SYMPOSIUM EE
Organic/Inorganic Hybrid Materials

November 29 - December 3, 2004

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SESSION EE1: Films, Layers and Surfaces
Chair: Ulrich Schubert
Monday Morning, November 29, 2004
Room 302 (Hynes)

8:10 AM OPENING REMARKS 8:15 AM *EE1.1
Controlled Surface Nucleation of Latex Nuclei as Disymmetric organo-modified Nanoparticles.
Etienne Duguet¹, Stephane Reculusa², Franck Perez³, Adeline Perro⁴, Serge Ravains², Marie-Helene Delville², Elodie Bourgeat-Lami³, Christophe Mingotaud² and Anne-Francoise Mingotaud²; ¹ICMCB, CNRS & University of Science and Technology of Bordeaux, Pessac, France; ²CRPP, CNRS & University of Science and Technology of Bordeaux, Pessac, France; ³LCP, CNRS & CPE, Villeurbanne, France; ⁴LMHCP, CNRS & University Paul Sabatier, Toulouse, France.

The “Janus particles” term refers in Roman religion to Janus God who was usually represented with two heads placed back to back. Indeed, such objects may present original properties such as (i) an amphiphilic character if an hydrophilic face may be combined with an hydrophobic one, (ii) a giant dipole moment if the surface charges may segregate onto separate poles or (iii) a discriminatory reactivity behavior if two types of chemical functions may be concentrated onto separate homophases. In a pioneering work, glass microspheres were deposited on a solid support covered with a cellulose varnish film of controllable thickness protecting one part of the spheres whereas the other one was treated with octadecyltrichlorosilane, which is commonly used to make a surface hydrophobic. After removal of the varnish that let the protected surface hydrophilic, amphiphilic particles were obtained. In the most general case, Janus particles are prepared from symmetrical ones. Several dissymmetrization procedures, i.e. chemical or physical-chemical symmetry altering the composition and thickness of the precursor particles, have been investigated: partial contact with reactive media through Langmuir or Langmuir-Blodgett-derived techniques or toposelective surface chemical modification in directional fluxes and fields. Nevertheless, the low amount of produced Janus particles remains a limitation. That is why we are investigating and developing a new dissymmetrization technique derived from our experience of the controlled surface nucleation of polystyrene latex particles onto silica beads. This novel concept is based on the nucleation of one latex particle per inorganic seed particle in order to obtain dumbbell-like hybrid particles. This route is successful if the nucleation step is favored at particle surface thanks to an adequate preliminary surface modification by PEO-based macromonomers for instance. Such hybrid particles are amphiphilic Janus particles, but more interestingly the polymer part may also act as a partial mask of the inorganic surface. Indeed, the non-protected hemisphere may be surface modified by a first reagent, then the mask is removed under the high shear of ultracentrifugation or ultrasonication and lastly the depleted surface may be modified by a second type of reagents. This new method is an extension of the pioneering varnish technique without restricting in any way the size of the precursor particles (typically from 50 to 150 nm in diameter). The aim of this communication is to present this route in the context of those previously reported, to be more specific about the experimental conditions and to discuss the results and the expected applications of such new colloidal systems.

8:45 AM EE1.3
Novel Organosilanes for the Preparation of High Refractive Index Silicone Coatings. Pierre Maurice Chevalier¹ and Duan Li Ou²; ¹SISC, S&T, Dow Corning S.A., Seneffe, Belgium; ²S&T, Dow Corning Ltd, Barry, United Kingdom.

In its continuing efforts to develop an in-depth understanding of the process-structure-property relationships, Dow Corning is investing, through the Surface and Interface Solutions Center (SISC), in innovative technologies that can be used in combination with improved properties towards current and future applications. As such, we wish to present herein the design and synthesis of novel organosilanes for the preparation of coatings having good dimensional stability and exhibiting high refractive indices (RI) without compromising the almost perfect optical properties required for optical lenses, optical amplifying fibers, or for hair care application. Two major approaches have been reported previously to enhance refractive index of inorganic resins and glasses. The first approach involves blending of silica and organopolysiloxane with well-known RI enhancers, e.g. titania and zirconia or by reacting silica precursors with titanium alkoxides. However, the RI of the final inorganic matrix is often much lower than the theoretical expected value because of in-homogenity in the dispersion of the oxides particles (scattering effect). In addition, brittle glass or inorganic material does not always fulfill the processability and mechanical requirements of specific applications. The second approach is focusing on the preparation of phenyl versus alkyl-containing silanes. Phenyldimethylsilanes, allowing for preparation of RI from 1.48 to 1.56, are promising materials for optical lenses and cosmetics have been described, confirming the importance of the organic group contribution onto the refractive indices. However, a need still remains for high refractive index, stable, curable and easily processable organic-inorganic hybrid coatings versus glasses or mixed metal oxides, having chemical resistance and well-balanced mechanical and thermal properties versus organic resins. Our current study is focusing on new synthetic routes to high refractive index curable polymers and hybrid, inorganic functional silicone resins with RI above 1.50 at 633 nm and ultimately with predictable and desired optical properties. Novel organosilanes containing arachnoneyl-, araphthyl- and iodoenyl-organic groups are synthesized and used as precursors for the preparation of stable and soluble aryl-functional silicone resins. Alternatively the direct iodination is also demonstrated onto preformed aromatic-functional resins. The curable resins are spin-coated onto silica wafers bare above 295°C and the RI of the refractive indices are measured by spectroscopic ellipsometry at 633 nm. To date we have demonstrated the preparation of silicone-based coatings with refractive index as high as 1.770. This is representing an RI enhancement of up to 0.21 as compared to traditional silicone and organic coatings, opening a new range of applications based upon improved thermo-mechanical and optical properties.

9:00 AM EE1.4
Polymerization on Surfaces of Nanoporous Silicas and Conversion of the Polymers to Nanoporous Carbons.
Michel Kent³, Bruno Dufour⁴, Eva B. Celer³, Tomasz Kowalowski⁴, Michael Paradies², Kristiania Stang⁵, Vincenzo Santoro⁴, Michael Tucek³, and Pierre A. Fouassier³; ¹Kent State University, Kent, Ohio; ²University of Bordeaux, Pessac, France; ³CRPP, CNRS & University of Science and Technology of Bordeaux, Pessac, France; ⁴S&T, Dow Corning S.A., Seneffe, Belgium; ⁵S&T, Dow Corning Ltd, Barry, United Kingdom.

