SYMPOSIUM N

Polymer Gels for Emerging Technologies

March 29 - 31, 2005

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* Invited paper

SESSION N1: Smart Polymer Gels
Tuesday Morning, March 29, 2005
Room 3007 (Moscone West)

8:30 AM N1.1
Title: Reversibly Swellable Polymers Made by Azide-Alkyne Cycloaddition. Chunmei Li[1] and M. G. Finn[2]; [1]Chemistry, Stephen F. Austin State University, Nacogdoches, Texas; [2]Chemistry, The Scripps Research Institute, Ja Lolla, California.

Here we describe a highly crosslinked hyperbranched polymer that rapidly swells and shrinks in dichloromethane solvent in response to the addition of acid or base. The polymer was based on 1,2,3-triazoles units conveniently synthesized under mild conditions in aqueous-organic solvent mixtures using Cu(I) catalyzed [3+2] cycloaddition of a diazide and an amine-containing trialkyne. The insoluble polymer swelled rapidly in trifluoroacetic acid-containing dichloromethane, and absorbed significant amount of solvent. Protonation of the tertiary amine and triazole moieties and concomitant charge-charge repulsion among sites in the polymer is likely to be responsible for the swelling behavior. After washing with dichloromethane, treatment with triethylamine-containing dichloromethane causes the material to retain its expanded architecture but lose most of its trapped solvent mass. Many cycles of acid/base treatment were performed with little or no loss in the measured retention of solvent. Characterization of the polymer before and after swelling showed different morphologies.

8:45 AM N1.2
Experimental Determination and Modeling of Phase and Calorimetric Properties of Gel-Forming Polymers with a Lower Critical Solution Temperature (LCST).
Francisco J. Solis[1], John Larance[2], Rachel Weiss-Malik[3] and Brent Vernon[2]; [1]Integrated Natural Sciences, Arizona State University West, Phoenix, Arizona; [2]Harrington Department of Bioengineering, Arizona State University, Tempe, Arizona; [3]Yale University, New Haven, Connecticut.

We discuss the gelation, phase-separation, and calorimetric properties of copolymers composed of N-isopropylacrylamide (NIP) and maleic (MAc) or acrylic acid (AAc).These copolymers exhibit a lower critical solution temperature (LCST) as well as a liquid to gel transition. In these polymers both gelation and phase separation occur on temperature increase. The gel transition temperature is near the human physiological temperature. This property makes these polymers useful in drug-delivery systems. The transition temperature depends on the degree of copolymerization, the pH of the environment, and the polymer concentration. We present a simple theoretical model to describe the properties of these and related families of LCST gel-forming polymers. The central assumption of the model is that the properties of the system are determined by the release of water molecules associated with the polymers at low temperatures. We assume that the water release is a local phenomenon in which the monomers act non-cooperatively. Experimental results for NIP-Mac and NIP-AAc copolymers, and results derived from the model exhibit several common features: (1) a weak dependence of both gelation and phase separation temperatures with concentration, (2) a gelation temperature decrease with increased concentration, and (3) peaks in the specific heat associated with both gelation and phase separation.

9:00 AM *N1.3
Hydrodynamic Theory of Active Polar Gels.
Jean-Francois Joanny, Karsten Kruse, Frank Julicher, Jacques Prost and Ken Sekimoto; Physico Chimie Curie, Inst. Curie (Paris), Paris, France.

Activ materials are non-equilibrium systems where energy is contantly injected. These include many biological systems such as the actin-myosin gels but also vibrated sand piles or even bird flocs. The cell cytoskeleton is mostly composed of actin filaments interacting with myosin motors. It is active in the sense that energy is consumed; the energy is provided by the hydrolysis of AdenosineTriPhosphate. We generalize here the Maxwell visco-elastic model to describe the actin-myosin complex. We explicitly take into account the active character of the material, the polarity of the actin filaments and treadmilling which is the continuous polymerization and depolymerization of the actin filaments. Following the lines of the classical Martin Parodi Pershan hydrodynamic theory of nematic liquid crystals, we write Onsager relations between genearalized forces and fluxes and define all the active Onsager coefficients associated to the myosin molecular motors. We then give examples of applications of this theory to problems inspired by cell motility. We discuss the formation of a lamellipodium at the leading edge of advancing cells and present an eversimplified model of the motion of fish keratocyte skin cells.

9:30 AM *N1.4
Directed Motion and Cargo Transport through Propagation of Polymer Gel Volume Phase Transitions. Ulrich Wiesner[1], Lilit Yeghiazarian[2], Surbhi Mahajan[1], Claude Cohen[3] and Carlo D. Montemagno[2]; [1]Materials Science & Engineering, Cornell University, Ithaca, New York; [2]Biological Engineering, UCLA, Los Angeles, California; [3]Chemical & Biomolecular Engineering, Cornell University, Ithaca, New York.

One of the fundamental problems in biotechnology is the transformation of energy into directed motion and load transport on very small scales. Hybrid devices driven by molecular motors have been engineered but are often limited through required specific environmental conditions. Here we demonstrate a prototype position controlled synthetic soft device built from a thermosensitive polymer hydrogel for which motion is based on a mechanism different from those employed in earlier gel-based devices. The moving gel is capable of transporting cargo and can be stopped and restarted at any time. We generate the directional motion of cylinder-type hydrogels by spatially controlled propagation of the volume phase transition along their length, demonstrating velocities of about 15 micrometers per second for cylinder diameters of the order of a millimeter. Since gel volume changes are diffusion controlled, miniaturization to the micron scale can be expected to dramatically enhance gel speeds beyond what is currently observed in small scale devices. We anticipate that this principle will be widely utilized in a variety of areas in biotechnology including microfluidics, robotics and drug delivery.

10:30 AM *N1.5
Polymer Gels for Remote Manipulation: In Vivo Adjustable Intra-Ocular Lens. Julia Kornfield[1], Eric Pape[1], Robert Grubbs[1], Dan Schwartz[2], Chris Sandstedt[3] and Shiao Chang[3]; [1]Dept of Chemical Engineering, California Institute of Technology, Pasadena, California; [2]UCSF, San Francisco, California; [3]Calhoun Vision, Pasadena, California.

To achieve optimal outcomes with medical implants it is necessary to account for the body's inherently unpredictable wound healing response. A significant example is the implantation of intraocular lenses in the human eye to provide refractive correction after cataract surgery: over 13 million lenses are implanted annually worldwide. The final position of the lens and the ultimate shape of the eye are not precisely known until wound healing has stabilized; consequently, most patients require spectacles to correct residual refractive errors. Here we describe a material that possesses a latent ability to change shape, which can be triggered in a spatially resolved manner using light to non-invasively adjust an implanted lens. The physics of diffusion and swelling in elastomers are applied to create a transparent silicone suitable for making a foldable intraocular lens that can be reshaped using near ultraviolet light. A crosslinked silicone matrix dictates the initial shape of the lens, while "macromers"-short silicone chains with polymerizable end groups-and photoinitiator enable shape adjustment using light: polymerization of the macromer in the irradiated regions, followed by diffusion of free macromer causes local swelling. To model these systems, we have synthesized and measured mechanical properties of a systematic series of crosslinked polydimethylsiloxane (PDMS) matrices. Equilibrium swelling properties and penetrant diffusivities were determined using several molecular weights of an acrylate endcapped PDMS macromer. The swollen elastomeric matrix was subsequently photopolymerized and final physical properties were characterized. Interaction parameters, modulus and penetrant diffusivities can then be used to create a theoretical model describing these systems.

11:00 AM N1.6
N-isopropylacrylamide Copolymer with Dimethyl-γ-Butyrolactone Acrylate with Hydrolysis-Dependent Lower Critical Solution Temperature.
Zhanwu Cui and Brent Vernon; the Harrington Department of Bioengineering, Arizona State University, Tempe, Arizona.

Temperature sensitive poly(N-isopropylacrylamide) (poly(NIPAAm)) and its copolymers have been of high research interest for biomedical applications, such as cell immobilization, drug delivery, etc. The low critical solution temperature (LCST) of poly(NIPAAm) copolymers can be controlled by varying the type and content of the comonomers. Incorporation of hydrophobic monomers leads to a lower LCST and hydrophilic monomers to a higher LCST. Neradovic et al(1). reported the synthesis of a new type of thermosensitive NIPAAm copolymer with hydrolysable lactate ester side groups with the increase in LCST after hydrolysis. Synthesis of NIPAAm with cyclic monomer, 2-methylene-1,3-dioxepane (MD), and its biodegradable properties have been described by Sun, et al(2). Here, a novel thermosensitive, biodegradable NIPAAM copolymer is proposed that would have no low molecular weight byproducts. Copolymer poly(NIPAAm-co-butyrolactone) was synthesized by radical polymerization. The biodegradability of the copolymer is attributed

to the increase in LCST due to hydrolysis of the ester bond in the butyrolactone ring. Properties of the copolymer were characterized by DSC, HPLC, FTIR, and acidic titration. The copolymers showed decreased LCST from 31°C to 16.3°C with the increase in butyrolactone content. The time-dependent hydrolysis study was conducted in 0.1N PBS solution of pH 7.4 at 70°C and it showed that the LCST increases for each butyrolactone content with time. This increase resulted from the change of the hydrophobic butyrolactone ring to a more hydrophilic structure after hydrolysis. FITR was conducted for time-dependent hydrolysis. It was indicated that the copolymer are hydrolyzed with time. Two peaks at 1782 cm-1 and 1750 cm-1 were found in the FTIR spectra for the copolymers before hydrolysis and these two peaks are assigned to the two carbonyl groups in butyrolactone. The heights of these two peaks changed after time-dependent hydrolysis indicating the hydrolysis of the butyrolatone. After hydrolysis for 10 days, the LCST increased 1 to 6°C depending on butyrolactone content (See Table). These results indicated that poly(NIPAAm-co-butyrolactone) could be a potential biodegradable thermosensitive material for controlled drug delivery or tissue engineering applications, due to its LCST increase with hydrolysis time. 1. Neradovic et al, Macromolecular Rapid Communications, 20, 577-581 (1999). 2. Sun et al, Macromolecular Bioscience, 2003, 3, No.12, 725-728

11:15 AM N1.7
Abstract Withdrawn

11:30 AM N1.8
Thermoreversible Gelation of Methylcellulose in Water: Effects of Ionic Surfactants. Lin Li, School of Mechanical & Production Engineering, Nanyang Technological University, Singapore, Singapore.

Methylcellulose (MC) is one of typical cellulose derivatives, which can form thermorevesible hydrogels in water upon heating. When the solubility of MC or the hydrophobicity of a solvent (water) is modified by an additive such as a salt or a surfactant, the sol-gel transition of MC is expected to change. In addition, a surfactant may be bound to polymer chains to form an associated structure with polymer so that the gelation behavior and rheological properties of a MC aqueous solution will be different. In this work, we studied the effects of anionic surfactants on the sol-gel transition of aqueous methylcellulose solutions by means of micro differential scanning calorimetry (micro DSC) and rheology. It is found that the heating process is endothermic while the cooling process is exothermic for MC solutions with and without an anionic surfactant. At low surfactant concentrations, the addition of the surfactant does not change significantly the patterns of gelation and degelation of MC. However, the gelation of MC can be completely modified when surfactant concentration is high. It is considered that the surfactant molecules can surround the hydrophobic groups of MC to form the micelle-like cage that prevent MC chains from aggregation. This is an effect similar to the salt-in effect, but with a different mechanism.

11:45 AM N1.9
Molecular Motions of PNIPAM Microgels in the Swollen and Collapsed States Studied by Neutron Scattering. Enrique Lopez Cabarcos[1,2], Jorge Rubio Retama[2] and Beatriz Lopez Ruiz[3]; [1]Physics, University of California Santa Cruz, Santa Cruz, California; [2]Pharmaceutical Chemical Physics, University Complutense of Madrid, Madrid, Spain; [3]Analytical Chemistry, University Complutense of Madrid, Madrid, Spain.

