.[1] They still remain on the wish list of synthetic chemistry. To tackle this problem, a C_{3v} symmetric cyclic monomer has been designed in which three 1,8-anthrylene units[2] are bridged by *m*-terphenylenes (Fig.1a).[3] The monomer synthesis has been done successfully.[4] Preliminary studies using model compounds confirm that the polymerization proceed via successive [4+4] cycloaddition of the anthrylenes under UV irradiation (λ = 350–400 nm).[4,5] Studies on the monomer preorganization properties in order to arrive at the target 2D structure (Fig.1b) are underway.

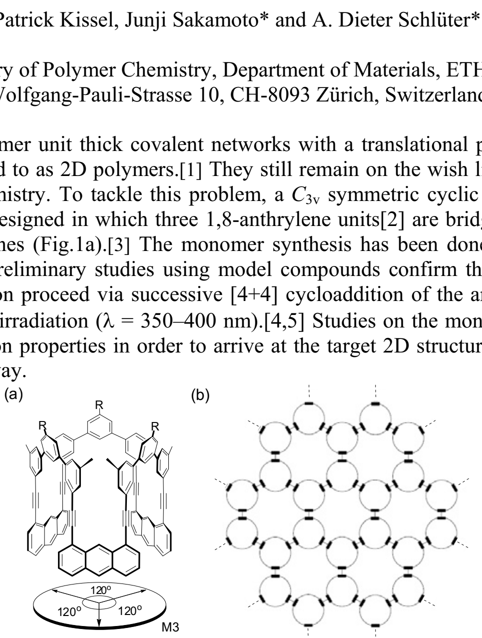

Figure 1. A C_{3v} symmetric cyclic monomer and a target 2D polymer structure

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Counterions and salt influence on titration curves and conformations of flexible polyelectrolytes

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The complexation of polyelectrolyte chains with oppositely charged nanoparticles has recently attracted much attention, because of their important potential applications in nanoscience, environmental chemistry and biology. In the vicinity of polyelectrolytes, small charged mobile ions interact strongly. In the case of weak (or annealed) polyelectrolytes, the amount of charged sites may vary with the pH leading to configurational and ion condensation changes. A common way to simulate such systems consists in performing Monte Carlo simulations according to the Metropolis algorithm using an electrostatic Coulomb potential with explicit objects (only the solvent is taken into account implicitly through its dielectric constant). In order to investigate the influence of parameters such as the monomer radius, salt concentration, salt multivalency and pH on the chain ionization degree, titration curves are calculated.

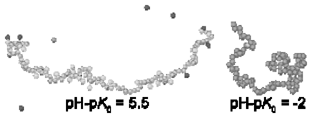

Fig. 1- Polyelectrolyte chain surrounded by counterions and salt for pH-pK_0=5.5 and -2

The chain degree of ionization ranges from 0 at low pH to 1 at high pH. The deprotonation process is more efficient for larger monomers while the chain energy is smaller. The explicit counterions counterbalance chain energy leading to a higher chain degree of ionization. By introducing trivalent salt, the electrostatic interactions between salt and chain are still stronger. As a result, fully charged polyelectrolytes remain folded even at high pH and a decrease of the expansion factor is observed.

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Synthesis of Kinked Polyphenylenes by Suzuki Polycondensation

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Polyarylenes attract increasing interest not only in academic research but also for industrial applications due to their useful mechanical and optoelectronic properties. Suzuki Polycondensation (SPC) is recognized as the most robust method for the synthesis of this class of polymers.[1] Most of the related studies focus on the synthesis of poly(*p*-phenylene) derivatives including polyfluorenes, whereas only few reports deal with other polyphenylene types, e.g., those with kinked main-chain backbones. We are currently working on the synthesis of poly(*meta*-phenylene) and poly(*para-meta*-phenylene) derivatives[2] by SPC (Figure 1). These kinked structures are to be used as key motif to design high molar mass new foldamers[3] as well as tough amorphous polymers[2] with considerable chemical and thermal stability.

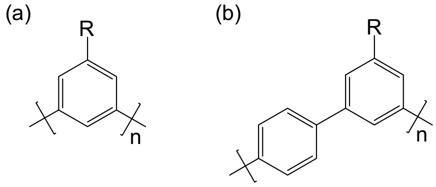

Figure 1. SPC synthesis targets in the present study, (a) poly(*meta*-phenylene)s and (b) poly(*para-meta*-phenylene)s

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Novel Alginate-PEG Hydrogels for Immobilization and Delivery: Synthesis and Physical Properties Assessment

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Since the pioneering work of Lim and Sun[1], alginate (alg) based hydrogel spheres became major studied materials for cell immobilization intended for subsequent transplantation. However, these hydrogels frequently suffer from mechanical stability deficiency, limited durability, and permeability drawbacks. Coating of the initially formed alg beads with polycations only partially solved the problems. Such positively charged molecules can provoke fibrosis. It was also shown that the polycation cannot be completely covered by further external alg layers and thus can activate host macrophages[2].