The grafting of polymers on surfaces of nanoporous materials is very interesting from the point of view of basic research, and potentially highly important as a method to obtain nanomaterials with designed composition and surface properties, including those suitable for applications. Various methods are available to introduce polymer layers on surfaces of nanoparticles, and the interest in such materials has been largely unexplored. To explore these opportunities, we studied the grafting of polyvinylpyrrolidone (PAN) from surfaces of nanoporous silicas of different pore diameters. The obtained silica-PAN nanocomposites were converted to silica-carbon composites, and the carbons were isolated via dissolution of the silica matrix. The porous silicas used as the substrates for the polymerization, the silica-polymer nanocomposites, the silica-carbon nanocomposites and the carbons were extensively characterized using a variety of techniques, including nuclear adsorption, thermogravimetry, transmission electron microscopy and powder X-ray diffraction. Moreover, the polymer formation on the silica surface was confirmed by size-exclusion chromatography. The amount of PAN formed in the nanocomposites was found to depend on the polymerization time and the reaction mixture composition. The silica-PAN nanocomposites exhibited accessible porosity, the silica nanoparticles diameter was sufficiently large and the amount of PAN introduced was significantly smaller than the amount necessary to fill the entire nanopore space. In these cases, there was evidence of the formation of faceted thin polymer layer on the silica nanoparticles, conversion of PAN to carbon via its stabilization by heating to 700°C under air and 800°C under nitrogen was successfully achieved, and the dissolution of the silica substrate allowed us to obtain mesoporous carbons with high specific surface areas (300-1000 m² g⁻¹) and large pore volumes (0.8-2.4 cm³ g⁻¹). The carbons exhibited high adsorption capacity and yet very low microporosity, which makes these materials different from most mesoporous carbons reported to date, which exhibited significant microporosity or had quite low adsorption capacity. We have demonstrated the applicability of ATRP for the introduction of polymer films on nanoporous surfaces, and showed some remarkable opportunities in the conversion of surface-grafted polymer to nanoporous carbon.

9:15 AM EE1.5
One-Dimensional Assembly and Selective Orientation of Lander Molecules on an O-Cu Template. Roberto Otero Martín¹, Yoshitaka Naitoh¹, Federico Rossi¹, Ping Jing², Peter Thostrup³, Andre Gourdon², Erik Laegsgaard¹, Ivan Stensgaard³, Christian Joos² and Flemming Besenbacher¹; ¹Department of Physics and Astronomy, University of Aarhus, Aarhus, Denmark; ²CEMES, CNRS, Toulouse, France.

Properly functionalized organic molecules are promising building blocks for nanoscale electronic circuits [1]. A major challenge is to develop a novel technology to assemble such molecular elements in a
Andre functionalization using novel silylation reagents and by grafting of structural properties of SBA-1, SBA-6 and SBA-16, surfactant and silica precursor. Detailed information about the surface [11]. Herein we report the synthesis and characterization of size, which can be tailored by carefully varying the synthesis of 3-10 nm, will produce superior materials for catalytic applications.

The family of cage-like mesoporous silicas comprise hexagonal SBA-2 (P63/mmc), and SBA-12 (P6/mmm) as well as cubic KIT-6 (Fm3m) [3], FDU-1 (Fm3m) [4], SBA-16 (Ia3d) [2], and SBA-1 (Pm3m) [1]. In addition, cage-like periodic mesoporous organosilicas, PMOs, such as hexagonal HMM-2 (P6/mmm) [5], cubic HMM-3 (Pm3n) [6], and cubic MOMO with HMM group [7] have been reported recently. It is assumed that their overall zeolite-like architecture, featuring an array of cages with diameters in the range of 3-10 nm, will produce superior materials for catalytic applications as well as for sorption/separation and sensing processes. The cages are three-dimensionally interconnected by smaller windows of uniform size, which can be tailored by carefully varying the synthesis conditions like temperature, pH-value, and the molar ratio of surfactant and silica precursor. Detailed information about the pore/cage architecture was obtained by (i) electron crystallography [1b], successfully applied by Ryo et al. for the determination of the structural properties of SBA-1, SBA-6 and SBA-16, (ii) nonlocal density functional theory [8], (iii) chloroform-based surface studies [9], (iv) templating mechanism [10], and (v) investigation of the adsorption of bulky organic molecules on the silica surface [11]. Herein we report the synthesis and characterization of highly ordered two- and three-dimensional mesoporous silicas including a topologically new organosilica. Advanced organic-inorganic hybrid materials were obtained via surface functionalization using novel silylation reagents and by grafting of tailor-made organosilanes with various functionalities to modulate their chemical and physical properties.

The first Mesoporous Templated Structure (MTS) preparation of powders with periodically organized mesoporous domains within alumina aerogels was described in literature in 1992 ever since. The increasing amount of time was dedicated to the research of new amphiphiles templates, inorganic compositions and their applications (heterogeneous catalysis, depollution, separation, etc.). The preparation of MTS shaped as thin films was first reported in 1996. Their preparation by Evaporation Induced Self Assembly (EISA) is only possible via a precise and simultaneous control of the sol-gel processing and the evaporation process. These are promising materials for nanotechnology science attending that one can easily control their structure (separately tuned pore size, pore composition and inorganic wall composition) to modulate their chemical and physical properties. The present work is dedicated to the investigation of the self-assembly pathway and creating a unique bio/nano interface. As a new direction in self-assembly, we have exploited mechanically-based reassembly to create superhydrophobic, fractal silica surfaces mimicking those of the Lotus leaf and desert beetle. These surfaces are self-cleaning and fundamentally affect flow, making them of general interest for containerless fluidic Microsystems.
Hydrolysis and condensation reactions of alkoxysilanes such as tetramethoxy- or tetraethoxysilanes are the key reactions in the synthesis of porous silica-based materials. However, the sol-gel process with these precursors is limited in its potential, especially when it comes to the synthesized monolithic materials due to the obligatory presence of the solvent as compatibilizing agent (typically an alcohol) and the catalyst to start the network forming reactions (acid or base). Diol- or polyol-modified silanes, such as tetraethoxysilane (TEOS) or glycidoxypropyltrimethoxysilane (GPTMS) or the glycerol and propylene glycol derivatives as precursors, have some distinct advantages since they can be condensed without a co-solvent, under neutral conditions (no catalyst is required to start the sol-gel reactions), and the diol/oligonol released upon hydrolysis show a very good compatibility with lyotropic phases of surfactant molecules. In this work, we present the preparation of large mesostructured silica monoliths from diol/polyol modified silanes, which exhibit a highly regular and ordered arrangement of the mesoscale order within different inorganic replicas of the initial block copolymer structures. While we have focused on silica and titania as the inorganic components, we expect this approach can be generalized to a variety of inorganic species.