Many potential applications of gels are limited by the slow response time of these systems to external stimuli. The main advantage of microgels with respect to gels is that reducing the gel size to mesoscopic dimensions increases the response time by orders of magnitude [1]. The dimension of the thermosensitive poly(N-isopropylacrylamide) (PNIPAM) microgels, prepared with 0.25% w/w bisacrylamide cross-linking are in the so-called ultra-micron region. The hydrodynamic radius of the PNIPAM microgels [2] changes from 1050 nm at 293 K (swollen state) down to 275 nm at 319 K (collapsed state) presenting a sharp decrease around 306.8 K at the volume phase transition. These microgels were used to investigate the molecular dynamics of the polymer chain in the swollen and collapsed states using incoherent elastic (IENS) and quasielastic (IQNS) neutron scattering. The experiments were carried out at the ILL (Grenoble, France) using the spectrometer IN10 with energy resolution 2 micro-eV. The incoherent scattering cross section of hydrogen is very large in comparison with the coherent and incoherent scattering cross sections of other atoms such as carbon, oxygen and nitrogen. For PNIPAM the incoherent scattering is 93% of the total scattering. Accordingly, from the measurements we obtain the incoherent scattering function for the H atoms and hence, we can infer the dynamics of the polymeric chain. IENS was measured during a heating and cooling cycle between 190K and 340 K and IQNS was recorded at 290 K and 327 K corresponding to the swollen and collapsed states of the microgel. The IENS increases at the volume phase transition temperature indicating that chain segmental motions which were allowed in the swollen state are hindered in the collapsed state. From the IENS the root mean square amplitude of the vibrational motion of the chain segments was obtained analyzing the q dependence (being q the scattering vector) of the elastic intensity at fixed temperature. The linear variation of the amplitude with T, (harmonic behavior) disappears at the transition temperature in which starts to oscillate exhibiting a sharp increase. The IQNS spectra of the microgels in the swollen state resembles that of polymers in solution whereas in the collapsed state is similar to the one in the solid sate. For the analysis of the IQNS spectra we have considered the molecular motion formed by the combination of a vibrational motion and a translational diffusion motion which appears as a lorentzian component in the quasielastic spectra. The half width at half maximum of the quasielastic component as a function of q follows a Fickean centre of mass diffusion equation which allows to derived the diffusion coefficient D. References 1.- Pelton R., Adv. Colloid Interface Sci., 2000, 85, 1 2.- Fernandez-Barbero A, Fernandez-Nieves A, Grillo I and Lopez Cabarcos E, Phys.Rev.E, 2002, 66, 051803

SESSION N2: Bioinspired Polymer Gels
Tuesday Afternoon, March 29, 2005
Room 3007 (Moscone West)

1:30 PM N2.1
Nonaqueous Gels with Broad Temperature Performance. Joseph L. Lenhart and Phillip J. Cole; Sandia National Laboratories, Albuquerque, New Mexico.

A gel is a cross-linked polymer highly swollen by solvent. Mechanically the solvent creates a "soft solid", which is easily deformable yet still recovers from deformation due to the elastic nature of the permanent cross-links in the polymer. Polymer gels have potential use in a variety of emerging technical applications including drug delivery, biomedical implants, artificial muscles, food and cosmetics, separation systems, display devices, electronics, batteries, optical devices, and sensors to name a few. While varying solvent types and loading provides a wealth of potential applications, the high solvent loading invokes unique materials challenges because the solvent-polymer partitioning impacts the gel properties. Solvent-polymer partitioning in a gel can be critical for the performance of devices. For example, polymer gels can undergo a volume phase transition when external conditions such as temperature, pH, solvent, or concentration of chemical or biological analytes, is altered. In some applications, this swelling-shrinking phenomenon can potentially be exploited to make devices. Examples are sensors for biological and chemical contaminants, controlled lubrication layers, etc. In other applications it is undesirable to have a gel exhibit phase separation, particularly when gel adhesion to a substrate is critical for the device performance. The objective of current research is to design a polymer gel that will perform over very broad temperature ranges both above and below room temperature. Key to this objective is a fundamental understanding regarding the role of the polymer-solvent interactions on the gel phase behavior, partitioning, microstructure, and properties. A combination of neutron scattering, rheological testing, and adhesion testing is presented illustrating the role of the solvent on the gel mechanical and adhesion properties, and on the gel microstructure and phase behavior.

1:45 PM N2.2
Probing Weak Adhesive Forces with Surface Modified Tri-Block Copolymer Gels. David A. Brass and Kenneth R. Shull; Materials Science and Engineering, Northwestern University, Evanston, Illinois.

Highly compliant materials, like polymer gels, are sensitive to weak adhesive interactions. Polymer gels consisting of poly(styrene-ethylene/butene-styrene) triblock copolymers in mineral oil are excellent model systems because of their ease of formation and water resistance. These gels were used in "JKR" contact experiments, in both air and water. In water, strong adhesion was experienced for unmodified gels, which is attributed to hydrophobic interactions and viscoelastic dissipation of the gel. Viscoelastic contributions to the adhesion were largely eliminated by adhering glassy polystyrene layers to the contacting gel surfaces. To further modify the surfaces, polystyrene-poly(ethylene oxide) diblock copolymer layers were deposited onto the polystyrene layers. In water, the diblock modification further reduced and virtually eliminated all of the hydrophobic interactions, giving non-adhesive gels, suitable for subsequent modification with specific adhesive molecules.

2:00 PM *N2.3
Polypeptide Hydrogels: Structure and Function. Timothy Deming, UCLA, Los Angeles, California.

The use of low-valent metal complexes for the polymerization of alpha-amino acid-N-carboxyanhydrides (NCAs) will be presented. Using these initiators, we have prepared block copolypeptides containing a variety of both hydrophilic and hydrophobic domains. The hydrophilic chains are composed of either cationic or anionic residues and the hydrophobic chains are composed of natural non-polar amino acid residues such as leucine, valine and phenylalanine. We have focused our efforts on the self-assembly of block copolypeptides in solution, primarily employing water as the solvent. By working with polypeptides, we expected that the secondary structures present in the block domains would substantially alter the structures of the polymers. The controlled aggregation of block copolypeptides into discrete ordered structures would yield materials valuable for biomedical and materials applications. Examples would be drug and gene delivery, where the shape of the complexes would favor selective interactions with different biological surfaces. The properties of hydrogel-forming amphiphilic block copolypeptides will be discussed.

2:30 PM *N2.4
Enzymatically Crosslinked Hydrogels: The Role of Polymer Composition in Gelation and Adhesion at the Biomaterial/Tissue Interface. Bi-Huang Hu, Marsha Ritter Jones, Roger Warren Sands and Phillip Messersmith; Biomedical Engineering Department, Northwestern University, Evanston, Illinois.

With increasing frequency, polymer hydrogels intended for wound repair and tissue engineering are being designed with the capability of in-situ gelation from a liquid precursor, allowing minimally invasive administration via syringe and needle. The catalytic activity of biological enzymes can be exploited to form polymer hydrogels under physiologic conditions without the need for polymerization initiators, monomers and other potentially harmful compounds necessary for gel formation by other methods. In this talk I will briefly describe our efforts to utilize protein crosslinking enzymes, such as transglutaminase, to induce rapid gelation of polymer-peptide conjugates. The use of combinatorial methods leading to optimization of the polymer composition for rapid gelation will be described. Due to the ability of the enzyme to crosslink peptide-polymer conjugates to extracellular matrix proteins of connective tissues, an added benefit of this approach lies in the potential enhancement of adhesion between the biomaterial and adjacent native tissues. Preliminary results demonstrating chemical coupling between hydrogel components and tissue surfaces will be presented.

3:30 PM *N2.5
Environmentally Responsive Hydrogels with Tunable Rigidity Constructed via Peptide Folding and Consequent Self-Assembly. Darrin J. Pochan, Materials Science and Engineering, University of Delaware, Newark, Delaware.

By using peptidic molecules in the materials self-assembly design process, one can take advantage of inherent biomolecular attributes, intramolecular folding events and secondary structure, in addition to more traditional self-assembling molecular attributes such as amphiphilicty, to define hierarchical material structure and consequent properties. Importantly, intramolecular folding events impart a molecular-level mechanism for environmental responsiveness at the material level (e.g. infinite change in viscosity of a solution to a gel with changes in pH, ionic strength, temperature). Design strategies based on small (less than 24 amino acids) beta-hairpin peptides will be discussed. The self-assembly construction process is predicated on the peptides first intramolecularly folding into the beta-hairpin conformation from a random coil conformation. Importantly, the scaffold assembly is completely reversible with pH or temperature by reversibly folding and unfolding the constituent peptides that, in turn, assembles or disassembles the scaffold, respectively. In addition, the rigidity of the gel scaffold can be tuned via the magnitude of the environmental stimuli, e.g. gels triggered with temperature form a more rigid network when assembled at higher temperatures due to faster folding and self-assembly kinetics. Local hydrogel structure, both fibrillar struts and crosslink points, can be altered by changing peptide length. Finally, the hydrogel networks are also mechanically responsive in that they can quickly reheal into a rigid material after shear thinning due to the self-assembled nature of the underlying network. The molecular design and self-assembly principles, including a model to explain the inherent tunability of the final gel networks that underlie the observed morphological and rheological material, will be presented. Laser scanning confocal microscopy, cryo transmission electron microscopy, oscillatory rheology, small-angle and ultrasmall-angle neutron scattering, spectroscopy, and cytotoxicity results will be presented.

4:00 PM N2.6
Surface-Patterned Hydrogels with Controlled Bioactivity. Peter Krsko, Jennifer Sipics and Matthew Libera; Stevens Institute of Technology, Hoboken, New Jersey.

We are interested in controlling the spatial distribution of proteins on surfaces at cellular and subcellular length scales using patterned hydrogels. To do this, we have been using a focused electron beam in a field-emission scanning electron microscope (SEM) to radiation crosslink water-soluble polymers such as poly(ethylene glycol) [PEG] and poly(carboxylic acids). We can simultaneously pattern the resulting hydrogels on silicon or glass surfaces with nanoscale and microscale feature sizes. Using hydroxy-terminated PEG 6800 we have learned to create gels with swell ratios between unity and fifteen depending on the degree of radiation crosslinking, and the swelling properties can be modeled using the Flory-Rehner formulation modified for one-dimensional swelling. While lightly-crosslinked PEG gels resist protein adsorption and cell adhesion as expected, highly crosslinked PEG gels adsorb such proteins as fibronectin and laminin and consequently become adhesive to fibroblasts, macrophages, and neurons. By spatially modulating the degree of crosslinking we can localize these cells and, for example, direct neurite outgrowth. If instead of using hydroxy-terminated PEG we use amine-terminated PEG, we introduce the additional flexibility of creating high-swelling PEG gels which resist nonspecific protein adhesion but to which specific proteins can be covalently bound. We use bovine serum albumin (BSA) to amplify the number of amine groups, and we further demonstrate that different proteins can be covalently bound to different hydrogel pads on the same substrate to create multifunctional surfaces. Finally, with the aim of making a three-dimensional hydrogel-based device, we have explored the interaction of focused electron beams with bulk hydrogels previously synthesized by conventional UV crosslinking methods, and we show that the local properties can again be modulated at cellular and sub-cellular length scales.

4:15 PM N2.7
Liquid Crystalline Gels Self-Assembled from Block Copolymers. Neal Scruggs, Rafael Verduzco and Julia Kornfield; Chemical Engineering, California Institute of Technology, Pasadena, California.

Block copolymers with long side-group liquid-crystalline (LC) midblocks and LC-phobic end-blocks form a physical network that swells readily in a small molecule LC to form nematic gels. Using ultralong ()800 kg/mol) side-group liquid crystal polymers (SGLCP) for the midblock enables gelation at relatively low concentration ($\sim$5% polymer). The materials provide model systems in which the molecular weight between crosslinks is well defined and determined by the length of the polymer midblock. Similar to LC elastomers, an initially unaligned, polydomain gel aligns under applied strain, creating a monodomain that is oriented well enough to generate clear conoscopic figures. Furthermore, a novel stripe pattern attributed to semi-soft elasticity forms when the gels are subjected to electric fields or when the order parameter of the LC solvent changes. When an electric field is applied to the gels the switch-on time is somewhat slower than that of the pure LC solvent but the polymer network exerts a restoring force that results in fast restoration of the original alignment state. We seek to develop an understanding of the molecular-scale architecture that is responsible for novel electro-optic and mechano-optic properties of these gels. Small-angle neutron scattering (SANS) in a perdeuterated LC solvent elucidates the dimensions and shape of the gels' network strands. Refractive index measurements and NMR measurements of the deuterium quadrupolar splittings yield the order parameter of the LC solvent. Comparison to experiments performed on an analogous SGLCP homopolymer allows the effects of network architecture to be isolated. Detailed knowledge of the network topology should allow rational design of gels exhibiting higher-order LC phases, such as ferroelectric gels.

4:30 PM N2.8
Enzymatic Cross-linking of Short Synthetic Peptides and Peptide-polymer Conjugates to Cartilage.
Marsha Elizabeth Ritter Jones and Phillip B. Messersmith; Biomedical Engineering Department, Northwestern University, Chicago, Illinois.

Hydrogels have been explored as matrices for cartilage regeneration, however the lack of adhesion of hydrogels to native cartilage is a major obstacle to their application. Tissue transglutaminase (tTG) is a member of the transglutaminase family of enzymes that catalyze the cross-linking reaction between lysine and glutamine residues of proteins. Tissue transglutaminase is found in cartilage and is considered to be one of the enzymes used to form permanent cross-links between cartilage extracellular matrix (ECM) components, such as osteonectin, osteopontin, collagen II and fibronectin. Some researchers have demonstrated that tTG can be used to create cartilage-cartilage bonds, and small synthetic tTG substrate molecules such as monodansylcadaverine have been found to couple to cartilage in the presence of tTG. Our lab has previously developed short tTG substrate peptides, Ac-FKG and Ac-GQQQLG, and has

used these peptides to modify polyethylene glycol (PEG) polymers and cross-link them into a hydrogel. Hypothesizing that interfacial adhesion between hydrogels and other tissue engineering constructs and native tissue will be important in successful repair or regeneration of cartilage, the current study sought to determine if these peptides have the capability to react with ECM components of cartilage. We examined the ability of these peptides, as well as peptide-modified polymers, to react with intact pieces of cartilage in the presence of tTG. Digested cartilage and commercially available ECM components of cartilage were reacted with these peptides in the presence of tTG and Western blot analysis used to determine which cartilage ECM proteins had reacted with the peptides. Our results demonstrate that these peptides are coupled to cartilage ECM components by tTG, suggesting the possibility that better integration of peptide based hydrogels with native cartilage is possible through enzymatic cross-linking to native tissue.