Novel spherical alginate-poly(ethylene glycol) hydrogels (alg-PEG) have been developed. Multiarm vinyl sulfone-terminated poly(ethylene glycol) (PEG-VS) was reacted with a thiol containing cross-linker via Michael-type reaction, while alg was simultaneously gelled ionotropically in presence of calcium ions. The alg-PEG hydrogel is formed in one step under physiological conditions containing the cross-linked PEG preferably in the core. The faster gelling surrounding calcium alg gel ensures a spherical shape. The molar ratio PEG/cross-linker (r) influences the core gel stability. However, only for r>2 PEG kept the spherical shape after alg dissolution. The degree of swelling was a suitable parameter to optimize r. The hydrogel stability and molecular cutoff can be controlled varying the PEG type as well as PEG and alg concentrations.

The microspheres can be used either as capsules, without removal of alg, or as beads after complete alginate dissolution.

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Origin of arrested phase separation in protein/polysaccharide-mixtures

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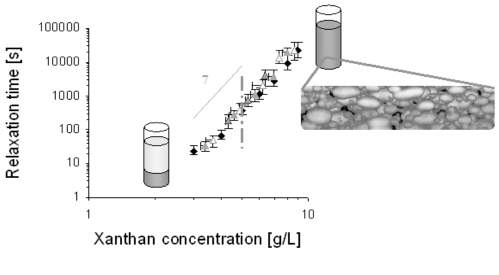
Colloid/polymer mixtures are known to exhibit phase separation due to the depletion induced attractions that arise from an unbalanced osmotic pressure when the polymer is excluded from the region between the colloids. We explore such depletion induced phase separation in mixtures of casein micelles and xanthan gum. Our investigations reveal that the phase separation process becomes arrested when the xanthan concentration exceeds a certain value, slightly above concentrations typically used in food products. Surprisingly, we find that this arrest is entirely due to the xanthan-rich phase, which exhibits a relaxation time that displays a remarkably strong dependence on concentration. This scenario of an arrested phase separation that is due to the unusual development of the relaxation time of the polymer-rich phase is in strong contrast to the one usually applying in colloid/polymer mixtures, where the arrest of phase-separation is due to the glassy arrest of the colloid-rich phase. It may generally apply to colloid/polysaccharide mixtures, thereby having an impact on a large class of food-systems.



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Vesicles as Templates for the Enzymatic Synthesis of Conductive Polyaniline

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Aniline and aniline derivatives can be polymerized into conductive polyaniline (PANI) by using hydrogen peroxide and horseradish peroxidase (HRP) as catalyst.(1-3) Depending on the chemical structure of the monomers, the presence of templates promotes the formation of the *para*-linked form of the polymers. The templates used so far include negatively charged polymers(3) and surfactant micelles(1, 3). In the absence of templates, highly branched products are obtained(1-3). For the HRP-catalyzed polymerization of aniline, we found that mixed anionic vesicles composed of sodium dodecylbenzenesulfonate (SDBS) and decanoic acid (1:1, molar ratio) are promising templates as well.(4)

The PANI synthesized in the presence of SDBS/decanoic acid mixed vesicles show a strong absorption at 1000nm which is a good indication for the formation of conductive PANI. FTIR and ^{13}C-NMR measurements confirm the formation of the linear emeradine form of PANI. The PANI synthesized in the presence of mixed vesicles possesses a high conductivity. Preliminary measurements indicate that the conductivity of PANI films cast from aqueous solution is around 10 S/cm. In addition, the presence of vesicles can stabilize the enzyme in the acidic aqueous reaction medium.

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A generalized model for the rate of aggregation of colloidal particles

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Aggregation of colloidal particles is a physical phenomenon having both fundamental interest and substantial practical relevance. As an example, coagulation of colloidal particles is a key step in processing of many particulate materials. For industrial applications, coagulation is typically carried out by shearing a suspension of charged particles after the addition of enough electrolytes to completely screen all electrostatic interactions. However, the addition of large amounts of electrolytes is not always beneficial for subsequent processing of the material and removal of electrolytes might be necessary, and operating below the critical coagulation concentration would be desirable. As another example, flocculation induced by sedimentation is commonly used to in waste water treatments. For the optimization of the process it is essential to quantify how fast gravity-induced flocculation proceeds under different conditions. All these examples justify the large amount of studies carried out to clarify the effect of different mechanisms on the rate of aggregation, such as inter-particle interactions, shear rate, gravity, and brownian diffusion. However, so far no general expression has been developed, which can accurately account for all of the aforementioned effects.
In this work, we have performed detailed simulations of the aggregation rate of colloidal nanoparticles and fractal clusters in the presence of linear shear flow and repulsive interactions, by numerical solution of the convection-diffusion equation for the pair probability function, *i.e.*, the probability of finding two particles (respectively two clusters) at a given relative position. In order to gain physical insight into the interplay between the various mechanisms affecting the aggregation, a simple but effective model is presented and used to interpolate the results of the rigorous calculations. This approach provides a simple but very general expression for the aggregation rate that can be effectively used in population balance equation calculations.