11:45 AM EE2.4
Hugh W. Hillhouse and Vikrant Urade, Chemical Engineering, Purdue University, West Lafayette, Indiana.

The synthesis of ordered mesoporous silica [1] via the cooperative self-assembly of surfactants and silica oligomers defined a new synthesis route that has been extended to other sol-gel systems to yield novel nanostructured materials. As a result, high surface area mesoporous frameworks have been synthesized from many metal oxides. Further, the development of evaporation induced (or evaporation controlled) self-assembly techniques [2] to yield continuous thin films of these materials has opened up the possibility of new applications in sensors, nanowire synthesis, low-dielectric, electrode materials, and photovoltaics that may exploit the high surface area, ordered pore structure, present in these films. A host of synthesis routes that have been extended to other sol-gel systems to accommodate a wide range of metal oxides. Despite the evolution of our understanding of these systems, well-ordered, thermally stable surfactant-templated mesoporous SnO2 films has remained elusive. Previously, researchers have reported disordered mesoporous SnO2 [3] as well as well-ordered, non-porous oxides. Further, the development of evaporation induced (or evaporation controlled) self-assembly techniques [2] to yield continuous thin films of these materials has opened up the possibility of new applications in sensors, nanowire synthesis, low-dielectric, electrode materials, and photovoltaics that may exploit the high surface area, ordered pore structure, present in these films. A host of synthesis routes that have been extended to other sol-gel systems to accommodate a wide range of metal oxides.

2:00 PM *EE3.2
Monolithic O/I-Hybrids with Hierarchically Ordered Mesos- and Macropores. Kazuki Nishikawa1, 2, Yukitaka Kobayashi1, Tomohiko Amamoto1, Kazuyuki Hiroi2 and Tetsuya Kodani3, 4, 5. Material Chemistry, Kyoritsu University, Graduate School of Engineering, Tokyo, Kyoy, Japan; 1Nanoarchitectonics Research Center, National Institute of Science and Technology, Tsukuba, Ibaraki, Japan; 2PRESTO, Japan Science and Technology Agency, Kawaguchi, Saitama, Japan.

Monolithic silica and siloxane-based gels with well-defined continuous macropores and highly ordered mesopores have been synthesized from silanol-terminated oligomer-diol precursors, and the mesoporous frameworks have been synthesized from many metal oxides. Despite the evolution of our understanding of these systems, well-ordered, thermally stable surfactant-templated mesoporous SnO2 films has remained elusive. Previously, researchers have reported disordered mesoporous SnO2 [3] as well as well-ordered, non-porous oxides. Further, the development of evaporation induced (or evaporation controlled) self-assembly techniques [2] to yield continuous thin films of these materials has opened up the possibility of new applications in sensors, nanowire synthesis, low-dielectric, electrode materials, and photovoltaics that may exploit the high surface area, ordered pore structure, present in these films. A host of synthesis routes that have been extended to other sol-gel systems to accommodate a wide range of metal oxides.

2:30 PM *EE3.3
Using Nanoarchitectonic Structure to Control Functionality in Inorganic/Surfactant Co-organization. Sarah H. Tolbert1, Brinson Waugh2, Xi Chen, Vijay Gupta3, William Morgan, Andrew Clark2, Dong Sun1, Andrew Biles1 and Scott Korey1, 2. Chemistry and Biochemistry, UCLA, Los Angeles, California; 2Mechanical and Aerospace Engineering, UCLA, Los Angeles, California.

Inorganic/surfactant co-organization is a powerful method for producing materials with complex and varied geometries on the nanometer length scale. Using a combination of self-assembly and hard-sphere chemistry, materials can be produced with a wide range of functionalities. More importantly, the nanostructured space provides a simple route to tune this functionality. In this talk, we will explore a number of systems where materials properties can be tuned and new behavior can be created by control of structure on various length scales. In the first example, templated nanomaterials are used to control the conformation and thus the optical properties of semiconducting polymers. In this way, new functionality, such as polarized or altered emission, can be created. If the nanoporous host is also an optically or electronically active material, the potential for

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**SESSION EE3: Porous Materials by Templating**

**Chairs John Bartlett and Jeff Brinker**

**Monday Afternoon, November 29, 2004**

**Room 302 (Hynes)**

1:30 PM *EE3.1
Hierarchically Structured Silica Monoliths.
Nicola Karola Huesing1, Doris Brandhuber1, Christina Rnab1, Viktoria Torma1 and Herwig Petekitt, 2. Chemistry, Vienna University of Technology, Vienna, Austria; 2Physics, University of Vienna, Vienna, Austria.
tuning materials properties is even greater. Thus, next we address the synthesis of new semiconducting frameworks and their combination with various host species. Both biological and natural systems will be addressed. Finally, on a structural level, we find that periodic inorganic/organic composites can be used to tune both stiffness and elasticity, creating materials with a unique combination of mechanical properties.

