

1-01

Nanostructured Materials Based on Polyelectrolyte Complexes

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Self-assembly processes in water are often driven by hydrophobic attraction; well known examples are common surfactant micelles and lipid bilayer vesicles. Other binding mechanisms can be very relevant, too, like metal coordination or electrostatic interaction. We discuss in this contribution polymer micelles consisting of oppositely charged polyelectrolytes, at least one of which is a diblock copolymer with a neutral, water soluble block. The core of these micelles consists of an insoluble complex coacervate formed by the ionic chains, and a corona made up of the neutral hydrophilic chains. Typical features of these micelles are that they (i) are formed only within a window of compositions around charge stoichiometry, and (ii) that they are fully reversible with respect to changes in polymer composition, pH and ionic strength in the solution. We have characterized micelles of this kind with a variety of techniques and using various polymers. In addition, we have studied their behaviour on solid surfaces.

1-02

Counterion Condensation and Complex Formation on Polyelectrolytes

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The effective charge of polyelectrolytes in solution is significantly lower than the nominal charge, since a considerable fraction of the counterions is not free to move away from the polymer, they are condensed on the polymer. Electrophoresis NMR combined with diffusion NMR permits the direct determination of the charge of molecules and complexes. The effective charge of poly(styrene sulfonate) is decreasing with increasing ionic strength of the solvent. For low molecular weight the effective charge equals the nominal charge. With increasing molecular weight the hydrodynamic friction increases, resulting a reduced diffusion coefficient, while the electrophoretic mobility is constant after only an initial increase. From the combination of both effects an increasing fraction of condensed counterions is concluded. Amino acids can bind to macromolecules through electrostatic interaction. Glutamic acid in solution exhibits a negative electrophoretic mobility, that is increasing by value with pH. The lower magnitude of the electrophoretic mobility in the solution containing the polycation is due to exchange between bound and free acid on the time scale of the experiment. At high pH the acid is fully dissociated and strongly binds to PDADMAC resulting in an electrophoretic mobility close to that of the polycation.

1-03

Design of Self Assembled Surfactant Nanostructures at Interfaces: Effects of Regio-isomeric and Stereo-isomeric Chemical Structure Changes

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The influence of regio-isomeric and stereo-isomeric changes in surfactant chemical structure on interfacial properties was studied using two sets of alkyl aromatic sulfonate surfactants. Two regio-isomeric sodium n-dodecyl xylene sulfonates: ortho and para isomers, and two stereo-isomeric sodium n-decyl stilbene sulfonates: dl and meso isomers were synthesized and their interfacial properties determined at the air-water, hydrocarbon-water and solid-water interfaces. For the regio-isomeric xylene sulfonates, the para-isomer exhibited a lower critical aggregation concentration and higher efficiency of interfacial tension reduction at the air-water, decane-water and solid-water interfaces. The dynamic interfacial properties i.e., rate of interfacial tension reduction and dynamic wetting were higher for the ortho isomer compared to the para isomer. Differences in molecular packing of the para isomer compared to the ortho isomer is key to account for the observed differences in interfacial properties. For the stereo-isomeric stilbene sulfonates, while the interfacial properties were not significantly different in water, in 0.1N NaCl solution differences in properties between the meso and dl isomers were observed. The meso isomer exhibited a lower critical aggregation concentration and higher efficiency of interfacial tension reduction at the air-water and decane-water interfaces. The dl isomer exhibited a higher rate of surface tension reduction at the air-water interface and marginally better dynamic wetting properties at the Teflon-water and Parafilm-water interfaces. Alteration of molecular packing at the interface accounts for these observations. This study demonstrates how subtle differences in molecular packing at interfaces due to regiochemical and stereochemical structural changes can impart significant interfacial property changes in self-assembling molecules. These findings impact the design of self-assembled surfactant nanostructures at interfaces and control of performance attributes such as foaming, emulsification and surface wetting.

1-04

Self-recognising Fluid Monolayers of DNA-based Surfactants: Properties and Applications

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We have designed novel DNA-surfactants prepared by covalent attachment of a hydrophobic anchoring group to the (3'- or 5'-) end of short DNA oligonucleotides. This anchoring group turns these DNA-strands into amphiphilic molecules. Such DNA-surfactants can adsorb at air-water and oil-water surfaces which orient them with respect to the liquid surface and can promote programmable interaction based on Watson-Crick pairing. We show that these materials are surface-active at various fluid surfaces, including air-water and oil-water interfaces, as well as lipid bilayers. We demonstrate that once adsorbed the DNA-surfactants used remain on the liquid surface upon hybridisation with a complementary DNA chain. Complementary DNA-surfactants are used to functionalise fluid surfaces and to program the interactions between them based on Watson-Crick pairing. By selecting the appropriate DNA base sequences the interaction between the fluid surfaces functionalised with DNA-surfactants can be programmed with the level of specificity as the enzyme-substrate interaction. We studied the adsorption of

DNA surfactants at the oil-water interface by Drop Shape Analysis and demonstrated that the interfacial tension isotherm at the oil-water interface depends strongly on the number of bases as well as the base sequence in the DNA surfactant. DNA hybridization at the oil/water interface was studied by measuring the interfacial tension of DNA surfactant during temperature jump across the melting point of complementary DNA-surfactants. Complementary sequences and non complementary sequence of DNA surfactant show clear difference during the temperature jump process. We also found that DNA surfactants can be immobilised on hydrophobic solid surfaces by hydrophobic interactions which allowed us to design a novel method for fabrication of DNA arrays based on microcontact printing of aqueous “inks” containing DNA surfactants on solid substrates. Novel type of aqueous inks based on DNA-functionalised small liposomes for micropatterning of solid surfaces with DNA by a microcontact printing technique has been used. We illustrate the capabilities of this technique by specific deposition of complementary DNA-functionalised liposomes onto DNA-micropatterned solid surfaces. Special attention is paid to the wetting properties of the ink with respect to the stamp and the solid substrates. The method allows for efficient attachment of DNA strands to solid surfaces and hybridisation with complementary fluorescently-tagged oligonucleotides. This new technology could be utilised for rapid preparation of DNA-assays and genetic biochips.