4:45 PM N2.9
Synthesis and Surface Properties of DOPA Modified Acrylic Triblock Hydrogels. Murat Guvendiren, Chi-Yang Chao and Kenneth R. Shull; Materials Science and Engineering, Northwestern University, Evanston, Illinois.

There has been a considerable interest on bio-hydrogel adhesives that can solidify in situ and form strong and durable bonds. In this study a Poly(methyl methacrylate)-poly(tert-butyl methacrylate)-poly(methyl methacrylate) (PMMA-PtBMA-PMMA) triblock copolymer was synthesized via anionic polymerization. The midblock was then converted to methacrylic acid (MAA), and L-3,4-dihydroxyphenylalanine (DOPA) was attached to the MAA midblock. The adhesive properties of DOPA containing hydrogel were studied via an axisymmetric adhesion test. A rigid flat punch coated with Titanium (Ti) was brought into contact with flat hydrogel surface. The two surfaces were pulled apart, and the energy of separation was measured by breaking the interfacial bonds formed when the surfaces were in contact.

SESSION N3: Poster Session: Polymer Gels
Tuesday Evening, March 29, 2005
8:00 PM
Salons 8-15 (Marriott)

N3.1
Acid Exposure and Swelling Influences on Phosphate Uptake in Polymers. Anika Odukale[1], Edward A. Ross[2], William E. Scott[1] and Christopher Batich[1]; [1]Materials Science and Engineering, The University of Florida, Gainesville, Florida; [2]Division of Nephrology, University of Florida, Gainesville, Florida.

In recent years there has been a growing appreciation for the need to avoid calcium-based phosphate binders in patients with chronic kidney disease so as to prevent the long-term complications of accelerated vascular disease. The paucity of available medications has led to the overwhelming use of the nonabsorbable synthetic polymer, polyallylamine (sevelamer HCl, Renagel®, Genzyme Corp, Cambridge, MA). It is a highly effective binder due to the anionic charge of protonated amine groups, removing phosphate in vitro at approximately 3 meq (288 mg)/g drug. Rigorous pharmacokinetics have not been published so as to describe the need for the rather high doses of this expensive medication in clinical practice. Polymer-based drugs present unique challenges in that they may swell rather than dissolve in aqueous solutions. Their efficacy can thus depend on the kinetics of ligands in solution interacting with moieties having varying degrees of hydration. Conditions or medications that impair gastric acid might then partially explain the patient-to-patient variability in the number of tablets needed to control plasma phosphate levels with ostensibly similar dietary intakes. To investigate this hypothesis we studied phosphate uptake by Renagel® at pH 7, after an initial incubation phase in solutions at different levels of acidity. Our current studies also involve the synthesis of novel polymer systems for phosphate binding. Within this, a large effect of altering pH on the amount of water uptake and hydrogel formation is noticeable to impressionable degrees. This is consistent with the literature describing increased swelling of various polymers as the pH falls below the pKb of the molecule/s base. Although sevelamer/s phosphate binding has been characterized at different pHs, we hypothesized that transient pre-treatment in an acid milieu would greatly enhance hydration, which could then permit more phosphate uptake. Polymer swelling was examined at different solution pH levels, as to imitate small intestine conditions in-vivo. Results showed that the polymer in its dry state initially showed significant swelling of 50-70% upon 1-hour exposure to a pH solution at or below 7. However, a negligible degree of swelling occurs when this hydrated sample is further exposed to an acid solution of pH 1. One hypothesis that arises from these results is that perhaps the polymer particles are crosslinked to an extent such that large-scale swelling is not possible. Instead phosphate uptake may be the result of binding to available protonated sites that create more of a hydrating effect of the polymer.

N3.2
Multiple Stamping of Arrays of Supported Lipid Bilayers with Different Lipid Compositions using Micropatterned Hydrogel Stamps. Sheereen Majd[1] and Michael Mayer[1,2]; [1]Biomedical Engineering, University of Michigan, Ann Arbor, Michigan; [2]Chemical Engineering, University of Michigan, Ann Arbor, Michigan.

Screening for binding of drugs to arrays of lipid bilayers would be useful to explore pharmacologically-relevant drug-membrane interactions. Ideally many copies of an array of different bilayers could be exposed to different drug candidates. Techniques for rapid preparation of multiple copies of arrays of supported lipid bilayers with different lipid composition are, however, limited. Here we present a stamping technique for parallel and repetitive formation of arrays of different lipid bilayers using patterned agarose stamps. We inked individual posts (diameter 200-1000 μm) on patterned hydrogel stamps manually with minute volumes ($\sim$1-3 μL) of different suspensions containing liposomes with varying lipid composition. During stamping, islands of lipid bilayers formed by diffusion of small unilamellar liposomes (diameter 20-80 nm) through the agarose stamp followed by spreading of liposomes onto the regions of contact with a glass slide. We demonstrated that agarose stamps inked with liposome suspensions can be used for rapid (contact time $<$ 7 s), repetitive stamping of more than 100 copies of the same pattern without the need for re-inking. We stamped arrays of lipid bilayers having different lipid compositions (up to 50% negatively charged lipids) on glass slides. We performed a membrane-binding assay with annexin V on paterns of bilayers with a gradient in phosphatidylserine (PS) and confirmed that the binding constant increases with increasing percentage of PS. Fluorescence recovery after photobleaching (FRAP) experiments revealed that the lipids in the supported bilayers were fluid at room temperature. Patterned spots of bilayers were stable in PBS buffer for at least 2 weeks. The technique presented here uses biocompatible agarose stamps and does not require drying of the molecules to be stamped; it might therefore be amenable to stamping of proteoliposomes. We currently explore the usefulness of supported lipid bilayers with different composition of lipids or membrane proteins for screening of drug-membrane interactions.

N3.3
Viscoelastic Characterization of Model Physical Gels through Instrumented Indentation. Aaron Michael Forster[1], Peter L. Drzal[2] and Mark R. VanLandingham[1]; [1]Multifunctional Materials Branch, Army Research Lab, Aberdeen Proving Ground, Maryland; [2]Building and Fire Research Division, National Institute of Standards and Technology, Gaithersburg, Maryland.

Scientific and industrial interest in self-organizing physical gels has been steady over the last few decades. Polymer gels play an important role in our everyday life and can be found in a variety of applications such as medical technologies, cosmetics, pharmaceutics, and ordnance damage studies. Much has been learned about the mechanisms by which biopolymers or synthetic polymers form three dimensional networks using conventional rheological techniques. Recent advances in instrumented indentation techniques (IIT) have provided the capability to measure dynamic mechanical and quasi-static properties of polymers over much smaller length scales than are accessible through conventional rheometery. In this work we use a commercial instrumented indentation system to investigate the viscoelastic deformation properties of two model physical gels. The first model system was an ordnance gelatin, a model biopolymer that forms aqueous polymeric gels through a time dependent association of single helixes into physical crosslinking sites. Ordnance gelatin is the material of choice for evaluating the damage inflicted by ballistic events on the human body. The second model system was a synthetic gel composed of a styrene-isoprene-styrene triblock copolymer dissolved in a midblock selective solvent where the polystyrene end blocks aggregate to form physical crosslinking sites. This triblock copolymer is readily available as the precursor to pressure sensitive adhesive formulations. In this work we compare the viscoelastic deformation properties of these model gels to standard ordnance gelatin gels using several different radius flat punch indenters. The small strain frequency dependent moduli over a range of frequencies (10−200 Hz) along with stress relaxation experiments were used to investigate differences in the stress dependent deformation behavior of the two different gel systems. Our goals in characterizing these systems are two-fold: 1) develop a methodology to reliably characterize a soft gel (E = 1 $<$ MPa) with IIT and 2) demonstrate the advantages of the model synthetic physical gel relative to a standard ordnance gel. For example, ordnance gelatin must be //calibrated// with a test shot before use as a target. This calibration provides a qualitative approach to understanding the relationship between inflicted damage and the gelatin structure and mechanical properties, which can vary due to the nature of ordnance gelatin. A

better understanding of the stress dependant deformation behavior of the test gel before testing will ultimately provide more quantitative information about the ballistic event after the test is completed. The physical gels are a route to achieving the required understanding of the deformation behavior.

N3.4

Structures of Hydrophilic Polymer-Silica-Phosphoric Acid Composites and Applications in Intermediate Temperature Fuel Cells. Wenbin Hong[1], Ken Tasaki[2] and Galen Stucky[3];
[1]Mitsubishi Chemical Center for Advanced Materials, University of California, Santa Barbara, California; [2]Mitsubishi Research and Innovation Center, Goleta, California; [3]Department of Chemistry and Biochemistry and Materials Department, University of California, Santa Barbara, California.

Organic-inorganic hydrophilic polymer-silica hybrids doped with proton conducting acid H_3PO_4 were prepared using a sol-gel process. Polymer-xH_3PO_4-ySiO_2 composites were obtained for $x \leq 6.0$ and $y \leq 20\%$, where x was the molar ratio of PO_4^{3-} with polymer repeat unit and y was the weight percentage of SiO_2 in the composite. TGA data showed that the composites were thermally stable up to 200°C. The glass transition temperature of the composites dropped from 176°C to -46°C when x was changed from 0 to 6. Thin film FTIR and ^{13}C, ^{29}Si and ^{31}P NMR studies revealed that in addition to the hydrogen bonding between the hydrophilic groups of the polymer and the phosphoric acid, the silanol groups reacted with the PO_4^{3-} goups as well, which suggested a semi-IPN structure of the composites. The proton conductivity of the composites increased with acid content and relative humidity (R.H.). At high acid content ($x \geq 3$), the composites had higher conductivity than Nafion at low R.H., and comparable conductivity to Nafion at high R.H. (>60%). Therefore, the composites have potential applications in intermediate temperature fuel cells.

N3.5

Ion Transport in Decoupled Hybrid Organic-Inoganic Polyelectrolyte. Flavio Leandro de Souza, Edson Roberto Leite and Elson Longo; Materials Science and Engineering, UFSCar, Sao Carlos, Sao Paulo, Brazil.

In this work we described the chemical synthesis strategy to obtain helical free chain configuration of a single-phase hybrid organic-inorganic polymer electrolytes leading to a good Li ion conductivity at room temperature (~10-5 (ohm.cm)-1). The hybrid polymer studied here is prepared, by a sol-gel non-hydrolytic process, with citric acid, tetraethyl orthosilicate and ethylene glycol, forming polyester chains. It is well that the ionic transport above Tg (glass transition temperature), in typical polymer electrolyte, is strongly coupled to segmental motions of the polymer chain, resulting in a VTF ionic conduction behavior (after Vogel-Tamman-Fulcher). The hybrid organic-inorganic polymer obtained from this strategy showed a Tg of -79 øC and an Arrhenius behavior regarding temperature dependent ionic conductivity for temperatures higher than Tg was obtained. Such remarkable behavior characterizes a segmental motion decoupled polymer. This hybrid organic-inorganic polymer electrolyte (polyelectrolyte) showed activation energy of 0.23 eV, indicating a fast ion transport mechanism. Such characteristics indicate a fast ion transport mechanism in a segmental motion decoupled behavior is reported for a hybrid polyelectrolyte. For the best of our knowledge, this is the first time that a segmental motion decoupled feature is reported for a hybrid organic-inorganic polyelectrolytes.

N3.6

Properties of Galactose-Derivatized Thermo-Sensitive Hydrogels and Their Uses in Culture of Hepatocyes. Jyh-Ping Chen[1,2] and Shis-Chuang Chen[2]; [1]Graduate Institute of Biochemical and Biomedical Engineering, Chang Gung University, Taoyuan, Taiwan; [2]Department of Chemical and Materials Engineering, Chang Gung University, Taoyuan, Taiwan.