3:30 PM  **EE3.4**

Periodic mesoporous organosilicas with integral organic functionality derived from bridged organosilanes ([HOSi(R-Si(OR))3]) in the presence of surfactant have homogeneous distribution of organic fragments and siliceous moieties within the framework (1). The materials have uniform pores, high stability, and control on morphologies (2) and potential application in a variety of areas, including optoelectronics, sensing, enantioselective separation and catalysis. The main object of contemporary hybrid mesoporous materials synthesis is to control the geometry of a material at the molecular level of design. Changing the nature of the organic molecule in the hybrid mesoporous organosilicas are widely published and offer a wide range of opportunities to control the surface properties. Recently, we have described the surfactant-mediated synthesis of phenylene-silica hybrid mesoporous materials with precise control of the nanorarchitecture possessing well-oriented phenylene and silica fragments from 1,4-bis(triethoxy)silyle)benzene (3). The material has a hexagonal array of mesopores that can be further intercalated by swelling with organic molecules such as alcohols or alkanes. The addition of organic molecules to the pore wall structure. The addition of crystallinity to the pore wall of mesoporous materials has long been sought after and is a most important development in this research field. Very recently, we have also reported the synthesis of ordered mesoporous 4,4'-biphenylene-4,4'-biphenylene-1,4-phenylene-5 (silica hybrid materials with a crystal-like pore wall similar to that reported for 1,4-phenylene-silica material) (4). We have also functionalized the mesoporous aromatic-silica hybrid by attaching functional groups such as sulfonic group (SO3H) for the applications of solid-acid catalysts and electrolyte for fuel cells (6,7). Here we describe the synthesis and characterization of crystalline mesoporous systems to improve the framework functionality with physical and chemical properties. [References] (1) S. Inagaki, S. Guan, Y. Fukushima, T. Ohsumi, O. Terasaki, J. Am. Chem. Soc, 121 (2004) 9811. (2) S. Guan, S. Inagaki, T. Ohsumi, O. Terasaki, J. Am. Chem. Soc., 122 (2000) 5660. (3) S. Inagaki, S. Guan, T. Ohsumi, O. Terasaki, Nature, 416 (2002) 304. (4) M. Kapoor, Q. Yang, S. Inagaki, J. Am. Chem. Soc., 124 (2002) 15176. (5) M. Kapoor, Q. Yang, S. Inagaki, Chem. Mater., 16 (2004) 1209. (6) Q. Yang, M. Kapoor, S. Inagaki, J. Am. Chem. Soc., 122 (2000) 9864. (7) M. P. Kapoor, Q. Yang, S. Guo, S. Inagaki, Chem. Lett., 32 (2003) 914.

4:00 PM  **EE3.5**

4:30 PM  **EE3.7**
Synthesis and Application of Ordered Mesoporous Organic-Inorganic Hybrid Materials, Ferdi Schueth, Yanqin Wang, Chia-min Yang, Anja Rumplecker, Regina Palkovits and Bodo Zivovich; MPI fuer Kohlenforschung, Muelheim, Germany.

Cocondensation of alkoxysilanes and functionalized alkoxysilanes in the presence of suitable surfactants or grafting of organic species on the surface of ordered mesoporous materials are methods to create surface functionalized ordered mesoporous materials with high surface area and regular porosity. The current focus of interest lies on the synthesis of functionalized ordered mesoporous materials synthesized with blockopolymers, since these allow a higher degree of flexibility with respect to pore size and wall thickness compared to materials of the MCM-41 type. The contribution will highlight different pathways to synthesize such materials with various surface functional groups. The question of homogeneous distribution of the functional groups over the material will be addressed as well. From an application point of view, these materials offer many possibilities: They can be used as such, for instance carbohydrate functionalized materials in acid catalysis or ion exchange. Vinyl modified materials are also functionalized for the synthesis of other mesostructured functional oxides via the nanooasting pathway. It is thus possible to create ordered mesoporous C304 or CoFe204. Another application field of organically functionalized silica is the reversible anchoring of molecular catalysts and other functional molecules to the surface which may offer advantages with respect to the recovery of such species after use. The contribution will cover various aspects of these applications of ordered mesoporous organic-inorganic hybrid materials.

8:30 AM  **EE4.1**
Hybrid Materials and Self-Assembling Phases, Samuel I. Stupp, Materials Science, Chemistry, and Medicine, Northwestern University, Evanston, Illinois.

Most mineralized structures in nature such as bone and exoskeletons are hybrid materials in which proteins or other macromolecules mediate the growth of inorganic phases. The organic content in these hybrids is typically nanostructured in forms such as fibrils or microfibrils organized in crystalline lattices. These biogenic structures often have organic-inorganic epitaxial relationships or energy dissipating capacity under stress which are difficult to emulate in synthetic materials. Our laboratory has previously reported one biomimetic example where an organic-inorganic self-assembling relationship is established between self-assembling nanofibers of peptide amphiphiles and the hydroxyapatite crystals they nucleate. We report here on three hybrid systems in which two-dimensional or hierarchically organized matter that nature is providing, researchers are striving to reproduce those architectures in laboratories. One approach is based on combining soft chemistry or sol-gel processes with soft matter and more precisely metastable thermodynamic systems such as air-liquid foams or biliquid foams. In a first strategy, by using air-liquid foams as macroscale patterns we were able to prepare macromolecular mesoporous metal oxide scaffolds where both Plateau-border lengths and widths as well as cell morphologies (i.e. spherical or polygonal shapes) can be tuned on demand while offering mesoporosity with vermicular templates. This dynamic approach based on the liquid fraction during mineralization process has been applied to the synthesis of Si02 and anatase or rutile TiO2 as well as V205 monolith-type materials. In a second route we used concentrated direct biliquid foams to tune mesoporous void spaces of silica monoliths while providing mesoporous texture with micellar templates. In this approach by increasing the oil volume fraction we increase the emulsion viscosity. The increase of the viscosity enhances the shear stress applied to the droplets thus minimizing their sizes. By changing the oil volume fraction and the pH conditions to tune the wall textures that connect two adjacent cells providing either only internal cell junctions (windows that connect two adjacent cells) or both internal and external cell junctions (nodes connecting four adjacent cells). Those strategies allow to control the geometry of a material at the molecular level of design.
one-dimensional self-assembling phases template the formation of mineral structures. In one example silicas are nucleated in periodic structures of closely spaced columns of aluminosilicate that exhibit strong fluorescence and energy transfer. In two other examples, biomolecular nanoparticles can template one-dimensional semiconducting phases if their surfaces bind precursors ions to the inorganic phase.