1-05

Triggered Morphological Transformations in Block Copolymer Aggregates in Solution

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Ever since it was shown that block copolymer micelles can self-assemble in solution to give aggregates of a wide range of morphologies, interest in applications of such structures has grown considerably. For some applications, e.g. delivery of specific agents out of vesicles, it is useful to understand the factors which trigger morphological changes, as well as the mechanisms of such changes. In this presentation, several such mechanisms are reviewed, i.e. rod-to-vesicle and sphere-to-rod as well as the reverse transitions, in addition to the mechanism of size changes in vesicles. All these transitions can be induced, in the vicinity of phase boundaries, by small changes in one of the “morphogenic” factors, most conveniently the composition of the solvent. The rod-to-vesicle transition involves a progressive flattening and shortening of the rod, with a simultaneous generation of curvature in the flattened part (to a structure resembling a Chinese wok), the enlargement of the curved or bowl-like section at the expense of the rod, and finally closure of the bowl. Easily accessible relaxation times are of the order of tens to hundreds of seconds. The reverse transition involves a very rapid collapse of the vesicle. The sphere to rod transition involves initially the formation of a “bead necklace” like structure, and subsequent smoothing of the bumps, while the reverse transition involves bulb formation and the splitting-off of spherical micelles from the ends. Finally, vesicle enlargement involves contact and adhesion, coalescence and formation of a center wall, destabilization of the wall, asymmetric detachment of the wall at some point,

retraction into the outer wall, and smoothing into a spherical shape. Vesicle fission involves elongation, internal waist formation, narrowing of the external waist, and complete separation. The mechanisms are reminiscent of some biological processes, and are usually subject to two relaxation times.

1-06

Synthesis and Self-organization of Multiple Stimuli Responsive Amphiphilic Polymers in Aqueous Media

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Amphiphilic block copolymers undergo efficient self-organization in bulk and in solution. They form supramolecular aggregates, in particular in aqueous solution. In order to develop dynamic systems instead of purely static ones where the properties are defined once forever by the chemical structure, stimuli-sensitive polymers have been developed. They are generally aimed at changing the character of functional groups reversibly from hydrophilic to hydrophobic, or vice versa, in order to switch the system between an amphiphilic and non-amphiphilic state. In this context, a series of water-soluble AB-diblock and ABC-triblock polymers was synthesized by us via reversible addition fragmentation chain transfer polymerization (RAFT). This method is a powerful method to prepare functional polymers of complex structure. The new block copolymers were investigated concerning their aggregation in water, in dependence on external stimuli. In particular, the possibility of multiple switchable systems is explored for copolymers containing two stimuli-sensitive hydrophilic blocks. Orthogonal switching the hydrophilicity of a single or of several blocks by changing the pH, the temperature or the salt content demonstrates the variability of the various molecular designs, and exemplifies the concept of multiple-sensitive systems.

1-07

Nanostructured Materials Formulation and Synthesis via Self-Assembly and Directed Assembly of Amphiphilic Block Copolymers

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The interplay between (a) self-assembly properties of amphiphilic block copolymers (ABCs) and (b) synthesis and colloidal stabilization of nanoparticles (NPs) in liquid media containing ABCs is a central theme in our research. When dissolved in selective solvent, ABCs can provide nanoscale environments of varying and tunable dimensions and shape, local polarity, concentration, mobility, affinity to surfaces, and reactivity [Macromolecules 1995, 28, 8604; 1998, 31, 6935; 2000, 33, 5574; 2001, 34, 5979; 2002, 35, 4064; 2004, 37, 912]. ABCs can thus initiate NP formation, facilitate NP growth, control NP size and shape, modify NP surfaces for dispersibility in solution or a solid matrix, alter NP optical and electronic properties, and promote long-range NP organization. The relationship between ABC characteristics and NP structure is

beneficial for several applications. Examples will be presented from our work on ABC-structured pharmaceutical and coating formulations [J. Colloid Interface Sci. 2002, 252, 226; 2002, 255, 1; J. Phys. Chem. B 2002, 106, 10834], and ABC-templated synthesis of metal nanoparticles [Langmuir 2004, 20, 8426; J. Phys. Chem. B 2005, 109, jp046221z; Nanotechnology 2005, 16, S344].

1-08

Multifunctional and Responsive Behavior of ABC Terpolymers with Amphoteric Blocks

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ABC block terpolymers constituted of three different polymer blocks demonstrate numerous possibilities of self organization in the bulk, at interfaces and in solutions. This behavior has attracted great interest and caused recent rapid development of the ABC block copolymer synthesis and investigations. The ABC terpolymers exhibit a wide variety of tunable self-assembled morphologies with potential applications in nanotechnology and biomedicine. Here we report on a double hydrophilic stimuli responsive ABC terpolymer poly(2-vinyl pyridine)-b-poly(acrylic acid)-b-poly(n-butyl methacrylate) (P2VP-PAA-PnBMA) which exhibits a rich polymorphism and multifunctionality in aqueous media (multiple response). The properties of the copolymer aqueous solutions depend strongly on pH. At low pH three-compartment spherical micelles with positively charged outer corona are formed. The micelles are thermo-responsive around the upper critical solution temperature (UCST) of the PAA blocks. As pH increases the micelles are transformed to other micellar structures due to the progressive deprotonation of P2VP blocks and the neutralization of PAA blocks. At pH 6 a three-dimensional physical network is formed constituted of hydrophobic domains of P2VP and/or PnBMA blocks interconnected by negatively charged bridging PAA blocks. This physical hydrogel is sensitive to ionic strength which induces a closed loop Sol-Gel-Sol transition. The so formed gel exhibits the characteristic behavior of Telechelic Associative Polyelectrolytes [Macromolecules, 2005, 38, 1307].

1-09

Nanostructured, Smart Hydrogel Layers

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Photo cross-linkable hydrogels are of considerable interest as materials in microsystems (e. g. microactuators) and biotechnology, in which the gel sizes are reduced to the μm -range (gel thickness and gel extension). Both temperature and pH-responsive hydrogels have been applied for flow control in microfluidic devices requiring no external power supply. However, controlling interactions of hydrogels with biomolecules is still a challenge. For this purpose hydrogel layer assemblies have been investigated.

Novel PNIPAAm block copolymers have been prepared by using controlled radical polymerization. Due to the radical character of the polymerization a random copolymer block of NIPAAm and a chromophore could be attached to the macroinitiator. The volume phase transition of constrained hydrogel layers was studied by a combination of surface plasmon resonance (SPR) spectroscopy and optical waveguide spectroscopy (OWS) as a function of cross-linking density, and composition. This technique has been applied previously for random copolymers, and is now extended to photo cross-linkable block copolymers and hydrogel layer assemblies. The swelling behavior was affected by the macroinitiator content as well as the cross-linking density of the PNIPAAm phase.