In this study we examined the behavior of freshly isolated rat hepatocytes cultivated within thermo-sensitive hydrogels containing the monomer N-isopropylacrylamide (NIPAAm). Based on the difference in molecular structure created by the presence or absence of a cross-linker during polymerization, the hydrogels can be divided into two groups, a thermo-sensitive injectable hydrogel (cross-linked) and a thermo-sensitive polymer hydrogel (not cross-linked). These novel three-dimensional scaffolds can mimic the in vivo extracellular matrix for hepatic tissue engineering. Loosely cross-linked poly(NIPAAm-co-acrylic acid) [P(NIPAAm-co-AAc)] thermo-sensitive injectable hydrogels were synthesized with N,N'-methylenebis(acrylamide) as a cross-linker in buffer solutions. Thermo-sensitive polymer hydrogel was synthesized by copolymerizing NIPAAm and AAc in benzene with AIBN as an initiator. Galactose residues were introduced into the hydrogels by modifying the AAc groups with galactosylated derivatives (galacotosylamine) or by co-polymerizing with galactose-containing co-monomer (allyl galactopyranoside). By introducing galactose into the hydrogels, cell adhesion and metabolic functions are expected to be substantially improved by inducing specific interactions between hepatocytes having a galactose-specific receptor, and the polymer molecules. The hydrogels were characterized by NMR for chemical structures, GPC for molecular weights, UV-VIS spectrophotometer for lower-critical solution temperature, SEM for pore sizes and structures, dynamic rheometry for viscoelastic properties, and resorcinol sulfuric acid assay for galactose content. Freshly harvested rat hepatocytes were seeded into the hydrogels by injection into the hydrogel or by mixing with the polymer hydrogel. Hepatocytes could maintain their viability up to a month from MTT assays and Laser Scanning Confocal Microscopy by a LIVE/DEAD fluorescence assay. Phase-contrast microscopy, HE and Alcian Blue stains, and TEM were used to evaluate the morphology, distribution of extracellular matrix, and ultrastructure of hepatocytes aggregates. Metabolic functions of cells were confirmed by secretion of albumin and urea-N during the culture period for up to 3 weeks. These galactose-modified thermo-sensitive hydrogels can serve as a useful tool for studying cell-material interactions within 3-D structures and have the potential to be used as ideal scaffolds for hepatic tissue engineering applications.

N3.7

Characterization of H+Nafion®/Alcohol Gels. Steven Romel Givens, Christian Pellerin, John Papalia, John Rabolt and Bruce Chase; Material Science and Engineering, University of Delaware, Newark, Delaware.

Thermoreversible gels were formed by dissolving DuPont H+Nafion® perfluorosulfonic acid in several alcohols, including 2-propanol, 2-butanol, 2-pentanol, and 2-octanol. These gels show a reversible liquid/solid transition with each of these alcohols. This gel behavior was not seen in H+Nafion®/alcohol systems using the primary alcohol isomers. The short-range molecular structure of the thermoreversible H+Nafion®/alcohol gels was investigated using FTIR, absorption and ATR techniques, and Near-IR FT Raman scattering. Using previously characterized spectra of polytetrafluoroethylene (1) as a means of identifying the vibrations of the helical zigzag CF2 backbone of H+Nafion®, particular attention was given to interpreting the interaction of the pendant sulfonic acid group with the solvent. Hyper differential scanning calorimetry was used to determine the gel thermal properties and transition point as well as the enthalpies of these transitions. (1) Rabolt and Franconi Macromolecules Vol 11 No. 4 pp.740-745 1978

N3.8

Controlling Pore Size of Resorcinol Formaldehyde Foam Aerogels for ICF Shell Targets. Christopher A. Frederick, O. Acenas, D. G. Czechowicz, A. Nikroo and R. R. Paguio; General Atomics, San Diego, California.

Resorcinol Formaldehyde (R/F) foam aerogels have been used in the fabrication of shell targets for Inertial Fusion Confinement experiments at the University of Rochester. Recent cryogenic experiments with R/F shells have necessitated a larger pore size R/F foam than the standard R/F formulation. The R/F foams are synthesized by the polycondensation of resorcinol with formaldehyde in a slightly basic solution. A method for controlling the pore size of R/F foams has been investigated. It involves increasing the catalyst concentration in the polymerization process leading to reaction and diffusion limited aggregation which in turn leads to changes in the pore size distribution of the foam. Foams with varying pore size distribution have been made using this technique. These foams have been characterized using a variety of techniques including SEM, nitrogen adsorption porosimetry, and visible light scattering. Results of our study are presented in this paper.

N3.9

Sliding Friction of Gel under a High Load. Jian Ping Gong and Takayuki Kurokawa; Graduate School of Science, Hokkaido University, Sapporo, Japan.

Industrial or environmental problems caused by high frictional surfaces of materials always exist in our daily life. Looking for materials with a low surface friction has been one of the classical and everlasting research topics for material scientists and engineers. Studies on the surface sliding friction of water swollen hydrogels on solid surfaces as well as between gels reveal the richness and complexity of gel friction.[1, 2] Hydrogels exhibit a wide range of frictional coefficients from an order of 10-3 to 100 in magnitude, depending on the interfacial interaction between the polymer network and the opposing substrate. It is also elucidated that polymer brushes on gel surfaces can dramatically reduce the surface frictional coefficient to a value as low as 10-4 if the polymer brush has a

repulsive interaction with the sliding substrate. [3] The low friction of gel should have enabled the gel to find a wide application in many fields where low friction is required, such as articular cartilage. Unfortunately, conventional hydrogels, especially polyelectrolyte gels that show a failure stress less than 0.1MPa, are mechanically too weak to be practically used in any stress or strain bearing applications. This is far weaker than that of an articular cartilage, especially those of kneels and hips that sustains a daily compression of decades of MPa. The mechanical weakness has hindered not only the extensive application of hydrogels as an industrial and biomedical materials, but also the fundamental researches on the gel friction under a high pressure (> MPa). Recently, we discovered a general method to obtain strong hydrogels by inducing a double-network (DN) structure for various combinations of hydrophilic polymers. [4] The DN hydrogels, containing 60-90 % water, exhibit fracture strength of a few to several tens of MPa. This makes it possible, for the first time, to study the gel friction under a pressure range as high as 1-10 MPa, over which an articular cartilage works. In this study, we report the friction of high strength DN gel against glass under a load up to 2.5 MPa order. The friction of the gels swollen with different viscous solvents is investigated over a wide velocity range. A velocity-viscosity conversion relationship is established, which indicates that the motion of the polymer chain plays an important role on the gel frictionDFrom the velocity-viscosity conversion relationship, a master curve that is characteristic to the adsorption-hydrodynamic lubrication transition is obtained, which indicates that the adsorption model proposed by our previous work[2] still valid even under a load up to 2.5 MPa order. References [1] J. P. Gong, Y. Iwasaki, et al., J. Phys. Chem. B.1999, 103, 6001. [2] J. P. Gong and Y. Osada, J. Chem. Phys. 1998, 109, 8062. [3] J. P. Gong, T. Kurokawa, et al., J. Am. Chem. Soc., 2001, 123, 5582. [4] J. P. Gong, Y. Katsuyama, T. Kurokawa, Y. Osada, Adv. Mater. 2003, 15, 1155.

N3.10
The Volume Phase Transitions of Acrylic Acid/Kaoline Powder Superabsorbent Composite. Jihuai Wu and Jianming Lin; Huaqiao University, Institute of Materials Physical Chemistry, Quan Zhou, Fujian, China.

Superabsorbent possess the better volume phase transition properties, which have aroused widely interest and investigation since it was observed first by Tanaka in 1978, because it is possible to apply in molecular biological, imprinting technique, drug delivery, selective membranes and biosensors. A novel superabsorbent, sodium acrylic acid/kaoline powder composite was synthesized by using partly neutralized acrylic acid as monomer, N, N'-dimethylacrylamide as crosslink agent, K2S2O8 as a initiator agent and doping kaoline ultrafine powder in the aqueous solution polymerization reaction system. The volume phase transitions of superabsorbent in aqueous salt solutions of NaCl, KCl, CaCl2, Na2SO4, K2SO4 and CaSO4 were investigated, it was found that the volume phase transition of superabsorbent decreases with the increase of the ionic strength of exterior solution. The different anions do not affect the volume phase transitions of the superabsorbent composite. The volume phase transitions depend on the pH value of solution, the volume phase transitions of superabsorbent composite change sharply when the pH value of exterior solution varies from five to thirteen, and the volume phase transitions of the composite is the largest (800) when the pH value of the system equal to 7. The volume phase transitions of superabsorbent depend on the corsslinking density and the functional group on the superabsorbent. The group of the superabsorbent composite can be controlled by adjusting the neutralization degree of acrylic acid monomer during the preparation of materials, and the volume phase transitions of the composite can be realized suitable. This work was supported jointly by the National Natural Science Foundation of China (No. 59772034) and the Provincial Scientific and Technology of Fujian, China (No. 2004HZ01-3, No. 2002H002)

N3.11
Properties of Poly(*tert*-butyl acrylate) Gels Polymerized in the Presence of Solvents. Danielle R. Lewis and Jeffrey T. Koberstein; Chemical Engineering, Columbia University, New York, New York.

Gels are crosslinked polymeric networks that swell in organic solvents. Although much work has been done in this field [1], the role that entangled chains play in fully polymerized gels and how these entanglements affect the gel's physical properties has not yet been fully understood. In this work, we investigate the influence of solvent present during UV polymerization of poly(*tert*-butyl acrylate) [poly(*t*-BA)] gels. The gels are comprised of the monomer *tert*-butyl acrylate (*t*-BA), ethylene glycol dimethacrylate (EGDMA) crosslinker, and a UV initiator 2,2-dimethoxy-2-phenyl acetophenone (DMPA). Three different solvents were introduced to this monomer solution in increasing weight percent of the total solution, spanning 0 to 20 wt%. The solvents chosen have varying miscibility with *t*-BA and thus allow us to probe how solvation during polymerization influences physical properties such as modulus and degree of swelling. The effects of total solvent content on various material properties was also investigated. Swelling studies were performed in solvents whose solubility parameter ranged from 15.1 to 47.9 $MPa^{1/2}$. Solvent swelling experiments indicate that the swelling ratio increases with wt% of solvent present during polymerization. Rheological testing indicates a corresponding decrease in modulus with wt% of solvent. The results of equilibrium swelling experiments are compared to theoretical calculations and rheological data in order to estimate the solubility parameter and molecular weight between crosslinks for the gels. [1] K. Sivasailam and C. Cohen, *J. Rheol.* **44** (4), 897-915 (2000).

N3.12
Mechanical Properties in Large Deformations of Hydrogels. Rebecca Webber, Guillaume Micquelard, Dominique Hourdet and Costantino Creton; ESPCI, Paris, France.

Although the mechanical properties of polymer gels have been well studied, most of theses studies focus on their linear viscoelastic properties. However, gels often show a very poor resistance to fracture which is closely connected with the large strain deformation properties of the gel. Although empirical knowledge on how to strengthen the gel exists, very few systematic studies investigate the mechanical properties of the gel in this regime. Using our experience with soft hydrophobic adhesives, we will present some results on the deformation properties of gels in the large strain regime and on their fracture properties.

SESSION N4: Biomedial Applications of Hydrogels
Chair: Phil Messersmith
Wednesday Morning, March 30, 2005
Room 3007 (Moscone West)

8:30 AM N4.1
Abstract Withdrawn

8:45 AM N4.2
Characterization of Poly(vinyl alcohol)–Amino Acid Hydrogel Scaffolds for Tissue Engineering Applications. Elizabeth Donaldson[1] and Buddy Ratner[2]; [1]Materials Science and Engineering, University of Washington, Seattle, Washington; [2]Bioengineering, University of Washington, Seattle, Washington.

Tissue engineering aims to create functional tissue using cells seeded onto 3–D scaffolds, providing an alternative to traditional transplants. Tissue engineering can encompass diverse technologies such as growing patches of living tissue in vitro to regenerative therapies to re-growing healthy tissue in situ. Despite the wide differences between approaches, they share one common need: a scaffolding material with properties mimicking natural tissue. The work described here investigates a new group of synthetic organic materials for use as tissue engineered scaffolds, poly(vinyl alcohol) (PVA)–amino acid (AA) hydrogel foams. Previously our lab reported a unique interaction between PVA and AA monomers, resulting in the production of novel hydrogels [1]. We have previously shown that by combining PVA-AA hydrogels with colloidal gas aphron (CGA) techniques we can create foams containing uniform bubbles with diameters on a micrometer scale [2]. The size scale of these CGAs or microfoams makes them a favorable choice for tissue scaffolds, where pores between 100 and 200um are desired [3]. We have fabricated and characterized a series of these PVA-AA scaffolds to examine the effects of polymer Mw, amino acid identity and incorporation of collagen I on final material properties. The largest property differences were seen with changes in polymer Mw and the introduction of collagen I. Volumetric swelling ratio (Q) increased with decreasing Mw. Degree of crosslinking, calculated from volumetric swelling ratio and Flory's equation [4], was found to be unaffected by polymer Mw however crosslinking decreased upon the introduction of collagen I. SEM imaging of the scaffolds found pores ranging in size from 50–300um (FEI Sirion 30, 3kV beam). Degree of interconnectivity appears to increase with the introduction of lower Mw polymer, and preliminary permeability studies support this claim. In addition mechanical testing of the scaffolds tensile properties and a study of hydrolytic degradation of the scaffolds at 37°C are in progress. This work was supported by National Institute of Health grant R24HL64387, NSF-Engineering Research Center grant EEC-9529161 and an American Heart Association Pre-doctoral fellowship. 1. Nair P.D., et al. Biodegradable Porous Polymers Containing Amino Acid Networks as Scaffolds for Tissue Engineering. Society for Biomaterials Transactions, 2001 2. Donaldson E., et al. Novel Tissue Scaffold Materials Based on Poly(vinyl alcohol) and Amino Acid Hydrogels. in 7th World Biomaterials Congress.2004. Sydney, Australia 3. Jockenhoevel S., et al. Fibrin gel - advantages of a new scaffold in cardiovascular tissue engineering. European Journal of Cardio-thoracic Surgery, 2001. 19:424-430 4. Flory P.J. Principles of Polymer

Chemistry. 4th printing ed. 1964, Ithica, NY: Cornell University Press

9:00 AM *N4.3
Synthesis of Osteogenic Hydrogels for the Controlled Differentiation of Mesenchymal Stem Cells. Charles Nuttelman, April Kloxin and Kristi Anseth; Chemical and Biological Engineering, University of Colorado and HHMI, Boulder, Colorado.