9:00 AM *EE4.2


9:30 AM *EE4.3

The combination of organic and inorganic substrates in silsesquioxane hybrids offers unique possibilities for designing new synthetic routes to ordered nanomaterials. Hybrid materials with well-ordered mesopore structure was obtained by use of external organic surfactant templates as it was first reported in the synthesis of silica mesophases. The surfactant control of phase was extended to amphiphilic mixtures with a double-quantum (DQ) NMR experiment of the self-assembling organic species in such novel nanohybrid precursors.

Silicas and organosilicas with phenyl, vinyl and methyl groups have been prepared with cationic surfactants with C16 aliphatic chains and various polar head groups. In order to characterize the location of the various organic entities with respect to each other, high resolution 1H solid state investigation has been conducted, using one of the most sophisticated NMR experiments to explore dipolar coupling of the protons and thus spatial proximity : the double-quantum (DQ) NMR experiment under fast Magic Angle Spinning. These DQ experiments using the Back-to-Back decoupling sequence have clearly shown the existence of close contacts between the CFAB and silanol functions, in the case of the phenyl-functionalized samples. A detailed analysis of these experiments on the various samples will be presented, which can lead to a precise localization of the organic entities at the silica/surfactant interfaces.

10:30 AM *EE4.4
Structural Engineering of Self Assembled Nanohybrids via $\pi-\pi$ and H-bonding Interactions. Gerard Calleija, Iana Karachtevska, David J. Cossey, Dunbar P. Birnie, Bruno A. Latella, and Julie A. Plante. 1Department of Chemistry, ANSTO, Menai New South Wales, Australia; 2Department of Ceramics and Materials Engineering, Rutgers University, Piscataway, New Jersey.

Applications of nanohybrid coatings in optics, photonics and sensors requires precise control of the size and spatial orientation of organic and inorganic domains, to enable the properties of the materials to be modulated. Organic groups capable of self assembling by exploiting well defined interactions such as $\pi-\pi$-bonding, H-bonding, and size exclusion can be used to control the structural evolution of nanohybrids, leading to control of the size and spatial orientation of organic and inorganic domains within the nanohybrids. This study investigates the structural evolution of a series of nanohybrid powders and coatings incorporating self-assembling organic species based on complexes between aromatic carboxylic acids (e.g. benzoic (BZA) and trimesic (TZA) acid) and amine functionalised alkyltriarylalkoxysilanes (e.g. triisobutylsilyl-benzoate and N(3-trimethoxysilyl)propylenediamine). The structural evolution of conventional (non self assembling) nanohybrids based on methyltrimethoxysilane was also investigated for comparison. Self assembling in solution prior to incorporation into the gel network was studied by Raman and FT IR spectroscopy, NMR, light scattering and small angle X ray scattering (SAXS), while the nanostructure and properties of the corresponding thin films and nanowebers were investigated by XRD, AFM, TEM, SAXS, and Raman spectroscopy. The mechanical properties of selected coatings were examined using nanoincindentation and tensile testing. Coating solutions prepared by hydrolysing MTMS/TMOS mixtures at pH 2, with a H2O-Si(IV) mole ratio of 10 and equivalent SiO2 concentration of 5 wt%, exhibited weak, flat SAXS patterns, consistent with the presence of small, structurally diverse species in solution. In contrast, the corresponding solutions prepared from the acid/ammine complexes exhibited scattering patterns consistent with larger, more structurally defined species, suggesting that self assembled moieties were forming in solution prior to deposition of coatings and/or precipitation of nanocomposites. Raman spectroscopy indicated that the self assembled moieties remained intact during hydrolysis of the methoxy groups and evolution of the inorganic network. AFM and TEM images revealed the presence of well defined domains in the self assembled coatings (with dimensions of 20 to 100 nm), whereas the corresponding coatings produced from the MTMS/TMOS mixture were smooth and featureless. Tensile testing revealed that the self assembled nanohybrid coatings were well adhered to the substrates. These results clearly highlight the structure directing role of the self assembling organic species in such novel nanohybrid precursors that exploit H-bonding and/or $\pi-\pi$ interactions, leading to well defined nanosegregation of organic and inorganic domains. Methods for tailoring the structure of these organics to modulate the size and spatial orientation of the domains will be discussed.
techniques (see Maciel et al.). However, a “paradox” is often claimed in the literature: MAS and CP MAS experiments do not lead to comparable results in terms of quantification of the various species present in the gels. In this presentation, we show that this paradox can be solved by a careful analysis of the cross polarization data (CP) and that the published data, though “experimentally correct,” are misinterpreted. This approach is extended to a large number of hybrid silica gels involving organics components. Criteria related to “quantitative CP experiments” are established. We show also that 1H solid state NMR gives valuable informations concerning the H-H distances by solid state NMR (decoupling by multipulses, Lee-Goldburg decoupling under very fast MAS). Under Lee-Goldburg decoupling, the CP process is oscillatory in nature, allowing the direct measurement of H-Si distances, with the prerequisite that NMR active Si (cubane shaped silsesquioxanes), as well as amorphous gels, are examined. It is shown that molecular motion in the gels leads to the drastic averaging of the homonuclear H-H interactions, leading to strongly suppressed CP signals. Such oscillations are even observed in the case of weakly coupled spins, encountered in Si-CH3 groups.

1:30 PM EE5.1
Living-Anionic Polymerization Terminated to Nanoparticle Surface and Its Influence on Structure and Dynamics of PI/silica hybrids. Qiang Zhang and Lynden A. Archer; Cornell University, Ithaca, New York.

Surface initiated anionic polymerization has been the common approach to tether long polymer chains to silica nanoparticles. In this study, the opposite approach was adopted: living polystyrene (PS) chains were terminated and tethered to silica nanoparticles. Sec-BuLi was used to initiate the anionic polymerization of PS in a cyclohexane solvent. Silica surface was grafted with a layer of organosilane (cubane shaped silsesquioxanes), as well as amorphous gels are examined. It is shown that molecular motion in the gels leads to the drastic averaging of the homonuclear H-H interactions, leading to strongly suppressed CP signals. Such oscillations are even observed in the case of weakly coupled spins, encountered in Si-CH3 groups.