1-10

Nanofabrication via Block Copolymer Templates: From Nanoparticle Arrays to Optical Waveguides

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We present latest developments on the use of self-assembled block copolymer (BCP) thin films as templates and scaffolds for nanostructured materials. First, various simple routes to fabricate hexagonally patterned nanoparticle arrays are discussed. Asymmetric diblock copolymers of poly(styrene-co-ethylene oxide) (PS-b-PEO), poly(styrene-co-2-vinyl pyridine) (PS-b-P2VP), poly(styrene-co-methyl methacrylate) (PS-b-PMMA) with cylindrical microdomains were employed to generate arrays of gold (Au), titania (TiO₂), and composite Au/TiO₂ by chemical vapor deposition and sol-gel process, and photophysical properties of the resulting hybrid nanostructures are discussed. Second, the potential application of block copolymer thin films as planar optical waveguides is considered. PS-b-PMMA thin films with cylindrical PMMA microdomains oriented normal to the substrate surface were used to couple optical modes in the Kretschmann configuration and their waveguiding properties are investigated. The methodology provides a significant advance over other conventional analytical tools to monitor the nanofabrication processes occurring in the BCPs in terms of the simplicity and high-sensitivity.

1-11

Nanomolecular Valve Effect of Cu Complex Crystal in Gas Adsorption

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Adsorption of supercritical gases such as H₂, or CH₄ on microporous solids has gathered much attention with respect to energy or environmental technologies. A microporous metal organic solid has a great advantage for designing and construction of the porous framework appropriate for selective adsorption of the target molecules. Although general metal organic solids available for adsorption have open channels in the crystals, Cu complex-assembled microcrystal [Cu(bpy)(BF₄)₂(H₂O)₂(bpy)]_n (bpy = 4,4'-bipyridine)

has no open channels. However, Li and Kaneko found a remarkably specific adsorption behavior of high reproducibility for CO₂ in Cu complex-assembled microcrystal [Cu(bpy)(BF₄)₂(H₂O)₂(bpy)]_n (bpy = 4,4'-bipyridine) irrespective of no open channels. Thus, this Cu complex solid is denoted a latent porous copper crystal (LPC). CO₂ is vertically adsorbed and desorbed at specific pressures at 273K. The mechanism of such a nanomolecular valve effect has not been clear because the crystal structure was not understood after pretreatment for removal of water molecules from LPC. Recently we have constructed a model structure of LPC from the experimental data from in-situ FTIR, elementary analysis, TG, XRD, and so on. In the present paper, the mechanism of the nanomolecular valve effect will be presented based on the model structure.

1-12

Microcalorimetry and Scattering in Binary and Ternary PNIPA Systems near the Volume Phase Transition

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Poly(N-isopropylacrylamide) gels swollen in pure water exhibit a volume phase transition (VPT) at 34°C, above which the solvent is expelled. Data from isothermal and scanning microcalorimetry and small angle X-ray scattering (SAXS) observations confirmed that the gel collapse involves two stages. The first is prompt microphase separation in which the polymer chains form a foam-like structure: water bubbles several hundred nm in diameter are separated by 10 nm thick polymer film clusters. The second stage involves slow relaxation, with a mutual diffusion coefficient of about 10⁻¹⁷ cm²/s, characteristic of glassy materials. In contact with aqueous phenol solutions, these gels display a VPT already at 20 °C at aromatic acid concentrations that depend on the number of OH-substitutions. Dynamic light scattering measurements, in which light from the thermodynamic fluctuations is heterodyned by that from the large-scale network heterogeneities, show that $D_c R_{dyn}/\phi$ (D_c and R_{dyn} are the collective diffusion coefficient and the Rayleigh ratio, respectively, ϕ is the polymer volume fraction) is independent of the aromatic concentration. Thus, the friction coefficient of the polymer chains is not modified in the presence of the binary solvent and below the VPT concentration the phenols are not directly in contact with the polymer chain.

1-13

A Novel Method for Controlling the Size and Spatial Patterning of Defect Domains in a Smectic A Liquid Crystal

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Controlling the size and spatial ordering of defects in liquid crystals offers new possibilities for exploiting their unique optical and rheological properties. Recently, confinement of liquid crystals in silicon microchannels has been shown to create ordered defect patterns [PNAS, 2004, 101, 17340]. However, silicon micromachining is costly

and time consuming. We present an alternate, rapid, and inexpensive method for controlling defect patterns in smectic liquid crystals on PDMS films. We first show that as-prepared and PEI coated PDMS films impose homeotropic and planar boundary conditions, respectively. Next, by oxidizing a thin film of PDMS in oxygen plasma, a thin glassy surface is created. Applying a uniaxial stress breaks this glassy surface and creates microscale parallel cracks. A drop of smectic liquid crystal on the surface exhibits ordered toroidal defects between two crack lines. The distance between two adjacent cracks dictates the size of defects. Sandwiching liquid crystal between two parallel plates in which one surface is cracked shows that up to a certain gap thickness, cracks are still capable of controlling the size and order of defects.

1-14

Pore Expansion in Fluorinated Surfactant Templated Porous Silica Thin Films through Supercritical Carbon Dioxide Processing

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The effect of processing mesoporous silica thin films with supercritical CO₂ immediately after casting is investigated, with a goal of using the penetration of CO₂ molecules in the tails of CO₂-philic cationic fluorinated surfactant templates to tailor the final pore size. Well-ordered thin films with 2D hexagonal close-packed pore structure are synthesized through the liquid phase co-assembly of a homologous series of perfluoroalkylpyridinium chloride surfactants and an inorganic silica precursor. Hexagonal mesopore structures are obtained for both unprocessed films and after processing the cast films in CO₂ at constant pressure (69-172 bar) and temperature (25°C to 45°C) for 72 hours, followed by surfactant extraction. XRD and TEM analysis reveal controlled and significant increases in pore size for all CO₂ treated thin films relative to the unprocessed sample with increase of CO₂ pressure. The degree of pore expansion achieved is directly dependent on the length of the fluorinated tail throughout the homologous series of surfactants. These results demonstrate that combining the tunable solvent strength of compressed and supercritical CO₂ with the 'CO₂-philic' nature of fluorinated tails allows one to control the pore size in ordered mesoporous silica thin films through CO₂ processing.