Hydrogels provide a unique, largely aqueous environment for 3D cell culture, and when locally modified with appropriate signaling molecules, these synthetic niches can facilitate the regeneration of tissues. While the gel environment is often >90% water, the microscopic architecture and chemistry play an important role in dictating cell morphology, gel degradation and erosion, and the secretion and distribution of extracellular matrix molecules. In this work, hydrogels were synthesized to present local signals to human mesenchymal stem cells (hMSCs) that induce osteogeneis, maintain cell function, and promote mineralized tissue formation. While a significant amount of research has focused on the differentiation of hMSCs in monolayer culture, very little is known about their differentiation potential when cultured in a three-dimensional environment. In particular, results will demonstrate approaches to modify the structure and chemistry of hydrogel hMSC carriers to facilitate osteogenic differentiation and bone formation. First, the macroscopic hydrogel properties including water content, mesh size, and degradation rate were tuned to support 3D hMSC culture. Second, the composition of the extracellular hydrogel environment was varied and methods were developed to locally present osteogenic factors (e.g., dexamethasone) to induce hMSC differentiation. Third, the gel degradation rate was tailored and mineralization nucleators (e.g., pendant phosphate groups) were systematically introduced into the gel formulation to facilitate neotissue evolution. Specifically, hydrogels were synthesized by the photoinitiated polymerization of multivinyl macromolecular monomers, based on poly(ethylene glycol). This general approach to fabricate covalently crosslinked gels provides a robust platform to directly encapsulate cells under cytocompatible conditions and examine the influence of the gel structure and chemistry on cell differentiation and tissue evolution. Variations in the polymerization conditions, as well as the monomer molecular weight and functionality, were used to control the initial gel structure and properties. Dynamic changes in the gel structure were then controlled by the chemistry and the overall connectivity and architecture of the gel. The importance of tuning temporal changes in the network structure for tissue engineering applications is demonstrated through degradation-controlled proliferation of differentiating hMSCs. Single and multi photon imaging was used as a non-invasive technique to explore living cell behavior, especially differentiation of hMSCs, as a function of the local gel chemistry and delivery of osteogenic factors.

9:30 AM N4.4
Polysaccharide-Derivatized Polymers for the Noncovalent Assembly of Bioactive Hydrogels. Nori Yamaguchi[1,2], Le Zhang[1,2], Eric M. Furst[3] and Kristi L. Kiick[1,2]; [1]Department of Materials Science and Engineering, University of Delaware, Newark, Delaware; [2]Delaware Biotechnology Institute, Newark, Delaware; [3]Department of Chemical Engineering, University of Delaware, Newark, Delaware.

Protein-polysaccharide interactions play important roles in a myriad of physiological and pathological processes. Materials in which assembly, mechanical response, and biological properties are controlled by these interactions may therefore be responsive to the biological environment and find use in a variety of biomedical applications. Despite this potential utility, polysaccharide-peptide interactions have only recently been demonstrated as useful in the assembly of noncovalently associated networks. We report here the production of a heparin-modified, poly(ethylene glycol) star copolymer that can be used in the assembly of bioactive hydrogel networks via multiple strategies and that is also competent for the delivery of bioactive growth factors. The noncovalent assembly of hydrogels can be attained via interaction of the heparin-modified polymer with a variety of heparin-binding proteins and peptides. The rheological properties of the hydrogels have been measured via optical probe microrheology and bulk rheology methods and can be controlled by the specific peptide-saccharide interactions. The release of therapeutically important proteins from these heparinized hydrogels has also been demonstrated via immunochemical and cellular assays and is correlated with the erosion of the network. The ability to manipulate the properties of the hydrogels will provide novel materials for use in controlled drug delivery and other biomedical applications.

9:45 AM N4.5
Dihexyl Acrylamide Block Copolymer Nanogels for On-Chip Protein Adsorption and DNA Purification. Karl William Putz[1], Thomas N. Chiesl[1], Meena Babu[3], Chung-Yan Koh[2], Xihua Lu[1] and Annelise Barron[1]; [1]Chemical and Biological Engineering, Northwestern University, Evanston, Illinois; [2]Chemistry, Northwestern University, Evanston, Illinois; [3]Materials Science and Engineering, University of Illinois, Urbana-Champaign, Urbana, Illinois.

A series of dihexyl acrylamide/acrylamide block copolymer nanogels were fabricated for use as a sieving matrices that adsorb proteins and lipids and allow DNA to pass through in microchip electrophoresis. Lab-on-a-Chip technologies will be a powerful tool in the future due to their small sample volume, ease of use, small physical size, and rapid analysis, in such settings as biowarfare agent determination and third-world disease detection. While several DNA sensing technologies have pushed the limit of specific DNA marker detection, these technologies are easily fouled by the presence of proteins, thus requiring purified DNA, with strand length in the 25-125 basepair size range. Since typical lab techniques to purify DNA require several large pieces of equipment, it has been necessary to develop methods to purify DNA "on chip". Previous experiments have demonstrated that the inclusion of hydrophobic N-alykyl acrylamide blocks into linear polyacrylamide polymers create matrices that adsorb proteins during electrophoresis due to interactions between the copolymer and hydrophobic amino acids. Highly charged and hydrophilic DNA molecules were not only allowed to pass through the copolymers, but also separated based on their length. The current series of dihexyl acrylamide/acrylamide nanogels offers a range of advances on the block copolymers, including: lower viscosity, higher hydrophobe incorporation, and retention on a specific location on the microchip. These nangoels were synthesized by precipitating dihexyl acrylamide/acrylamide block copolymers and crosslinking the polymer chains using divinylsulfone. The hydrophobic content was verified by 1H NMR and the size of the nanogels was determined by dynamic light scattering.

10:30 AM *N4.6
Tissue Regeneration with Ultra-Thin Hydrogels: Cell Sheet Engineering for Regenerative Medicine utilizing Temperature-Reponsive Culture Surfaces. Masayuki Yamato, Institute of Advanced Biomedical Engineering and Science, Tokyo Women's Medical University, Tokyo, Japan.

The possibility of re-creating various tissues and organs for the purpose of regenerative medicine has received much interest. However, the field of tissue engineering has been restricted by the limitations of conventional approaches. A method to circumvent the need for traditional scaffold-based technologies is cell sheet engineering, which utilizes temperature-responsive culture dishes. On these surfaces, ultra-thin hydrogel layer is created by the covalent grafting of the temperature-responsive polymer, poly(N-isopropylacrylamide), by electron beam irradiation. This temperature-responsive layer is around 20 nm in thickness, and allows for the non-invasive harvest of cultured cells as intact sheets by simple temperature reduction. Since this cell sheet harvest doesn't require proteolytic treatment, cell-cell junctions, other membrane proteins and the deposited extracellular matrix all remain intact. Therefore, harvested cell sheets readily adhere and integrate with other cell sheets and tissues. Current research progress in the applications of cell sheet engineering for the reconstruction of various tissues including cornea, periodontal ligaments, cardiac tissues, urinary bladder, liver, and esophagus will be shown. In addition, the early clinical outcome will be also provided. We believe that cell sheet engineering, which utilizes temperature-responsive intelligent surfaces, will overcome the problems that have limited conventional approaches and establish a new basis for regenerative medicine.

11:00 AM N4.7
Colocalization of RGD and PHSRN Epitopes on PEG Surfaces Influences Osteoblast Function. Danielle S. W. Benoit[1] and Kristi S. Anseth[1,2]; [1]Chemical and Biological Engineering, University of Colorado, Boulder, Colorado; [2]Howard Hughes Medical Institute, Chevy Chase, Maryland.

Poly(ethylene glycol)-based hydrogels provide many ideal characteristics for cell delivery and tissue regeneration; however, synthetic platforms often require modification to present cells with ECM cues that actively and selectively stimulate desired cellular functions important for tissue growth and healing. Significant interest has emerged in the design of cell scaffolds that incorporate peptide sequences that correspond to known signaling domains in ECM proteins and study how this influences cell attachment and subsequent cellular functions. The cell-adhesive domains of fibronectin have been well studied, and an Arg-Gly-Asp (RGD) sequence is a critical site. Since its identification as a pervasive cell-adhesive peptide, RGD has been widely investigated in terms of biomaterial modifications. More recently, a Pro-His-Ser-Arg-Asn (PHSRN) sequence, although itself not biologically active, was found to enhance the cell-adhesive activity of RGD. In this work, we synthesized macromolecular PEG monomers with pendant RGD functionalities, RGD and PHSRN spaced by a 13-mer of glycine that mimics the 40$\AA$ spacing of these epitopes in fibronectin (RGDG13PHSRN), and a scrambled peptide sequence of

no biological significance (RDGG13HPRNS). These monomers were copolymerized with divinyl PEG macromers to produce hydrogels used to present cells with a controlled surface chemistry. Osteoblasts were seeded on these surfaces to determine the effects, if any, of the synergistic epitope sequence on cell attachment and function. Gels incorporating RGDG13PHSRN increased osteoblast adhesion and spreading, cytoskeletal organization, and focal adhesion formation compared to surfaces modified with the singular RGD peptide and controls. At a maximum (2 week time point), only 53 and 65% of the initial seeding density of cells attached, respectively, on the unmodified and scrambled peptide-modified hydrogels. On the RGD modified surface, cell density was somewhat higher than the negative controls for all three time points; however, the RGDG13PHSRN modified hydrogels had a significantly higher cell density compared to the RGD modified gels. Proliferation, as determined by the total amount of DNA normalized by the total number of cells, was statistically higher for cells seeded on the RGDG13PHSRN gels at all time points, compared to all other surfaces. To monitor cell activity on the various peptide-modified PEG surfaces, MTT and alkaline phosphatase (ALP) production assays were employed. The highest metabolic activity and ALP production at all time points was exhibited by cells seeded on the RGDG13PHSRN modified surfaces. While cell density, proliferation, metabolic activity, and levels of alkaline phosphatase production were augmented by cells on the colocalized peptide-modified surfaces, ECM production was down-regulated.

11:15 AM N4.8
Maintenance of Undifferentiated Human Embryonic Stem Cells on RGD Functionalized Hydrogels. Ying Jun Li[1], Eugene H. Chung[1], Ryan T. Rodriguez[2], Meri T. Firpo[2] and Kevin E. Healy[1]; [1]Bioengineering, University of California Berkeley, Berkeley, California; [2]Center for Reproductive Sciences, University of California San Francisco, San Francisco, California.

Human embryonic stem cells (hESCs) are being studied as a possible source of cells for the treatment for many diseases (e.g. diabetes, Parkinson's, leukemia). However, it is difficult to control the maintenance of hESCs, since conditions for self-renewal are incompletely understood. As such, hESCs are typically grown on a feeder layer of mouse cells (i.e., irradiated but viable cells) and are considered xenografts and cannot be used clinically. Control of hESCs growth and differentiation on a synthetic system offers several advantages. If hESCs can be derived and maintained on a synthetic hydrogel system, then it may be possible to eliminate pathogen transmission associated with mouse or human feeder layers. Also, the hydrogel system can increase the reproducibility of culture conditions and elucidate the requirements for hESC maintenance. In this study, hESCs were grown on a hydrogel consisting of loosely crosslinked poly(N-isopropylacrylamide-*co*-acrylic acid) (p(NIPAAm-*co*-AAc)). The p(NIPAAm-*co*-AAc) was crosslinked with an acrylated peptide (QPQGLAK-NH_2), a sequence designed to be cleaved by matrix metalloproteinase-13 (MMP-13) and other collagenases.(1) In addition, a semi-interpenetrating polymer network was synthesized by the addition of polyacrylic acid-*graft*-RGD (p(AAc)-*g*-RGD), to provide cell binding domains, during the polymerization of p(NIPAAm-*co*-AAc). An important feature of this hydrogel is that the gel stiffness is tunable by varying the concentration of: (a) the crosslinker, and (b) the linear p(AAc)-*g*-RGD chains. The hydrogel undergoes a lower critical solution temperature (LCST) at $\sim$35 °C. Rheological measurements were performed over a frequency range of 0.001 Hz - 10 Hz to determine the complex modulus (G*) and loss angle. The mean G* at 22 °C at 1 Hz was 77.4Pa ±30.3 (SE), and at 37 °C at 1 Hz was 129.1 Pa ± 61.6 (SE). The hydrogel was polymerized in 12-well plates and sterilized by the use of ethanol. hESCs were cultured on the hydrogel surface and optimal hESC culture conditions were used.(2) hESCs were evaluated by morphology, live/dead stain (calcein AM and Ethidium Homodimer), and immunofluorescence against the Oct-4 transcription factor, a highly specific and necessary hESC marker. Initial results indicate that the hydrogel was able to support short-term hESC self-renewal in the absence of a mouse or human feeder layer. The hESC colonies were morphologically intact and live / dead stain indicated a combination of living and dead cells. Finally, immunofluorescence revealed positive Oct-4 expression in the hESC colonies. Further studies are necessary to understand the long-term effects of growing hESCs on the hydrogel. References 1.S. Kim, K. E. Healy, Biomacromolecules 4, 1214-23 (Sep-Oct, 2003). 2.M. S. Bodnar, J. J. Meneses, R. T. Rodriguez, M. T. Firpo, Stem Cells Dev 13, 243-53 (Jun, 2004).