1:45 PM EE5.2
One-step Hydrothermal Synthesis of Metal Oxide Nanoparticles whose Surface is Covalently Bound with an Organic Monolayer. Sachiko Sata, Tetsuya Matsumoto, Masahiro Tsuchida, and Masato Isoda; Tohoku University, Sendai, Miyagi, Japan.

We report one-step hydrothermal synthesis of a hybrid nanomaterial where a metal oxide nanoparticle was covalently covered with an organic monolayer. The organic monolayer can be tuned to alter the surface properties of metal oxide nanoparticles. Our method relies on the dehydration between an organic molecule and a hydroxyl group on the growing surface of metal oxide nanoparticles under hydrothermal conditions. We note that organic reagents become miscible with water at higher temperature due to decreased dielectric constant of water. Therefore, metal oxide nanoparticles can be tethered with longer alkyl chains under anhydrous conditions in the next step. Finally, living PI chains were terminated by these chrolosilane groups and therefore chemically attached to silica nanoparticles. Hairy particles with various PI molecular weight and narrow molecular weight distributions were synthesized. These hairy particles were characterized by gel permeation chromatography, thermogravimetric analysis, dynamic light scattering, atomic force microscopy, etc. The relaxation dynamics of tethered chains were studied by dielectric spectroscopy and structure and dynamics of hybrid materials containing linear PI chains and such particles were investigated using x-ray microscopy.

2:00 PM *EE5.3
Nanoparticle-Polymer Nanocomposites prepared by the Incorporation of Organic-Functionalized Metal and Metal Oxide Nanoparticles into Polymers. Guido Kinkel and Dieter Holzinger; Institute of Materials Chemistry, Vienna University of Technology, Vienna, Austria.

Nanocomposites formed via the incorporation of inorganic nanoparticles into organic polymers offer many interesting applications in fields like optics, electronics, magnetic materials, etc. Major challenges in the preparation of these materials are to avoid agglomeration and phase separation and to obtain a good chemical link between the inorganic and organic moiety. Probably the most promising method to get homogeneous nanocomposites is the surface functionalization of the inorganic nanoparticles with organic groups that act as both, compatibilizers and linkers that covalently bind to the organic polymer matrix via polymerizable or initiating groups. In this contribution we present the controlled preparation of metal (Au) and metal oxide (MOx; M = Ti, Zr, V, Fe, Sn, Y) nanoparticles and nanorods and their organic functionalization via post synthetic treatment or via in situ surface modification. Gold dendrimeric procedures was the controlled preparation of both, the inorganic nanoparticles and the organic polymers. Gold nanoparticles and nanorods were surface-modified with thiol groups or a silica shell that was further modified and incorporated into various polymers. The optical properties of the final materials revealed that the inorganic nano building blocks were homogenously distributed in the polymer matrix and the materials respond to environmental, such as mechanical, changes. Metal oxide nanoparticles were dispersed in microemulsions using either metal alkoxides or metal salts as precursors. Their surface was functionalized during synthesis via an intra approach using modified alkoxides that contained bidentate ligands or via the use of silane coupling agents after synthesis. Applying these approaches initiator groups for atom transfer radical polymerization (ATRP) were attached to the surface and various polymers were grafted from the surface of the thus obtained macrorinitiators resulting in inorganic-organic core-shell nanoparticles.

2:45 PM EE5.5
Core-shell Nanocapsules and Drug Detoxification on Mycoyo/Microelectrode Array Devices. Randy S. Duran; Aleka Jovanovic; Mark Pottek; Christiane Thielemann; Jorge Chavez; Wolfgang Knoll; Chemistry, Univ of Florida, Gainesville, Florida; Max Planck Institute for Polymer Research, Mainz, Germany.

Polymerizable alkoxysilane compounds find broad use in applications ranging from self-assembly to sol-gel materials. We are interested in synthesizing core-shell nanocapsules from these compounds for eventual drug detoxification applications. Specifically, we have investigated the chemical polymerization of these compounds confined to a free surface of a microemulsion droplet. By varying conditions, monodisperse nanocapsules over a large range of sizes can be obtained. Drug uptake results probed by neonatal myocytes plated over microelectrode array devices will be discussed.

3:30 PM EE5.6
Encapsulation and Controlled Release of Bioactive Molecules from Sol-Gel Nano-Particles. Chris J. Barbe, Linggen Kong, Hu Qi, Qiang Lin, Kim Finnie, Scott McIvor, Mark Blackford and David Cameron; Materials & Engineering Science, ANSTO, Menai, New South Wales, Australia.

We present a generic approach to the synthesis of sol-gel silica matrices for encapsulating bioactive species, and controlling their subsequent release over periods ranging from hours to months. The bioactive species are incorporated into the matrix during gelation at, or near, ambient temperature, and remain entrapped until the gels are immersed in solution. The release profile can be tailored by...
controlling the internal structure of the gels (pore volume, size and tortuosity, and surface chemistry). In turn, the gel structure can be precisely tailored by varying such sol-gel processing parameters as the water-to-alkoxide ratio, pH, alkoxide concentration, aging, drying time and temperature. Hence, the release rate of the encapsulated species is controlled by the structure of the internal pore network to the physical properties of the drug molecule. Combining emulsion synthesis with sol-gel technology enables the carrier to be produced in the form of mono-dispersed spherical particles, with an average size that can be varied from 50 nm to 50 microns. The diameter is determined by the size of the reverse micelles, which is controlled by the hydrophile-lipophile balance between the surfactant, aqueous phase and non-polar solvent. The release rate of the encapsulated species is controlled by the internal nanostructure of the spheres, which can be tailored (as in bulk gels) by varying the sol-gel chemical parameters. The ability to independently control the release rate and particle size renders this technology particularly attractive for passive, in-vivo targeting of different drugs. Preliminary in-vitro and in-vivo bioavailability results, as well as comparisons with alternative controlled-release carriers based on polymers and liposomes, will also be presented.