1-15

Dynamic Manipulation of Proteins and Colloidal Scale Objects with Smart NanoTextured Surfaces

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Using planar surfaces with 10-nm scale regions of controlled surface chemistry, we are able to manipulate the adhesion dynamics of a variety of objects, ranging from small proteins (3-4 nm in size) to micron-scale colloidal particles. The surfaces exert both

selectivity and tunability in the adhesion dynamics. The key to these behaviors is that the surface chemistries making up the nanopatterns exert substantially different forces on the approaching objects / molecules, setting up lateral competition between attractions and repulsions. In the case of protein adsorption, we demonstrate the ability of small adhesive islands to capture individual fibrinogen molecules, or to hold up to 4 lysozyme molecules in relatively close proximity. Surfaces of similar chemistry are shown to give controlled adhesion rates of micron-scale colloidal particles, from a flowing suspension. In the case of the colloidal particles, the adhesion rates depend on the spacing on the attractive islands on the opposing surfaces. The observations suggest a dynamic pattern-recognition mechanism where lengthscales set up by the particle and ionic strength (through fluctuations) mate with those of the surface at the threshold conditions for adhesion.

1-16

Stimuli-Responsive Polymeric Films from Colloidal Dispersions

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Colloidal dispersions have been of interest for a long time, and recent advances in phospholipid (PL) chemistry combined with traditional monomer polymerization or crystallization in the presence of PL resulted in the development of a new generation of colloidal films that exhibit unique film formation properties. This presentation will focus on the developments of non-spherical colloidal particles and the effect of particle morphologies on film formation and stratification near the film-air (F-A) and film-substrate (F-S) interfaces. Using biologically active PLs it is possible to induce the formation of surface localized clusters (SLICs) that may serve as rafts for other applications.

1-17

Stimuli-Responsive Layer-by-Layer Polymeric Films and Capsules

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We discuss the role of hydrogen bonding and electrostatic interactions in pH- and temperature-responsive multilayer films and capsules, which contain a weak polyelectrolyte as one of the multilayer components. We will contrast fundamental differences between electrostatic and hydrogen bonding layer-by-layer polymer self-assembly, including charge regulation and charge imbalance within the film. Along with the systems where hydrogen-bonded and electrostatically adhered polymers are incorporated into different stacks of hybrid films, we introduce copolymers that combine centers for electrostatic and hydrogen bonding in one molecule, such as polybetaines containing carboxylate groups and quaternized derivatives of poly-4-vinylpyridine with pyrrolidone moieties. Such copolymers can be self-assembled via electrostatic mechanism at neutral pH values, but they also yield robust multilayers with polycarboxylic acids at low pH in salt solutions where the films are stabilized by hydrogen bonding. Temperature responsiveness can also be imparted to films by

introducing poly(vinyl methyl ether). Strategies to stabilize films at high pH values by introducing covalent cross-links will also be discussed. The permeability of self-assembled layers and capsules to small molecules is strongly pH- and/or temperature-dependent, showing potential for controlled release applications.

1-18

Patterning of Polymeric and Biomolecular Nanostructures: Approaches and Challenges

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Fabricating stimulus-responsive, smart polymeric and biomolecular structures on surfaces and the control of their architecture on the nanometer length scale is important for applications in biosensors, proteomic chips and nanofluidic devices. Here we present methods that we have developed that allow for molecular-level control in the fabrication of polymeric and biomolecular nanostructures. First we describe the fabrication and characterization of stimulus responsive, elastin-like polypeptide (ELP) nanostructures grafted onto functionalized thiolates patterned onto gold surfaces with dip-pen nanolithography (DPN). ELPs undergo a reversible, hydrophilic-hydrophobic phase transition in response to external stimuli, such as a change in temperature or ionic strength. This phase transition behavior was exploited to reversibly immobilize a thioredoxin-ELP (Trx-ELP) fusion protein onto the ELP nanopattern above the lower critical solution temperature (LCST) demonstrating the potential for ELP nanoarrays in reusable lab-on-chip devices for protein purification or nanoscale analysis. Next we describe the fabrication of stimulus-responsive, poly(N-isopropylacrylamide) (pNIPAAm) brush nanopatterns in a “grafting-from” approach that combines scanning probe lithography and e-beam lift-off lithography, with surface initiated polymerization using atom transfer radical polymerization (ATRP). We demonstrate the reversible, stimulus-responsive conformational height change of these nanopatterned polymer brushes by inverse transition cycling in water, and water-methanol mixtures. Our nanofabrication approaches are generic and can likely be extended to a wide range of vinyl monomers. Finally we discuss surface-initiated ring-opening metathesis polymerization (ROMP) of cyclic monomers on silicon oxide nanopatterns fabricated by atomic force microscope (AFM) anodization lithography. The combination of anodization lithography and surface-initiated ROMP allows us to fabricate small, nanoscale features on silicon surfaces either by solution or vapor phase introduction of the monomer. We will describe our results characterizing these sample surfaces using TappingMode and potential gradient AFM imaging.

1-19

Nanoscale Functionalization and Site-Specific Assembly of Colloids by Particle Lithography

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The production of a simple localized and nanoscale charge distribution on the surfaces of individual colloidal microspheres is realized here using our technique of “particle lithography”. In this technique, parts of the microspheres are masked off, while polyelectrolytes (or other molecules) cover the remaining portions of the microspheres. The result is a microsphere with a functionalized patch of controlled size. The effectiveness of this process is demonstrated by the accurate and reproducible production of colloidal heterodoublets composed of oppositely-charged microspheres. The particle lithography technique is advantageous since it is not limited by the resolution of photolithography or by functionalizing chemistries, and the technique opens the door for complex site-specific functionalization of particles. The size of the functionalized patch may be tailored through the use of polyelectrolytes (or any masking agents) of different sizes, or by adjusting the salt concentration (i.e. adjusting the Debye layer thickness). The particle lithography process and its degree of accuracy will be better understood through modeling.

1-20

Xerogel from Silica and Naphthanediiimide, an Efficient Photoredox Agent

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A nanohybrid xerogel composed of N, N'-bis(2-phosphonoethyl)-1, 4, 5, 8-naphthalenediimide (DPN) with silica was obtained by doping the sol-gel with DPN during the TEOS condensation reaction. Physical and chemical aspects of the xerogel were obtained by FTIR, TA and BET. Morphological analyses reveal that DPN are located inside the particle pores. Photochemical studies in the presence of Tryptophan (Trp) showed that the xerogel is efficiently promoting the photosensitization of Trp radical formation. Photophysical studies demonstrated the presence of J-aggregates of DPN. The splitting model of exciton theory was used to determine the distance between DPN molecules (~7Å). The silica sterical hindrance and the DPN geometry inside the silica particles are main factors for the good photosensitizing efficiency of the xerogel. Sponsors: FAPESP, CNPQ and CAPES.