11:30 AM N4.9
Sol Gel Scaffolds as In-Vitro Platforms for Neural Network Development Analyses. Shalini Prasad, [1]EE, University of California Riverside, Riverside, California; [2]ECE, Portland State University, Portland, Oregon.

Transparent nanostructured substrates with are suitable for functioning as cell scaffolds. Not only do they provide support to the developing cells but also allow for in-situ optical monitoring. The sol-gel process is used to prepare inorganic and hybrid organic-inorganic host structures. In this process, a suitable silicon alkoxide and/or an organosilicon precursor is mixed with water in a mutual solvent such as methanol. During sol-gel formation, the viscosity of the solution gradually increases as the sol becomes interconnected to form a rigid three-dimensional, porous structure - the gel. Materials with tailor made porosity, morphology, and chemical functionality are particularly important in the development of highly directed biological neural networks. Three dimensional porous gel scaffolds are created using polymer sol gel chemistry and fundamental optical lithography. These three dimensional matrices are then used to map the morphological growth changes both optically and electrically. Sol gel has the same chemical make-up as glass - silicon dioxide - Unlike glass, though, sol gel is porous and can be made at low temperatures. This property is used to optically visualize the encapsulated neural networks. The cells are stabilized in the matrix, but retain and exhibit their natural properties. These three dimensional biological neural network matrices would be suitable platforms for understanding neuron proliferation and understanding cell-cell communication in in-vitro environments

11:45 AM N4.10
In-Situ Gelation and Tissue Adhesive Potential of Mussel Adhesive Protein Mimetic Hydrogels. Sean Burke and Phillip Messersmith; Biomedical Engineering Department, Northwestern University, Evanston, Illinois.

Marine and freshwater mussels are notorious foulers of natural and manmade surfaces, secreting protein adhesives for rapid and durable attachment to the substrates upon which they reside. Given the strong and water-resistant nature of mussel adhesive proteins (MAPs), significant potential exists for mimicking their adhesive characteristics in bioinspired synthetic polymer materials. An important component of MAPs is L-3,4-dihydroxylphenylalanine (DOPA), an amino acid found in high concentration in several MAPs. DOPA is believed to contribute to cohesive strength of MAPs through oxidation and crosslinking reactions responsible for solidification of mussel glue, and has also been speculated to enhance interfacial adhesion. Our group has synthesized MAP mimetic polymers by coupling DOPA and DOPA-containing peptides to a number of synthetic polymers. One goal of our work is the development of polymers that have the ability to solidify in-situ, a property that facilitates their use as adhesive gel-forming materials for drug delivery and tissue repair. In this paper, we describe the use of stimuli responsive liposomes to induce rapid thermal gelation of DOPA-modified polymers. Liposomes containing entrapped sodium periodate were mixed with DOPA-modified polymers to create a viscous liquid capable stable during storage at room temperature. Warming of the liposome/polymer mixture to body temperature induced release of periodate from liposomes and rapid crosslinking of polymer into a hydrogel. Finally, we report the preliminary results of tissue adhesion experiments in which the shear strength of porcine skin tissue slices adhered by in-situ formation of hydrogel between tissue surfaces was determined.

SESSION N5: Device Applications of Polymer Gels
Chair: Ken Shull
Wednesday Afternoon, March 30, 2005
Room 3007 (Moscone West)

1:30 PM N5.1
Micropatterning of Poly(ethylene glycol) Hydrogels: Applications in Cell Screening and BioMEMS.
Alexander Revzin[1] and Mehmet Toner[2]; [1]Biomedical Engineering, UC Davis, Davis, California; [2]Center for Engineering in Medicine, Harvard Medical School, Boston, Massachusetts.

This paper describes a surface modification procedure whereby poly(ethylene glycol)-diacrylate (PEG-DA) is photopatterned to manufacture micron-scale hydrogel microstructures on glass or silicon. This approach mimics traditional photoresist lithography in that a polymer solution is spin-coated on the surface and exposed to UV light through a photomask. However, rather than form a barrier to penetration of etching agents, fabricated PEG micropatterns resist protein or cell adhesion. Because of similarity to a "top-down" photolithography process and utilization of traditional semiconductor processing equipment (e.g. spin-coater, mask aligner) large glass or silicon substrates can be micropatterned with PEG hydrogels. Furthermore, PEG photolithography can be combined with registration steps to form cell-repellent PEG microstructures on top of existing microfabricated layers. Utility of this surface modification strategy for creating high-density arrays of single mammalian cells on glass surfaces will be described. In addition, potential for integration of cells with microdevices will be demonstrated.

1:45 PM N5.2
Dynamic In Situ Spectroscopic Ellipsometry of Thin Polymer Films. Three Case Studies. Nebojsa Pantelic, William R. Heineman and Carl J. Seliskar; Chemistry Department, University of Cincinnati, Cincinnati, Ohio.

Dynamic *insitu* studies of three different chemically-selective films used in sensors are presented. A thin polymer film, usually of optical quality, represents a crucial element in a chemical sensor. Film properties like selectivity, ability to pre-concentrate an analyte, stability, and strong bonding to a solid support are important factors in making robust and useful sensors. We have used spectroscopic ellipsometry to measure film property changes in time upon exposure to a variety of aqueous environments. The three film materials studied were quartenized poly(4-vinylpyridine) (QPVP), poly(vinyl alcohol)-poly(acrylic acid) composite (PVA-PAA), and Nafion®.The first of these, QPVP, was well-behaved. Dynamic characterization revealed great stability. Dry film exposures to supporting electrolyte (aqueous KNO_3) showed a 90% thickness increase relative to the dry state. The sorption of aqueous model analyte $Fe(CN)_6^{4-}$ obeyed a Fickian kinetic. The second, PVA-PAA, consists of a composite of high molecular weight PAA dispersed in a cross-linked PVA host matrix. Exposure of the dry films to aqueous environments gave the expected large increase in film thickness and reduced refractive index. However, slow shrinking of the composite then followed rapid swelling as the film approached an equilibrium state. Coincident with the latter stage thickness decrease, the film refractive index increased. Subsequent exposure to aqueous model analyte ($Ru(bpy)_3^{2+}$) caused additional swelling. The films displayed crazing dynamics when exposed to water for a long period. In some cases, the polymer network fragmented after ~1 hour. An ESEM investigation of such films showed micro-cracks and overlapped segments. The quantity of cross-linking agent could be increased in these cases thus improving adhesion and stability of the polymer matrix. The third film material consists of Nafion. We have previously reported on a spectroelectrochemical sensor for aqueous iron. In this sensor the ligand 2,2′-bipyridine (bpy) was pre-loaded into a Nafion thin film. When the film was then exposed to aqueous ferrous ion *insitu* complexation of the ion with bpy was detected by the formation of the strongly absorbing complex, $Fe(bpy)_3^{2+}$. The stability of the ligand and ferrous iron species within the polymer film was probed in detail. The results revealed detailed information on the stability on both Nafion-bpy and Nafion-$Fe(bpy)_3^{2+}$ systems. Mass transport during film exposure to bpy solution revealed a non-Fickian diffusion mechanism with a curve shape resembling two-step response. Our work exemplifies the power of spectroscopic ellipsometry in monitoring the detailed kinetics of a chemical reaction, *insitu*, in a porous polymer film. In general, by performing dynamic studies we were better able to describe the conditions under which chemical sensing occurs as well as to characterize the mechanism of mass transport at the liquid/solid interface.

2:00 PM *N5.3
Hydrogel Micro and Nano-Environments as Functional Units in Microfluidic Devices. Jaisree Moorthy and David Beebe; Biomedical Engineering, University of Wisconsin, Madison, Wisconsin.

The 'omics' era promises a better understanding of cellular processes at the molecular level facilitating the development of more efficient drugs to cure diseases. A comprehensive characterization of the biomolecules, their mutual interactions and drug studies would require a platform that is capable of performing large number of studies simultaneously and with limited sample volumes. Microfluidic devices allow for accurate manipulation of nano-fluids through micron sized conduits and have demonstrated their potential in high throughput studies. These systems require various components for transporting fluids (e.g. pumps and valves) and carrying out specific tasks in a biological assay such as separation and reaction. Here we describe the use of hydrophilic polymers (hydrogel) as functional units at both the micro and nano scales. Hydrogel based microfluidic components are fabricated in situ via liquid phase photo-polymerization where pre-polymer mixture containing monomer, cross-linker and photo-initiator is shaped into a 3D polymeric construct by irradiating with UV light through a mask. The advantages of using hydrogel as opposed to 'hard' materials (e.g. silicon, glass) are that the polymer offers a large range of material properties which can be tuned to fit the application. The polymer can be made responsive to external stimuli such as pH, ions, temperature and electric field by incorporating polarizable chemical moieties (e.g. -COOH, -NH2) and choosing appropriate monomers. At the micron scale, the volumetric changes due to swelling of hydrogel were used to develop valves and fluid dispenser units. At the nanoscale, hydrogels can also be used as environments for storing proteins and as vehicles for drug delivery. The nano-environment parameters such as pore size and charge distribution can be controlled by the choice of the monomer. We propose to use hydrogel structures in microfluidc networks to study biomolecular interactions. Proteins can be transported into the hydrogel structure via diffusion and their interactions studied using fluorescence resonance energy transfer. It has been shown that the thermodynamics of biomolecular interaction is different in polymeric solutions as compared to the dilute solutions that are often used in biological assays. Polymeric networks are more realistic as they can mimic the structure of the cytoskeleton and the "crowdedness" of the cellular interior. We intend to explore this hypothesis by using the hydrogel structures as "cell mimics". The extent of crowding in cells is not uniform and also changes with time. This variation can potentially be mimicked by changing the cross-link density or decreasing the pore size. In order to maximally capture the complexity inherent in spatio-temporal dynamics of cellular processes, we will use arrays of hydrogel structures each of which would represent a specific snapshot of the cell in terms of density and distribution of the "crowding effect."

2:30 PM N5.4
Development of an Ultra-Lightweight and Uncooled Protein/Polymer Thermal Sensor Array. Lawrence L. Brott, Morley O. Stone and Rajesh R. Naik; Air Force Research Laboratory, WPAFB, Ohio.

The use of thermal sensors and imaging devices has become so widespread that numerous applications ranging from military sensors to firefighting equipment rely heavily upon this technology. There is a desire, however, to improve upon the sensitivity of uncooled sensors while reducing the complexity of their fabrication. Our research takes a biomimetic approach through the incorporation of a thermosensitive protein to enhance the properties of the infrared sensing device. The TlpA protein of *Salmonella* is a natural choice since it shows an incredibly fast response time, exhibits large conformational changes in response to slight variations in temperature, and most importantly, exhibits rapid, renaturation uncharacteristic of a protein response. By integrating this protein into a poly(vinyl alcohol) gel doped with plasticizer, a relatively simple and reliable thermally sensitive chip can be fabricated. Here, we describe the development of several arrays for various applications, from simple imaging arrays to tracking and guidance systems.

2:45 PM N5.5
Cytocompatibility of PEG Hydrogel Constructs for Photo-Initiated Layered Manufacturing. John Jongchun Bang[1,2], Karina Arcaute[1,2], Lindsay Adams[1,2], Luis Ochoa[1,2] and Ryan Blaine Wicker[1,2]; [1]Mechanical and Industrial Engineering, University of Texas at El Paso, El Paso, Texas; [2]W. M. Keck Border Biomedical Manufacturing and Engineering Lab, El Paso, Texas.

Polymeric hydrogels have received extensive examination for use in tissue engineering. However, cytocompatibility remains a critical issue in their application. As part of a continuing feasibility study for using stereolithography (SL) layered manufacturing to develop precise implantable PEG hydrogel constructs, cytocompatibility of NIH/3T3 cells with photopolymerized PEG hydrogels at different concentrations of two photoinitiators was investigated. SL has been used extensively in industrial applications and its benefits are beginning to be recognized by the tissue engineering community. In particular, by way of layered manufacturing and optically-based reaction kinetics, SL affords the opportunity for fabricating PEG hydrogel constructs with precisely located bioactive agents for use in guided angiogenesis, nerve regeneration, and other applications. NIH/3T3 cells were seeded on photocured PEG hydrogels in 24-well dishes with different concentrations of Irgacure 2959 and HMPP for two experimental conditions: one design tested the effect of different photoinitiator concentrations on cell survival and the other tested the osmolarity effects of PEG hydrogels on cell survival. The photocuring process was conducted in a cell culture lab with a portable UV source. The PEG monomer solution containing photoinitiators was filtered before UV exposure. For each design, seeded cells in the 24-well dishes were examined for their morphologic changes and growth patterns. Four relevant observations were made for future SL applications in PEG hydrogel production. First, the intrinsic cytocompatible characteristics of the photoinitiators could be manipulated by concentration adjustment. For example, low concentration of HMPP allowed compatible levels of cell survival without compromising optimal physical properties of the hydrogels. Second, the level of homogeneity of the hydrogels used for cell growth seems to influence cell growth pattern on the hydrogels. Third, osmolarity seems to influence cell growth behavior. A dramatic difference in cell growth pattern was observed between 24-hour DMEM pretreated hydrogels and non-treated ones. Fourth, the surface contact conditions between cells and supporting scaffolds (porous PEG hydrogels or Petri dishes) influence the cell survival. In both pretreated and non-treated hydrogel settings, there was a distinctive difference between the Petri dishes (without covering hydrogels) and dishes covered with hydrogels in terms of cell growth. The discrepancy observed in cell growth on

different surfaces narrowed in the experiment using DMEM pretreated PEG hydrogels. Further evaluations on the variables investigated in this preliminary study with various types of cells are warranted so that the information can be utilized in a variety of SL PEG hydrogel construct fabrication applications so that the gels can be precisely tailored for the application.