4:35 PM EE5.7
Bion conjugation of CdTe Nanoparticles & Nanowires and Au Nanoparticles: Plasmon-Exciton Interaction. Jaehoon Lee1, Nicholas A. Kotov2 and Alexander O. Govorov2; 1Chemical Engineering, University of Michigan, Ann Arbor, Michigan; 2Physics and Astronomy, Ohio University, Athens, Ohio.

Photoluminescence (PL) enhancement of CdTe nanoparticles (NPs) and nanowires (NWs) is presented from the bion conjugation of hybrid semiconductor-metal nanoparticles system. D-biotin and streptavidin for biol conjugation were used to connect NPs and NWs in solution. In the presence of metallic nanoparticles, excitonic light emission of CdTe nanoparticles is strongly enhanced. The enhancement effect is explained in terms of plasmon-assisted absorption of incident light and plasmon-induced increase of nanoparticles dipole moments. This supermolecules and bion conjugates system can be useful to build further efficient photonic devices and biological sensors.

4:00 PM EE5.8

Nanoparticles with sizes in the range of 1-3 nm have between 50 and 90% of all their atoms at surface positions, so surfactant adsorption can modify the electron density as well as the interatomic distances. This changes the electronic properties of the nanoparticles such as optical absorption and magnetic susceptibility. We report studies of the effect of binding of organic ligands or surfactants to metal clusters of Au, Ag and AuAg and Co. These nanoparticles were investigated using size-exclusion chromatography, (SEC) by using clusters by size, and chemical affinity chromatography, (CAC), to investigate the effect of ligand binding to the cluster surface. We demonstrate that addition of alkyl thiols to metal clusters results in etching of the cluster surface producing especially small sizes with Au. We find that the length of the thiol determines the etching rate, with the shortest chains, which actually bind most weakly to the cluster surface, having the largest effect on the size dispersion. We also show that deposition of Ag onto the surface of Au clusters weakens the binding of thiols to the surface while alloying the surface of Ag with Au strength the bond. In the case of 1.8 nm Co particles in dilute solution we show that the magnetic response depends strongly on the surfactant deposited onto the surface, with alkyl amines producing a nearly linear response at high fields, but not altering the low field susceptibility. Studies of the deposition of magnetic atoms onto the surface of Co clusters reveal an initial quenching of the moment followed by recovery of the magnetic response due to redistribution of the atoms on the cluster surface. Acknowledgments: Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

4:15 PM EE5.9

Metal nanoparticles hold promise for many scientific and technological applications, including single electron transistors, sub-diffraction limit waveguides, and bio-chemical sensors. Understanding and controlling the behavior of these nanoparticles is essential for the development of reliable devices. We study the electronic and optical properties of metal nanoparticles stabilized by a dense monolayer of organic ligands. Modulation of both ligand and core parameters can influence the behavior of the nanoparticles. The synthesis procedure for these nanoparticles allows for control of solvent, stabilizer, and the radius of the nanoparticle, on the electro-optical characteristics of the nanoparticles. Specifically, we investigate the optical absorption of nanoparticles in solution, the (V) characteristics of individual nanoparticles, and the changes in the size across the surface in a function of the above parameters. For example, we show that by simply varying the ratio of low-ε to high-ε molecules in the ligand shell, it is possible to tune the position of the optical absorption resonance, as predicted by Mie theory. Additionally, controlling the composition (and hence the dielectric properties) of the ligand shell can cause the nanoparticle to act as a superluminescent diode. We also demonstrate the ability to easily and controllably tune the electronic and optical behavior of ligand-coated metal nanoparticles.

4:30 PM EE5.10
Formation and Reaction of Metal-containing Nanoparticles in Organic/Inorganic Hybrid Aerogels. Chunhua Yao and William Rieau; Chemistry, Brown University, Providence, Rhode Island.

Synthesis of hybrid aerogel materials that contain both selectively reactive nanoparticles and nanoparticles with appreciable magnetic susceptibilities will be reported. This has been achieved by first synthesizing silica-biodebased polymer hybrid aerogels, then incorporating metal ions sequentially and finally carrying out photochemically induced chemical reductions or decompositions. Thus, for example, silical-thioanion hybrid gels were prepared, Au(III) ions were coordinated to the thioanion and, after photochemical reduction, Au(III)-silica-thioanion aerogels could be obtained. This shows that the method could account for the preparation of hybrid nanoparticles with both magnetic and non-magnetic properties.

4:45 PM EE5.11
Jet Blowing of Polymer Micro and Nanofiber Composites with Inorganic Materials. John V. Bading, Ayusman Sen, Sachin Borkar and Bin Gu; Chemistry, Pennsylvania State University, University Park, Pennsylvania.

We have developed a jet-based technique, which we call jet-blowing, that is useful for the fabrication of micro and nanofibers of difficult to process polymers such as polytetrafluoroethylene. The technique is applied to the preparation of composite micro and nanofibers containing both polymer and inorganic nanoparticle components. Physical blending or in-situ oxidation of metal carbonyls has been used to load inorganic phases such as palladium nanoparticles and metal oxide nanoparticles into the polymer matrix. The composite material is characterized by electron microscopy, Raman spectroscopy, X-ray diffraction, differential scanning calorimetry, and BET surface area measurements. Preliminary results suggest that the resulting composites have high surface areas and may be useful as catalytic materials.

SESSION EE6: Structural Characterization

Chair: Florence Babonneau

Wednesday Morning, December 1, 2004
Room 302 (Hynes)

8:15 AM **EE6.1
In situ SAXS/XRD Investigations of the Formation of Mesoscopically Ordered Surfactant-Silica Mesophases. Mika Linden1,2, Silaine V. Teixeira1, Heinz Amenitsch1, Viveka Alfredsson1 and Freddy Kleitz2; 1Dept. of Chemistry, Abo Akademi University, Turku, Finland; 2Department of Heterogenous Catalysis, Max-Planck Institute for Coal Research, Muelheim/Ruhr, Germany; 3Austrian Academy of Sciences, Graz, Austria; 4Physical Chemistry I, Lund University, Lund, Sweden.