1-21

Synthesis and Rearrangement of Block Copolymer Brushes

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The synthesis of tethered block copolymer brushes *via* the use of controlled/‘living’ free radical polymerization techniques presents many significant advantages over traditional free radical polymerization techniques. In our group, we have found that the most versatile controlled/‘living’ free radical polymerization techniques are atom transfer radical polymerization (ATRP) and reversible addition fragmentation transfer (RAFT)

polymerization. Both diblock and ABA type triblock copolymer brushes have been synthesized using either ATRP or RAFT. Of particular interest with block copolymer brushes, are their ability to reversibly rearrange upon treatment with selective solvents. This rearrangement of block copolymer brushes can result in the formation of unusual surface morphologies that have been attributed to the formation of either ‘pinned micelles’ or ‘folded’ structures. We have demonstrated the other external stimuli besides block-selective solvents can be used to induce brush reorganization such as temperature and treatment with supercritical CO₂. We have recently been studying the use of block rearrangement to control flow and permeability.

1-22

Ultrahydrophobic Surfaces through Surface-attached Ultrathin Polymer Films

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The leaf of the lotus plant has, like a variety of other plant surfaces, strongly ultrahydrophobic surface properties due to a series of micro- and nanostructures spanning a wide spectrum of length scales. Water cannot wet the surfaces, even upon impact, and rolls easily off the surface, collecting dust and other particles along the way. The study of these unusual wetting properties of such natural surfaces has suggested to introduce such a concept into a variety of different engineering applications. The transfer of this concept into artificial materials, however, had only somewhat limited success so far. After having very good initial properties, the ultra-hydrophobicity of such surfaces usually deteriorates rather quickly. One of the major problem has been that artificial surfaces, unlike plant surfaces, do not have a possibility to regenerate after physical damage of the micro- or nanostructures and once the surface is mechanically damaged, the surface properties are changed irreversibly. We present new techniques to obtain ultrahydrophobic surfaces through a combination of surface-attachment of fluorinated polymers and microstructure generation. The polymer molecules are either grown on the surface of the substrate through surface-initiated polymerization or become attached through a photochemical process.

1-23

Binary Polymer Brushes: Structured Surface with Reversibly Tunable Wetting Properties

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Grafting of two incompatible polymers onto a substrate one prevents macroscopic phase separation and the laterally self-assembled thin film structures exhibit reversibly tunable wetting properties. Self-consistent field calculations utilizing the Gaussian chain model and a virial expansion for the interactions predict a rich phase diagram of laterally periodic morphologies as a function of solvent quality, composition of the brush, incompatibility of the two polymer species and grafting density, however, the structures observed in experiments lack long-range periodic order. We employ Monte Carlo

simulations of a coarse-grained off-lattice model to investigate the influence of spatial correlations of the grafting points onto the morphology of one-component brushes in a bad solvent and binary brushes. Comparing different self-assembled structures on identical sets of grafting points we observe a pronounced correlation between the average morphology of the brush and density fluctuations of the grafting points. These fluctuations in the grafting points prevent long-range order. Rather than a sharp thermodynamic transition, we observe a gradual building up of structure upon increasing the incompatibility and the structure formation occurs at smaller incompatibility and the length scale is slightly larger than in case of grafting on a regular lattice. Chain length polydispersity has only a much smaller influence on the structure. Different morphologies as a function of composition give rise to very similar structure factors but can be well distinguished by their Euler-characteristics.

1-24

Mixed Polyelectrolyte Brushes: Adaptive and Responsive Polymer Surfaces

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We have shown in the past that different binary polymer brush layers at solid surfaces reveal responsive and switching behavior. This can also be shown for polyelectrolyte brushes which are sensitive on pH. Mixed polyelectrolyte - non polyelectrolyte and mixed oppositely charged polyelectrolyte brushes were synthesized by "grafting to" and "grafting from" approaches on solid substrates (Si-wafers and polymer films). The mixed brushes exhibit responsive properties via exposure to organic solvents and water of different pH resulting in switching of the brush morphology, surface energetic state, wettability, and thickness. From AFM investigations different nanostructures are distinguished.

1-25

Nanoprobing of Switchable Polymer Surfaces

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An overview of recent author's results on atomic force microscopy (AFM) probing of nanomechanical and tribological properties is presented and discussed for a wide range of switchable surfaces. We focus on mono- and binary polymer brushes (grafted to, grafted from, and Y-shaped) studied under various conditions (in air, in fluid, and at elevated temperatures), patterned surface films, and photochromic monodendrons of different generations.

1-26

Synthesis of Segregated Binary Polymer Brushes

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Communication is focused on synthesis of binary polymer brushes with phase-segregated morphology. Namely, polystyrene/polyethylene glycol methyl ether methacrylate (PEGMA) brushes were fabricated by combination of “grafting to” and “grafting from” techniques of the polymer anchoring. A ultrathin film consisting of carboxyl-terminated polystyrene (PS) and poly (methyl methacrylate) (PMMA) blend was first deposited on a substrate modified with poly(glycidyl methacrylate) and annealed at 120 °C. As a result of the grafting islands of PS brushes were created. To complete formation of the segregated binary brushes, surface initiated polymerization (ATRP) of PEGMA was carried out. Surface rearrangements of the segregated brushes were studied by contacting them with selective solvents.

1-27

Synthesis of Mixed Homopolymer Brushes on Silica Nanoparticles by Living Radical Polymerization Techniques

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By using two different living radical polymerization techniques, atom transfer radical polymerization (ATRP) and nitroxide-mediated radical polymerization (NMRP), we successfully synthesized mixed poly(*t*-butyl acrylate) (PtBA)/polystyrene (PS) brushes on silica nanoparticles. Silica particles were prepared by the Stöber process and were functionalized with an asymmetric difunctional initiator-terminated monolayer. Surface-initiated ATRP of *t*-butyl acrylate was carried out in the presence of a free initiator. Kinetics study showed that the polymerization was well controlled. By cleaving PtBA off the particles, the molecular weights of the grafted and free polymers were found to be essentially identical. Mixed PtBA/PS brushes were obtained by NMRP of styrene from PtBA particles. The M_n of the grafted PS was found to be the same as that of the free PS formed from the free initiator. Amphiphilic mixed poly(acrylic acid) (PAA)/PS brush-coated nanoparticles were synthesized from mixed PtBA/PS particles by hydrolysis of PtBA with iodotrimethylsilane. Tyndall scattering experiments and ^1H NMR study showed that the mixed PAA/PS particles can be dispersed and form a stable suspension in CHCl_3 , a selective solvent for PS, and also in CH_3OH , a selective solvent for PAA, demonstrating the capability of these hairy nanoparticles to undergo chain reorganization in response to environmental changes.