3:30 PM *N5.6
Using Enzymes and Biological Materials for Biofabrication. Gregory F. Payne and William E. Bentley; Center for Biosystems Research, University of Maryland Biotechnology Institute, College Park, Maryland.

Nature provides ample evidence for construction over a hierarchy of length scales. Most efforts to fabricate using natural materials or nature-inspired materials focus on their self-assembling capabilities (to organize into supramolecular structures). To complement self-assembly approaches, we are examining enzymes to selectively introduce covalent bonds into biopolymers to generate tailored macromolecular architectures. The first enzyme, tyrosinase, catalyzes the grafting of proteins (via their tyrosine residues) to the amino-polysaccharide, chitosan. Tyrosinase-catalyzed reactions between gelatin and chitosan yield a transient gel network with thermally-responsive properties (gelatin confers thermal-responsiveness). Tyrosinase-catalyzed reactions with the globular green fluorescent protein (GFP) yield a GFP-chitosan conjugate that can be spatially-localized in response to applied electrical signals (chitosan confers this responsiveness). The second enzyme, transglutaminase, catalyzes reactions between lysine and glutamine residues, and when this reaction is performed with gelatin, a covalently crosslinked hydrogel network is generated. This enzymatic crosslinking reaction occurs under mild conditions, and is being explored for in situ cell entrapment, and as a soft tissue adhesive. These results indicate that the potential of biological materials for fabrication extends beyond their self-assembling capabilities - biological materials often offer stimuli-responsive properties and they can be acted upon by highly selective biological catalysts.

4:00 PM N5.7
Hydrogel Multilayers for Sensing and Actuating Applications. Ryan Toomey[1] and Juergen Ruehe[2]; [1]Department of Marine Science, University of South Florida, St. Petersburg, Florida; [2]Institute of Microsystems Technology (IMTEK), University of Freiburg, Freiburg, Germany.

Surface-attached polymer networks offer a powerful route towards soft surfaces with well-defined mechanical, physical and biochemical properties. Polymer networks not only provide a 3-dimensional scaffold capable of hosting a wide-array of functionalities, ranging from proteins to inorganic nanoparticles, but they can also undergo substantial swelling and contraction in response to specific stimuli, making them excellent candidates for "smart" surfaces with sensing and actuating characteristics. We introduce a facile method for fabricating hydrogel multilayers from photo-cross-linkable copolymers that can be comprised of hydrophobic, hydrophilic, or charged functionality. The strategy involves integrating the photoreactive monomer methacroylbenzophenone (MaBP) along a polymer backbone, which is capable of forming covalent cross-links with aliphatic groups upon exposure to UV radiation at 365 nm. The approach is general in nature and facilitates the rapid fabrication of cross-linked multilayers through sequential deposition/irradiation steps with few restrictions as to the types of polymers that can be incorporated. In order to understand the swelling properties of such films, we have studied their swelling behavior with multiple-angle null ellipsometry in an ATR configuration, an analytical technique that yields information about the thickness and refractive index profile of the swollen layers. Ellipsometric measurements reveal that the volume fraction profiles of the swollen surface-attached networks can be controlled by the MaBP content; however, attachment of the network to a surface effectively constraints swelling to approximately the square-root of the value measured in the unconfined state. To demonstrate that these layers can be sequentially layered, bilayers of two different types of networks were fabricated and verified with ellipsometry. Upon swelling, a discontinuous change in the volume fraction of the film could be found where the two layers were joined.

4:15 PM N5.8
Inorganic-Organic Hybrid Surfaces by In-situ Self-Assembly for Controlled Drug Delivery - Detecting Pores by Positron Annihilation Lifetime Spectroscopy. Hubert Koller[1], Ansgar Boegershausen[1] and Anita Hill[2]; [1]Institute of Physical Chemistry, University of Muenster, Muenster, Germany; [2]CSIRO Manufacturing & Infrastructure Technology, Clayton South MDC, Victoria, Australia.

The oral application of drugs often requires encapsulation of the active component into a matrix that releases it with a controlled kinetic protocol. The first goal of this study was to explore the drug release kinetics for inorganic-organic hybrid gel matrices which are self-assembled in the presence of the incorporated drug molecule. The second topic was the characterization of pore space which is responsible for storage and delivery capacity. Dipyridamol (Persantin) is a drug that is used for expanding the coronar vessel system. It was incorporated in situ into silica hybrid gels which are synthesized from tetraethylorthosilicate (TEOS), and a second molecular precursor, R-Si(OEt)3. By variation of the organic component in the drug carrier system, the interaction between host and guest was tailored to optimize the release behavior. At least three parameters determine the release kinetics: the hydrophobicity of the organic group, R, the synthesis pH value, and the presence of organic functional groups which introduce hydrogen-bond capabilities or aromatic moieties into the host matrix. The introduction of organic side groups in the matrix (phenyl, benzyl groups) leads to a very stable interaction between these groups and Persantin which has an aromatic core and aminoalkyl side groups. A higher release was observed for alkyl groups (methyl, propyl) in the sol-gel matrix. Aromatic as well as alkyl groups increase the retarding properties of such drug carrier systems. On the other hand, acetoxypropyl side chains lead to a faster release, when these functional groups are increased in concentration. The single-precursor gel (TEOS), and most hybrid gels show an increasing microporous specific surface area after the dissolution experiment. Surprisingly, the materials with acetoxypropyl side chains show no increase in specific surface area after drug release, even though these gels have released the highest amount of Persantin. Therefore, we used positron annihilation lifetime spectroscopy (PALS) as an alternative means to study the porosity of the gels. Positrons can penetrate matter and localize in pores without the need for pore accessibility from the external surface. Positrons have a reduced lifetime due to pick-off annihilation with electrons from the surrounding environment. The lifetime depends on the size of the pores. Therefore, PALS is well suited to detect porosity developing upon drug release, independent of whether or not the pores are directly connected to the external surface. With this tool, it was possible to clearly detect the evolution of pores depending on release time. It is concluded that acetoxypropyl groups block the pores for nitrogen adsorption. PALS is a very useful method to characterize the porosity of such biologically relevant internal surface structures.

4:30 PM N5.9
Anisotropic Porosity of Hybrid Organic/Inorganic Polyisocyanate Sol-Gel Films. Jonathan M. Stoddard and Douglas A. Loy; MST-7, Los Alamos National Laboratory, Los Alamos, New Mexico.

The ability to form polymeric liquid crystalline assemblies coupled with a relatively low depolymerization temperature (<150 oC) make polyisocyanates excellent candidates for preparing thin films with functionalized, anisotropic porosity. In this study, we have prepared poly(3-triethoxysilylpropyl isocyanate) by a cyanide initiated anionic polymerization to provide a rigid-rod polymer that can be sol-gel polymerized into highly crosslinked matrices. A variety of formulations were attempted in the preparation of liquid crystalline films with reagents (acid, base, and/or tetraethylorthosilicate and bis(triethoxysilyl)methane) introduced to induce crosslinking of the pendent triethoxysilyl groups. The crosslinked films were liquid crystalline, but cracked upon drying with and without the addition of drying control additives such as DMF. Biphasic formulations made crack-free, monolithic films from suspending a dilute organic solution of polyisocyanate in toluene or xylene on top of an aqueous solution of acetic acid, water, and additives (ethylene glycol, triethylene glycol, or glycerol). The IR, porosity, solid state NMR, birefringence, SEM, and TGA were used to assess the morphology, surface area, and chemical functionality of the sol-gel films.

4:45 PM N5.10
Use of Stimuli-Responsive Organosilica Hydrogels in Controlled Intake/Release of Molecules. Dave C. Bakul and Mukti S. Rao; Chemistry and Biochemistry, Southern Illinois University, Carbondale, Carbondale, Illinois.

This presentation will focus on the use of organosilica sol-gels as environmentally responsive hydrogels. The organosilica sol-gels exhibit bulk volume changes with respect to different stimuli such as pH, temperature, light, salt, and solvents. These volume changes result in altered porosity of the gel matrix, which can be utilized as a means for externally regulated separation, release, and delivery of dopant molecular entities. The results on use of organosilica sol-gels as hydrogels responsive to external stimuli will be presented. The externally controlled release/intake of specific molecules by these materials will be evaluated in terms of their potential utility as matrices for stimuli-controlled delivery/release.

SESSION N6: Mechanics and Adhesion of Polymer Gels
Thursday Morning, March 31, 2005
Room 3007 (Moscone West)

8:30 AM N6.1
Nonlinear Elastic Properties of Entangled and Non-Entangled Polymer Physical Gels. Costantino Creton[2], Alexandra Roos[2], Fanny Deplace[2], Patrice Roose[3] and Francois Simal[3]; [1]ESPCI, Paris, France; [2]Laboratoire PPMD, ESPCI, Paris, France; [3]R&D Acrylics, Surface Specialties, Bruxelles, Belgium.

In a general sense, all gels can be viewed as comprised of a network, which gives the solid character, and a liquid phase which dilutes the network and controls also the dissipative properties. In between rubbers, where the network is essentially undiluted and classical polymer gels where the polymer fraction typically varies between a few percent and 20%, exists an intermediate category of materials where the polymer fraction is of the order of 50%, which are widely used as soft adhesives. Although the adhesive properties of these materials have been extensively investigated, the material characterization has been mostly limited to the linear viscoelastic properties. Yet, their non-linear elastic and viscoelastic properties play an important role in their final application properties. An important aspect of these concentrated gels is the role played by entanglements both in the nonlinear elastic properties and in the viscous dissipative properties. We will present some new results and interpretation on both entangled systems based on styre-isoprene copolymers, and on unentangled systems based on methymethacrylate-2ethyl-hexyl acrylate copolymers.

8:45 AM N6.2
Abstract Withdrawn

9:00 AM *N6.3
Tough Hydrogels with Double Network Structure. Jian Ping Gong[1], Y. Kurokawa[1], R. Kuwabara[1], Y. H. Na[1], Y. Tanaka[2] and Y. Osada[1]; [1]Graduate School of Science, Hokkaido University, Sapporo, Japan; [2]Creative Research Initiative "Sousei", Hokkaido University, Sapporo, Japan.

Hydrogels are composed of three-dimensional hydrophilic polymer network in which a large amount of water is interposed. Due to their unique properties, a wide range of medical, pharmaceutical, and prosthetic applications have been proposed. However, most of them are suffered from the lack in mechanical toughness, and only very limited applications have been realized. Recently, we have overcome the problem by discovering a general method to obtain high strength gels. The high strength gels are synthesized by a sequential two-step polymerization, forming a double network (DN) structure for various combinations of hydrophilic polymers[1]. The DN gels, containing about 90 wt% water, possess both hardness (elastic modulus of 0.3 MPa) and toughness (fracture stress of 10-20 MPa). It has been found that the combination of first and second networks, the cross-linking density of the two networks, and the molar ratio of the two polymers are crucial in improving the resistance against stress. The optimized conditions are 1) Rigid polyelectrolyte as the first network and flexible neutral polymer as the second one; 2) the first network is highly cross-linked, and the second is slightly cross-linked or even without cross-linking; 3) the molar ratio of the second network to the first one is in a range of several to a few decades. The dynamic light scattering (DLS) analysis of the DN gels shows a slow mode besides the gel mode (fast mode) for the DN gels with a loosely cross-linked 2nd network, which correlates with the increase in the strength of DN gels. The dynamics of slow mode cannot be explained in terms of reptational motion of the second component in the first network but it is similar to the translational motion of the 2nd polymers in a semi-dilute solution. As the highly cross-linked first network has a high Young's modulus but is quite brittle on its own, we consider that large voids of first network may exist and the loosely cross-linked second network, exist in voids act as molecular crack-stopper by dissipating the fracture energy, preventing the crack from growing to a macroscopic level. [2] References [1] Gong, J. P.; Katsuyama, Y.; Kurokawa, T.; Osada, Y. Adv. Mater., 2003, 15, 1155. [2] Na, Y-H.; Kurokawa.T; Katsuyama, Y.; Tsukeshiba, H; Gong, J. P.; Osada, Y; Okabe, S.; Karino, T.; Shibayama, M. Macromolecules 2004, 37(14), 5370.