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Rheology of suspension of colloidal aggregates

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The rheological behaviour of colloidal solution is of interest in many fields. The rheology of suspensions of solids is governed by the geometry, orientation and concentration of the contained particles, and the magnitude of the applied flow. A century ago Einstein[1] put forward the first prediction for the estimation of the bulk viscosity of a dilute suspension of uniform sized rigid spheres in a Newtonian fluid. Jeffrey[2] extended his work for the case of suspension of ellipsoidal particles. No studies are available that extend these concepts to objects usually encountered in processing colloidal suspensions with more complex geometry, such as cluster made of identical spherical colloidal particles. The motion of such clusters in fluid flow is of significant fundamental and industrial interest, but poorly understood due to intricate couplings of hydrodynamic interactions between constituent particles.
In the present work, a large library of clusters generated using a combination of different Monte-Carlo simulations, with fractal dimensions ranging from 1.8 to 3 has been used. The grand resistance matrix was estimated by the Stokesian dynamics[3]. Rigid body equations were applied to the Stokesian dynamics model to construct generalized rigid body resistance matrix, which is then averaged for different orientations of a cluster and for different clusters with the same mass and fractal dimension. The averaged rigid body matrix is then used to estimate the contribution of clusters of different shapes and sizes to the viscosity of suspension. Additionally, the average motion of clusters in different flow conditions has been investigated.

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Stimuli-responsive Dendronized Diblock Copolymer

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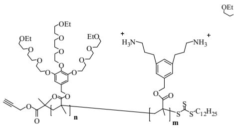
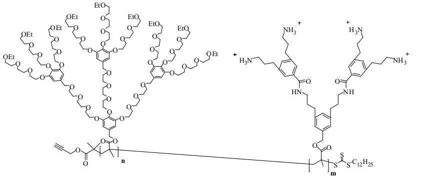
Stimuli-responsive block copolymers have been found widespread applications in nanobiotechnologies, drug delivery, and separations, due to their tunable conformation and properties trigged reversibly by external stimuli.[1] Dendronized polymers are a well-established class of linear polymers bearing pendant dendrons on the repeated units.[2] Here we present the synthesis of a series of novel stimuli-responsive dendronized diblock copolymers, which consist of a thermoresponsive oligoethylene glycol (OEG)-based dendronized block and a pH-responsive positively charged dendronized block. Their pH- and thermo-induced aggregation behaviors in aqueous medium were investigated in details by UV/vis spectroscopy and dynamic laser light scattering. The possible effects of the thickness of the dendronized blocks on their stimuli-responsive aggregation behavior will also be described. It can be expected that such stimuli-responsive dendronized block copolymers might represent a promising new direction in the field of macromolecular design and nanobiotechnology within the context of both academic studies and practical applications.



PG1-*b*-PG1



PG2-*b*-PG2

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Is thickness of linear chains a new variable in polymer chemistry?

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Thickness of dendronized polymers (denpols), an important but rarely studied aspect, can be tuned by varying the dendron generation and branching multiplicity. [1] For a study of related effects, a polymethylmethacrylate was systematically thickened by attaching dendrons generation by generation to each repeat unit. This way two homologous series of dendronized polymers were synthesized up to the sixth generation ($P_n = 1200$ and 6900). The structural perfection of the obtained denpols was determined by quantitative UV measurements. The AFM images of mixtures of denpols with different generations indicate differences in chain stiffness and apparent heights. The thickness produced by the dendronization chemistry described is unique in that the density distribution in the cross-sectional area is not homogeneous. Free volume rather mediates responsivity to external stimuli. In an earlier experiment, it has been observed by AFM imaging that G2 and G3 denpols self-fold to duplex superstructures upon peripheral charging (external stimulus). [2] Such a phenomenon has not been reported for conventional (better: thin) polyelectrolytes. The responsive thickness postulated for denpols is believed to play an important role in this unprecedented observation in that it facilitates the internal reorganization. The densely packed charged surface by duplex formation can better shield the hydrophobic interior from unfavoured interactions with the surrounding water.

This is the first experimental evidence that thickness represents more than just modifying persistence lengths of linear chains.

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