1-28

Novel Smart Core-Shell Microgels: Synthesis and Characterization

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Colloidal microgels that are able to alter their volume and properties in response to environmental stimuli, such as pH, temperature and ionic strength are attractive candidates for many potential applications. Recently, microgels with more complex

structures, such as a multi-responsive core-shell, have received increasing attention due to the tuneable properties of the individual responsive components. In this presentation, a new method to prepare smart microgels that consist of well-defined temperature-sensitive cores with pH-sensitive shells will be described. The microgels were obtained directly from an aqueous graft copolymerization of N-isopropylacrylamide and N, N-methylenebisacrylamide from water-soluble polymers containing amino groups such as poly(ethyleneimine) and chitosan. The microgel diameters ranged from 300 to 400 nm with narrow size distribution. The unique core-shell nanostructures exhibited tuneable responses to pH and temperature.

1-29

Collapse of Polyelectrolyte Brushes Driven by Ion Pairing Interactions

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Polyelectrolyte brushes are ideal building blocks for soft nanotechnology and the engineering of responsive surfaces. Changes in ionic strength, pH and solvent properties lead to markedly difference on surface properties due to transitions in the polymer brushes between stretched and collapsed states. The traditional framework in polyelectrolyte brushes describes collapse as the result of a significant screening of the charges of the pendants groups. However, a much richer behaviour should be expected when the specific chemical interactions between anions and cations are explicitly studied. The introduction of chemical triggers of collapse (rather than merely relying on ionic strength) will allow the development of surfaces which show responsive behaviour that can be exploited as sensors, as well as actuating mechanisms in fluidic devices. In this work we have investigated the critical role of ion-pairing interactions on the collapse of cationic 2-(methacryloyloxy)ethyl-trimethylammonium chloride (METAC) polyelectrolyte brushes. We observed that in the presence of ion-pairing interactions, the chemical nature of the electrically neutral polymer can be sharply switched from hydrophilic to hydrophobic. This chemical change of the monomer units leads to a collapse driven by hydrophobic interactions with the surrounding water. As a consequence, ion-paired collapsed polyelectrolyte brushes show very compact stiff structures markedly different from similar brushes whose collapse are driven by Coulombic screening.

1-30

Thermally Responsive Polymer Brushes with High Protein-Binding Affinity

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Polymer brushes with tunable protein affinities can be useful for protein chromatography or adsorptive pre-fractionation of crude cell lysate samples. Well controlled brushes of poly(dimethylaminoethylmethacrylate) (PDMAEMA) are grown from thiol-linked initiators on gold surfaces using atom transfer radical polymerization (ATRP). The lower critical solution temperature (LCST) of the brushes is controlled by statistical copolymerization with methylmethacrylate (MMA). The polymer grafting density is controlled by varying the relative amounts of initiator and inert thiol in solution during the initial gold surface modification and is quantified by surface plasmon resonance (SPR). At lower grafting densities, SPR measurements indicate that these brushes have an unexpectedly high affinity for proteins, adsorbing the equivalent of 10-15 monolayers of serum albumin within the brush, under good solvent conditions. Above the LCST, the extent of adsorption increases slightly, but the adsorption rate increases approximately ten-fold. In spite of the greater hydrophobicity of PDMAEMA-co-PMMA compared to PDMAEMA, the protein adsorption is approximately 40-fold slower for the copolymer brushes. This effect is tentatively attributed to a reduction in protein accessible volume within the copolymer brush. The effects of temperature, protein hydrophobicity, brush composition and grafting density on protein binding capacity will be discussed.

1-31

Strong Polyelectrolyte Brush at the Air/Water Interface

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We synthesized an ionic amphiphilic diblock copolymer having strong acid group; poly(hydrogenated isoprene)-b-poly(styrenesulfonic acid) (PIp-h₂-b-PSS) by living anionic polymerization, and the nanostructure of its spread monolayer on the water surface was directly investigated by in situ X-ray reflectivity (XR) technique. The monolayer of a diblock copolymer on a water surface had a smooth hydrophobic PIp-h₂ layer on water and hydrophilic layer consists of a dense 'carpet layer' just beneath the hydrophobic layer and 'brush-like layer' stretching into water. The surface pressure and PSS chain length dependence of its hydrophobic layer thickness and the brush nanostructure were quantitatively studied. Furthermore, the effect of salt concentration in the subphase was also investigated. The thickness of the PSS brush layer decreased at salt concentrations above 0.2M while no nanostructure change was detected below 0.2M. This critical salt concentration corresponds to be that of free counterions inside the brush layer. However almost all of counterions in the carpet layer might be condensed so that the carpet layer structure is hardly changed by compression, or salt addition.

1-32

Stimuli-Responsive Polymer Based Composite Microcapsules

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Polyelectrolyte capsules representing a novel type of nano-engineered multifunctional materials are made by layer-by-layer adsorption of oppositely charged polyelectrolytes on the surface of colloidal template particles of 0.05-20 μm diameter. A great variety of materials including synthetic and natural polyelectrolytes, proteins, multivalent ions, organic nanoparticles, lipids were used to build walls of hollow capsules. Many of them were functionalized to provide special surface properties of technical or biological relevance. The possibility of tailoring different functionalities, impregnating inorganic and organic substances both inside capsule volume and in polyelectrolyte shell, controlled release of encapsulated material provided continuous scientific and industrial interest for employing capsules as microcontainers and microreactors. Inorganic nanoparticles incorporated to polyelectrolyte shell makes possible the remote activated release. Smart polymers involved in capsule build-up exhibit reversible sensitivity to environmental conditions, i.e. capable of undergoing sharp physical or chemical modifications in response to external stimuli such as temperature, pH, ions, etc. Here we present the results obtained with hollow and filled capsules prepared with stimuli-responsive polymers and capsules filled with different polymers responsive to ions, pH and temperature. The possibilities for practical applications of such capsules are illustrated.

1-33

Connecting the Wetting and Rheological Behaviors of PDMS-Grafted Nanospheres in PDMS Melts

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Engineered nanocomposites are often formulated by grafting polymer brushes to the surfaces of colloids to optimally disperse them into viscous polymer matrices. In spite of the ubiquity of these filled materials, the essential mechanisms in producing an optimal dispersion have not been well quantified. To this end, rheological and light scattering measurements are made to connect the static wetting and dynamic flow properties of polydimethylsiloxane (PDMS)-grafted silica nanospheres in PDMS melts. By controlling the brush grafting density and the matrix chain length of these model systems, results indicate that the wetting and the flow behaviors can be quantifiably linked. Overall, these studies represent new ways of quantifying the factors that control the dispersion of polymer-grafted nanoparticles in viscous melts.