9:30 AM N6.4
Physical Properties of Interpenetrating Polymer Networks Determined by QCM-D. Elizabeth F. Irwin[1] and Kevin E. Healy[1,2]; [1]Bioengineering, UC Berkeley, Berkeley, California; [2]Materials Science and Engineering, UC Berkeley, Berkeley, California.

Polymer-based hydrogels have been exploited as coatings for devices and materials used in the medical and biotechnology fields. In this work, the physical properties of an interfacial interpenetrating polymer network (IPN) based on acrylamide and poly(ethylene glycol) [p(AAm-co-EG)] were investigated. The p(AAm-co-EG) IPN is a non-fouling coating that has minimized protein adsorption ($\leq$ 5 ng/cm^2) and eliminated cell attachment.[1] One possible application for the p(AAm-co-EG) IPN is a coating that is both non-fouling in biological environments and can deliver low molecular weight pharmacologic agents. In this context, it is necessary to have information about the IPN's thickness (δ_f), the molecular weight between crosslinks (M_C), and the mesh size of the network (ξ), which all play a role in drug diffusion, uptake, and release. To determine the physical properties of the p(AAm-co-EG) IPN, a quartz crystal microbalance with dissipation monitoring (QCM-D) was employed in network swelling experiments. In a QCM-D, an AC voltage is pulsed across a piezoelectric quartz crystal, causing it to oscillate in shear mode at its resonant frequency. The Sauerbrey relationship states that a change in mass of a film is directly proportional to a change in the resonant frequency of the crystal. The dampening of the shear wave is recorded simultaneously with the resonant frequency of the crystal as the dissipation factor (D), which provides information about the viscoelastic properties of the film.[2] Both Si/SiO_2 and Ti/TiO_2 surfaces were modified with p(AAm-co-EG) IPNs that were swollen in ambient humidity and in phosphate-buffered saline (PBS), pH 7.4. The IPNs swell from thin, rigid films when dry to expanded, viscoelastic films when hydrated. The Sauerbrey relationship was employed to obtain thickness of dry IPNs, and the data was validated by previously recorded spectroscopic ellipsometry measurements. Swollen IPN surfaces, however, could not be described by the Sauerbrey relationship, and were instead interpreted with a Kelvin-Voigt viscoelastic model. Modeling of the QCM-D swelling data yielded quantitative information such as the G* of the swollen IPN. Thickness and modulus data were used to calculate the important physical parameters of the IPN including the effective crosslink density (υ_e), polymer volume fraction (υ_{2s}), M_C, and ξ of the gel. The QCM-D is a powerful technique that can be used to determine the physical properties of thin viscoelastic polymer films at interfaces. 1. Bearinger, J. P.; Castner, D. G.; Golledge, S. L.; Rezania, A.; Hubchak, S.; Healy, K. E., P(AAm-co-EG) interpenetrating polymer networks grafted to oxide surfaces: Surface characterization, protein adsorption, and cell detachment studies. Langmuir 1997, 13, (19). 2. Rodahl, M.; Kasemo, B., A simple setup to simultaneously measure the resonant frequency and the absolute dissipation factor of a quartz crystal microbalance. Review of Scientific Instruments 1996, 67, (9).

9:45 AM N6.5
Use of the Quartz Crystal Microbalance in Contact Mechanics Studies of Polymer Gels. Kenneth R. Shull and F. Nelson Nunalee; Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois.

A contact mechanics methodology utilizing the quartz crystal microbalance (QCM) has been applied to study the spreading behavior of polymer solutions and gels. Changes in the series resonant frequency and in the dissipation are monitored as these materials are brought into contact with the electrode surface of the QCM. The primary application is in studies of elastic polymer gels, where spreading over the surface of the QCM is limited by the elasticity of the gel. Simultaneous measurement of the applied loads and displacements, along with measurement of the QCM/gel contact area, the frequency shift, and the dissipation, enable us to calibrate the QCM as a contact sensor. While the frequency shift and dissipation both depend linearly on the contact area, measurements of the dissipation provide a more reliable indicator. The relationship between the dissipation and the contact area is determined by the solvent viscosity, and by the high frequency intrinsic viscosity of the system of interest. This result is consistent with previous results on the high frequency rheological behavior of polymer solutions.

10:30 AM *N6.6
An Indentation Method for Characterizing the Elastic Properties and Permeability of Gels. Chung Yuen Hui[1], Yu Yun Lin[3], Fu-Chin Chuang[3], Wei-chun Lin[2] and Kenneth R. Shull[2]; [1]Theoretical and Applied Mechanics, Cornell University, Ithaca, New York; [2]Material Science and Engineering, Northwestern University, Evanston, Illinois; [3]Civil Engineering, National Cheng Kung University, Tainan, Taiwan.

When a saturated gel immersed in the same liquid is suddenly brought into contact with a smooth rigid indenter, the liquid cannot immediately flow out of the pores, so that the gel initially behaves as an incompressible material. This give rise to a pressure gradient in the liquid phase and the liquid flows until the pressure in it goes to zero everywhere, and all the stresses are transferred to the elastic network. As a result of the flow, the force needed to maintain a constant contact area relaxes with time. In this work, we study the feasibility of using an indentation test to measure of this time dependent force and to determine the elastic modulus, the Poisson ratio and the cooperative diffusion coefficent, D, of the network. Specifically, we

consider a two dimensional Hertz contact problem of a rigid circular cylinder indenting on a half space consisting of an elastic gel. The network of the gel is assumed to be linearly elastic and isotropic and liquid flow within the gel is assumed to obey Darcy law, which states that the flux is proportional to the pore pressure gradient. Exact expressions are obtained for the initial and final force required to maintain a given contact length. These expressions allow us to determine the elastic constants of the network. The permeability of the network can be obtained from the time dependent relaxation of the applied load. The relation between the applied load and the pore pressure is obtained in closed form. A finite element method is used to obtain the pore pressure. Our finite element results show that for short times, load relaxation is a linear function of the square root of Dt divided by a, where t is time and a is the contact width made by the circular indenter.

11:00 AM N6.7

Transport Properties of Polymer Gels. Wei-Chun Lin[1], Kenneth R. Shull[1], Chung-Yuen Hui[2], Yu Yun Lin[3] and Fu-Chin Chuang[3]; [1]Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois; [2]Department of Theoretical and Applied Mechanics, Cornell University, Ithaca, New York; [3]Department of Civil Engineering, National Cheng Kung University, Tainan, Taiwan.

When a saturated polymer gel comes in contact with an indenter during an adhesion test, a common assumption made is that the solvent flow out of the polymer network is negligible. However, this assumption is not always valid: Under such deformation, solvent flow in a gel occurs as a result of the pressure gradient that forms when the indenter comes in contact with the gel. The local pressure of the gel is not equal to the osmotic pressure of its environment, and as a result the polymer gel is strained as solvent is squeezed out. An analysis of the kinetics of such a system leads to a novel method, which determines the permeability and elastic constants of a gel. To determine these transport and mechanical properties of a gel experimentally, a flat punch indentation method is used to study the behavior of poly(n-isopropylacrylamide) (PNIPAM) hydrogels in phosphate buffer saline solution at temperatures below and above the lower critical solution temperature (LCST) of 32°C. Stress-relaxation and oscillatory experiments are used to probe the response of the gel over different time scales.

11:15 AM N6.8

Structure and Mechanical Properties of Gelatin - Clay and Gelatin - Oxide Nanocomposite Gels in Bulk and Thin Film Form. Margarita Darder[1], Anabel Ruiz-Hitzky[1], Patrick Amarellis[2], Eduardo Ruiz-Hitzky[1], Andre Dubault[2] and Henri Van Damme[2]; [1]ICMM, CSIC, Madrid, Spain; [2]PCPMD, ESPCI, Paris.

Gelatin - a denaturated form of collagen - forms non toxic biocompatible thermoreversible gels in water. Unfortunately for structural applications, the gel temperature is relatively close to room temperature and the mechanical properties are rather poor. The purpose of our study was to explore the possibility of increasing both the gel formation temperature and the gel mechnanical properties by building and entangled bicontinuous organic-inorganic network. Nanocomposite gels were prepared by mixing clays or oxide nanoparticles with gelatin. Nanoparticles with either lamellar (montmorillonite or laponite clays; perovskite oxydes) or fibrous (sepiolite clay; vanadium oxyde) morphology were used. The dispersion state of the mineral component in the aqueous organic phase was monitored by X-ray diffraction and transmission electron microscopy. The mechanical properties of the gel were investigated by conventional dynamical rheological measurements in stress-imposed shear strain conditions. The results show that large (lateral size) lamellar particles of nanometrer thickness are extremely effective for increasing the gel formation temperature and the mechanical properties of the gel. Thin (a few tens of micrometers) self-supporting and well transparent films are easily obtained by water evaporation. Surprisingly, fibrous particles are much less effective, even at concentration above the expected percoilation threshold. The mechanical properties of the organic-inorganic films will be compared with those of pure clay films. The organic-inorganic mixed nanocomposite gels are attractive materials for conservation of antique wall paintings.

11:30 AM N6.9

Adhesion between Polymeric Fluids using a Probe Method. Regis Schach and Costantino Creton; Laboratoire PPMD UMR 7615, CNRS/ESPCI, Paris, France.

Relatively few studies have been carried out on the adhesion between polymeric fluids, and the problem remains poorly understood. However, this problem is critical for industrial applications. For example, in the tire industry the cohesion of the different layers of a tire before the final crosslinking process is directly related to the polymer-polymer adhesion of uncrosslinked elastomers, which are polymeric fluids. A key experimental obstacle for the understanding of this problem is the separation of the surface and the bulk contributions to adhesion for such liquid materials. The probe tack experiment, used in the Pressure-Sensitive-Adhesive (PSA) industry, is a powerful analytical tool capable of evaluating adhesion and cohesion of adhesives against rigid surfaces [1]. In this test, a flat steel probe approaches the adhesive layer (which has been deposited on a glass slide) at a constant velocity, applies a controlled compressive force during a set contact time and is removed at a constant debonding velocity while a CCD camera allows the observation of the debonding mechanism. This technique cannot be directly applied to the study of self adhesion of elastomers because the adhesion between the two polymers is greater than between the polymer and the substrate causing the debonding to occur between the substrate and the elastomer. To avoid this problem, we use chemical grafting of mercaptosilanes to chemically bond the polymer to the substrates : a silicon wafer grafted with a 1 μm polymer layer is glued on the probe and the second polymer layer (100 μm) is grafted to the glass slide. This modification of the probe tack experiment allows us to study the autohesive tack of elastomers. We present here results on the self adhesion of SBR Rubbers. We used three SBR rubbers with the same microstructure (20% styrene, 42% vinyl, 19% cis and 19% trans) but with different molecular weights (80 000, 160 000 and 240 000 g/mol). We observed different debonding mechanisms depending on the time of contact, the debonding velocity and the polymer used. For short times of contact, fast debonding rates and hard polymers we observed an interfacial crack propagation, though for longer contact times, cavitation occurs in the polymer. For very slow debonding rates and with soft polymers, we observed a liquid-like mechanism of deformation. We found that these different behaviours are directly related to the bulk rheology of the polymer, especially its reptation time, which sets the limit between elastomeric and liquid-like behaviour as well as the interdiffusion time at the interface. Finally, we propose a map of the mechanism independent of the molecular mass of the polymers, using two reduced parameters, the ratio of contact time to reptation time and the Deborah number. [1] Creton, C. MRS Bulletin 2003, 28, 434-439

11:45 AM N6.10

Electric Field Effect on Adhesion of Poly(*N*-isopropylacrylamide) Gel. Victor Barinov, Robert Dabrowski and Kalle Levon; Chemical and Biological Sciences and Engineering, Polytechnic University, Brooklyn, New York.

Development of disbonding adhesive gels and physical-separation methods could have a major impact on technologies requiring reversible adhesion properties. The effect of applied electric field on the adhesion of poly(N-isopropylacrylamide) (PNIPA) hydrogel to aluminum was studied. PNIPA hydrogel was prepared by UV-induced polymerization. A pull-off adhesion test was employed to characterize the adhesion of a hydrogel sample to an aluminum dolly. Hydrogel was placed between two flat faces of aluminum dollies. By activating the load source, tensile load was increased within the system. When the load on either of two hydrogel-dolly interfaces becomes larger than the adhesion strength between the hydrogel sample and the dolly, separation occurs. The measured pull-off force was used to calculate the adhesion strength. The above-mentioned aluminum dollies were utilized as electrodes to apply a direct electric field on PNIPA hydrogel. Each of the dollies was attached to one of the power-supply terminals. The power supply produced a specified potential difference between two dollies. Pull-off adhesion tests were carried out while the electric field was applied to the system. The electric field was found to be a factor reducing the adhesion strength of PNIPA hydrogel to the aluminum surface. Separating-force decrease was found to be proportional to potential-difference increase. Failure in an adhesion layer occurs on the surface of the cathode dolly. Based on data obtained, the electric field can be used to regulate the adhesion strength of PNIPA hydrogel. This ability to control the adhesion strength could lead to a new type of advanced adhesive.