1-34

Ordering and Interactions in Electrorheological fluids

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Some fluids can respond to an applied electric field, switching from a disordered structure with a fluid-like response to an ordered structure with a solid-like response. More research on these fluids is performed in order to use them as hydraulic actuators in micro-devices or as electro-optical devices, e.g. sensors, switches, narrow-band filters, and wave guides. A critical feature in the performance of such fluids is the control of interparticle interactions. Indeed, the particles must repel each other at short distances, otherwise the field-induced aggregation is not fully reversible and the device cannot be switched repeatedly. In the present work, we combine numerical calculation and Small-Angle Neutron Scattering experiments to study the phase transitions in the structure of a fluid made of surface modified silica particles dispersed in silicone oil. We shall be using the Neutron small angle scattering instrument as a Surface Force Apparatus. When an electrical field was applied, a two-dimensional set of diffraction spots was obtained, located in the direction of chain alignment. The spacing of these diffraction spots yields the average interparticle distance, which is found to vary, from a complex way, with the electrical field, the field frequency and the surface chemistry of the silica particles.

1-35

Polymer-Capped Monodisperse Magnetic Nanoparticles

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We have prepared monodisperse magnetic nanoparticles following the organic route proposed by Sun et al. [JACS, 2004, 126, 273]. The particles are stabilized by oleic moieties, and in order to undergo further functionalization a surface ligand exchange reaction is performed by means of which the oleic moieties are replaced by ricinoleic moieties. The additional hydroxyl group of ricinoleic acid enables further reactions to take place. In particular the reaction with acid halides bearing halogen atoms allows one turn the nanoparticles into macroinitiators for Atom Transfer Radical Polymerization (ATRP). ATRP allows one to polymerize a large variety of monomers in controlled conditions, which can impart to the so obtained polymer-capped nanoparticles a wide range of properties. For example, by polymerizing PH or temperature sensitive monomers, one can obtain water soluble monodisperse magnetic nanoparticles showing PH or temperature induced reversible self-assembly. We have grown poly(meth)acrylic acid brushes from the nanoparticle surface through polymerization of trimethylsilyl (meth)acrylate, followed by hydrolysis to yield the PH responsive poly(meth)acrylic acid. The nanoparticles properties can be further tailored by making use of amidation chemistry to attach a variety of molecules and biomolecules to the carboxyl groups.

1-36

Improving Fuel Cell Performance by Controlling Polymer Membrane Architecture; Nanoparticles for Enhanced Proton Conduction

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A key limiting factor for the performance of proton-exchange membrane fuel cells (PEMFC) is the reduction in proton conductance, and hence, power output at “high” temperatures (100-150 °C). For standard Nafion™ based systems, this is primarily due to the loss of water. Hydration of the membrane is necessary for the percolation of self-assembled proton conduction channels in the ionomeric membrane. It has been hypothesized that incorporation of nanoparticles has proved to be beneficial for proton conduction at high temperatures/low humidity. In the work presented, select Nafion™ composite membranes were prepared by recasting from dispersions in which particles with known size and surface charge were incorporated. We investigated how colloidal Nafion™/silica-interactions in solution determine the structure of both the dispersions and the resulting membranes. Techniques include rheology, light- and X-ray scattering, light microscopy and scanning electron microscopy, altogether covering a wide range of length scales. The performance of the composite membrane regarding proton conductivity and half-cell activity will be presented and discussed in terms of the membrane microstructure and the water holding capacity of the membranes

1-37

Vapor Sensors Based on Gold Nanoparticle Interlinked with p-Oligophenyldithiols

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Recent efforts to control the physical and chemical properties of nanostructured materials through a molecular level design have generated enormous interest in thin films comprised of organically crosslinked metal nanoparticles. Here, we investigate films prepared by layer-by-layer self-assembly using solutions of dodecylamine-stabilised 4 nm Au-nanoparticles and oligophenyldithiols of different lengths. The resulting films are 7 to 30 nm thick, as determined by AFM and the dodecylamine ligands are exchanged by the crosslinking dithiols during film assembly as revealed by XPS. Additionally, two main sulfur signals (S-Au, S-H) are observed indicating that π - π interaction may be important for assembly. All films show linear current-voltage characteristics and conductivities independent from the length of the linking molecule. Conductivity measurements at variable temperature are consistent with an Arrhenius-type activation of charge transport. For investigating the vapor sensing properties, coated chemiresistors and quartz micro balances are dosed with vapours of toluene, 1-propanol, 4-methyl-2-pentanone and water. Their resistances increase only slightly whereas the mass uptake is significant in case of hydrophobic vapors. All results are compared with results from films interlinked with alkanedithiols of similar lengths (C₆, C₉, C₁₂).

1-38

Magnetic-field-guided Growth of Ferromagnetic Core-Shell Nanomaterials

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Our recent work on metal nanoparticles (Cu, Ni, Co) electrochemically deposited on an ultrathin polypyrrole film grown on a gold-coated silicon electrode shows that the

morphology (size, shape, density and distribution) of these nanostructured materials can be easily controlled by varying the wet deposition conditions (pH, electrolyte concentration, deposition potential, charge, and current density), and the thickness and morphology of the polypyrrole film. Using similar electrochemical techniques, we have recently obtained mono-sized, uniformly distributed Fe core-shell nanoparticles with two different morphologies: quantum dots of 4-10 nm in diameter and 20×110 nm “nano-surfboards” (<5 nm thick). These nanoparticles are found to primarily consist of a Fe metallic core and a mixed Fe oxides shell (2-3 nm thick). In the present work, we report the first evidence of morphological changes induced by an external magnetic field during growth. Implications of constructing patterned nanostructured materials using this technique will also be discussed.

1-39

Advanced Nanostructured Materials from Block Copolymer – Nanoparticle Assemblies

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The study of polymer based co-assembly (“bottom-up”) approaches to multifunctional polymer-inorganic hybrid materials is an exciting emerging research area interfacing solid state and soft materials and offering enormous scientific and technological promise. By choice of the appropriate synthetic polymers as well as nanoparticle precursors unprecedented morphology control down to the nanoscale is obtained. Tailoring of the polymer-inorganic interface is of key importance. The structures generated on the nanoscale are a result of a fine balance of competing interactions, a typical feature of complex biological systems. The potential for new multifunctional materials lies in the versatility of the polymer chemistry as well as that of the inorganic (nanoparticle) chemistry that can be exploited in the materials synthesis. In the present contribution the synthesis and characterization of advanced nanostructured hybrid materials will be presented with potential applications ranging from microelectronics to nanobiotechnology. In all cases cooperative self-assembly of organic and inorganic species is induced by amphiphilic macromolecules. Besides amorphous and crystalline oxide materials novel systems toward high temperature SiCN and SiC structures are introduced. Examples will include the preparation of mesoporous materials and superparamagnetic mesoporous materials with pore sizes ranging from 5-50 nm for separation technology and catalysis, solid hybrid polymer electrolytes for battery applications, the synthesis of nanoparticles with controlled shape, size, and composition for applications in the life sciences, as well as thin film materials with potential applications in microelectronics and nanobiotechnology.

1-40

Electric Field Directed Assembly of Colloidal Particles into Nanostructured Thin Films and Composites

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When an electric field is applied to a colloidal suspension, particles can exhibit a variety of electrokinetic responses that may be exploited to manipulate particles and control their assembly. For example, charged particles move to an oppositely charged electrode by electrophoresis, particles migrate in an electric field gradient by dielectrophoresis, or field induced dipoles on particles cause particles to aggregate in linear chains. Rod-shaped particles can be aligned by an electric field with the longest axis parallel to the applied field. Here we report the fabrication of thin films and composites containing aligned rod-shaped particles through a novel electric-field driven process. The alignment direction of rod-shaped particles in the composite material is controlled by the electrode geometry. Functional particles are selected that give the composite material anisotropic optical and transport properties that are dependent on the alignment direction. The films may find application in membranes and optical materials. The electric field-driven process is applicable to the directed assembly of a variety of types of rod or plate shaped particles to create advanced materials with controlled nanostructure.

1-41

Inversion of Emulsions Stabilised Solely by Ionisable Nanoparticles

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Certain solid nanoparticles act as excellent emulsifiers of oil and water in the absence of any surface-active agent and, since particles are strongly attached to interfaces, coalescence tends to be absent. However, different types of particles are needed to prepare either oil-in-water (o/w) or water-in-oil (w/o) emulsions in mixtures containing equal volumes of the two liquids. Here we describe a new class of solid particle emulsifier capable of stabilising both emulsion types efficiently. The spherical nanoparticles are those of polystyrene whose surfaces contain ionisable carboxylic acid groups. Inversion of the emulsion type is simply effected by either an increase in pH or salt concentration, both driving the inversion from w/o to o/w. The emulsions are studied using conductivity, optical microscopy and stability measurements. The origin of inversion is due to the change in the wettability of the particles at the interface, brought about by increasing the degree of dissociation of acid groups, rendering particles more hydrophilic as a result.

1-42

A New AC Electrokinetic Technique for Collection and Manipulation of Particles on Patterned Electrodes

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We report a new type of microfluidic chip that collects and concentrates colloidal particles from bulk liquid medium using AC electrokinetics. The alternating electric fields were applied to dilute suspensions of latex microspheres enclosed between a

patterned silicon wafer and an ITO-coated glass slide. The latex particles entrained by a liquid flow were collected in the center of the conductive "corral" patterns. The particle collection efficiency and speed depended only on the frequency and strength of the applied field and were independent of the material properties of the particles or the electrodes. The leading effect in the particle collection process is AC electrohydrodynamics (EHD). We discuss how the EHD flows emerge from the spatially non-uniform field and interpret the experimental results by means of electrostatic and hydrodynamic simulations. We demonstrate on-chip collection of latex particles, yeast cells and microbes. The technique allows three-dimensional microfluidic pumping and transport by use of two-dimensional patterns.

1-43

Temperature-Induced Phase Inversion of Emulsions Stabilized by Latex Particles Alone

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Aqueous dispersions of poly[2-(dimethylamino)ethyl methacrylate-block-methyl methacrylate] (PDMA-PMMA)-stabilized polystyrene latex particles (diameter = 150 nm) were synthesised and used as sole emulsifiers of hexadecane and water (1:1) at various temperatures. At low temperatures (≈ 50 °C) oil-in-water emulsions form which are stable to coalescence but exhibit creaming. At high temperatures (≈ 65 °C) water-in-oil emulsions form which are unstable to coalescence. At intermediate temperatures (55-65 °C), emulsions could be of either type. Thus transitional inversion takes place in the same direction as that occurring in nonionic surfactant-stabilised emulsions. Microscopy observations of the aqueous dispersions indicate flocculation of the particles with increasing temperature. Furthermore, the contact angles of a water drop under hexadecane on a glass substrate coated by PDMA homopolymer increase with increasing temperature, implying an increase in system hydrophobicity. A mechanism to understand this inversion involves consideration of changes in the hydration and ionization of the exterior amino groups on particle surfaces with increasing temperature.

1-44

The Synthesis of FePt Nanoparticles by Two-Liquid Mixing Method

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FePt nanoparticles have been synthesized continuously by mixing two precursor liquids: ferric acetylacetonate, $\text{Fe}(\text{acac})_3$, and platinum acetylacetonate, $\text{Pt}(\text{acac})_2$ in ethyleneglycol solution with dispersing agents. The reduction reaction of the mixed Fe and Pt ions to the FePt metal alloys in the reaction cell at a high temperature were aided by irradiating the high power of ultrasound continuously. The obtained FePt particle size was found by TEM photograph to be around 3~ 4 nm showing monodisperse and

nonagglomerating. The rate of production of the FePt nanoparticles was more than 30g per hour. The composition of Fe and Pt elements in FePt nanoparticles determined by ICP analysis was changed arbitrarily by controlling the flow rate of two precursor liquids. The ferromagnetic property of FePt nanoparticles was obtained by the annealing because as grown sample shows the nature of super-paramagnetic properties. The annealing condition was to keep the FePt nanoparticles at a high temperature for 30 min in an atmosphere of 15% of H₂ and 85% of Ar. The magnetic hysteresis loops of FePt nanoparticles were obtained by SQUID measurements. The highest room temperature coercivity ~up to 10 kOe was observed in Fe₅₃Pt₄₇ sample. The addition of Ag atoms to FePt nanoparticles in the nanoparticles synthesis lowered the annealing temperature of the sample as low as below 350°C. The magnetic properties of the FePtAg and FePt nanoparticles were compared by the measurements of SQUID and XMCD.