The formation of a variety of different surfactant-silicate mesophases has been studied by in situ synchrotron SAXS/XRD. The syntheses were carried out having the surfactant, the pH of the solution and the temperature as parameters, resulting in the formation of hybrid materials having a 2D hexagonal or one of several cubic structures. Careful analysis of both the scattering and diffraction patterns allows
the different stages of the formation to be described in some detail. The results are compared with literature data (if available) obtained with complementary techniques. It is shown that the formation mechanism is drastically different depending on the initial structure of the surfactant aggregates in solution. Thus, new synthesis approaches can be foreseen that allow the structure of the final hybrid mesophase to be rationally controlled.

8:45 AM *EE6.2
The Use of Multinuclear Solid State NMR for the Characterization of Sol-Gel Derived Hybrid Nanocomposites. Christel Gervais1, Beatriz Julian1,2, Elisa Cordonnico1, Purification Escrubano1, Mark E. Smith3, Florence Babonneau1 and Clement Sanchez1; 1Chimie de la Matiere Condensee CC174, Universite Pierre et Marie Curie, Paris, France; 2Departamento de Quimica Inorganicas, Universitat Jaume I, Castellon, Spain; 3Department of Chemistry, University of Warwick, Coventry, United Kingdom.

Properties of hybrid materials in which organic and inorganic components are combined in the nanometer range are strongly dependent on the extent and the nature of the interface between the constituents. Considering for example siloxane-metal-oxo nanocomposites prepared through hydrolysis and condensation of Me3Si(OEt)4-x (with 0 < x < 2) and M(OR)4 oxides (M = Ge(IV), Ti(IV), Zr(IV), Nb(V), Ta(V)), the degree of homogeneity of the final materials depends on the ability to favour heterogeneous condensation reactions between the precursors. The siloxane component can be characterized through vibrational spectroscopy and 29Si NMR, and the size or the average distance between metal-oxo nano-domains can be deduced from SAXS analysis. However, the characterization of the interface is a direct task. Evidence of the Si-O-M linkages may be obtained from FTIR measurements but the attribution of asymmetric Si-O-M stretching mode is not straightforward. For hybrid elastomers based on poly(dimethylsiloxane) (PDMS), 29Si MAS NMR experiments permit to distinguish and quantify mobile siloxane units from the rigid ones directly linked to the metallic atoms [1]. Such experiments give indirect information about the hybrid interface. 170 NMR experiments appear as a very straightforward tool to characterize the structure of these materials by probing directly and quantifying the small gyromagnetic ratios and moderately large quadrupole moments resulting in very large lineshapes. These factors combine to produce relatively low intrinsic detection sensitivity. Despite these problems, titanium NMR has a great potential for characterising titanium-siloxane hybrid systems. In this review, the use of the combination of NMR techniques for the characterization of hybrid materials and their interfaces will be presented. [1] B. Julian, C. Gervais, E. Cordonnico, P. Escrubano, F. Babonneau, C. Sanchez Chemistry of Materials, vol 15, 3005-3010 (2003); [2] C. Gervais, G.M. Smith, Journal of Physical Chemistry B, vol 105, 1971-1977 (2001). [3] B. Julian, C. Gervais, M.-N. Rager, J. Maquet, E. Cordonnico, P. Escrubano, F. Babonneau, C. Sanchez Chemistry of Materials, vol 16, 521-529 (2004). [4] C. Gervais, M.E. Smith, A. Pottier, J.-P. Jolivet, and F. Babonneau Chemistry of Materials vol 13, 462-467 (2001).

9:15 AM *EE6.3

Over the last years, solid state NMR has undergone significant developments both on the methods and hardware points of view. These developments lead improved sensitivity and resolution improvements, which open the way to new experiments able to probe the structure of advanced materials at different length scales. These experiments include homo and heteronuclear correlations, mediated by through bond or through space interactions. Illustration will be given with studies of mesoporous or hybrid or bioinspired materials[1-2]. In the case of hybrid materials, we have been able to identify and to locate at the interface the remaining alkoy groups. Moreover, the relative amount of these groups has been measured and related to the textural properties of the mesoporous spheres [3]. Current IH solid state NMR experiments are focused on hybrid mesoporous organosilica spheres is shown to be also particulary useful for the knowledge of self-assembly processes. [1] B. Alonso and D. Massiot, J. Magn. Reson., 163, 347-362 (2003). [2] Advanced Materials, in press [3] B. Alonso, A. Douchet, F. Babonneau, J. Pottier, M.-N. Rager and D. Massiot, J. Mater. Chem., 14, 2006-2016 (2004).

10:00 AM *EE7.1
Potential for polyolefin-clay hybrid. Arimitsu Usuki, Toyota CRDL, Aichi, Japan.

We have synthesized nylon 6 clay hybrid (NCH) in 1986. In the clay gallery, e-caprolactam is polymerized; the silicate layers were dispersed in nylon 6 to give a NCH. This is the first example of an industrial clay-based polymer nanocomposite. The modulus of NCH increased to 1.5 times that of nylon6, the heat distortion temperature increased to 140 degree from 65 degree, and the gas barrier effect was doubled at a low loading (2 wt. %) of clay. However, polyolefin clay hybrid could not be synthesized easily because polyolefin is hydrophobic and has poor miscibility with clay silicates. Octadecyl ammonium ion was used as a modifier for the clay and a maleic anhydride modified polyolefin was used so that the clay became more compatible. Thus polyolefin was directly intercalated into the clay gallery. There is also a direct-intercalation process in which polyolefin is modified using maleic anhydride, followed by melt compounding. It is a useful process from an industrial standpoint. Ethylene propylene rubber-clay hybrid (EPR-CH) is a useful process from an industrial standpoint. Ethylene propylene rubber-clay hybrid (EPR-CH) is prepared by copolymerizing ethylene, propylene, maleic anhydride modified EPR (EPR-MA) with organophilic clay, and their properties are examined. Silicate layers of organophilic clay are found to exfoliate and homogeneously disperse into the nanometer level in the hybrid by transmission electron microscopy observation. EPR-CHs exhibit higher tensile modulus compared to EPR-MA and the conventional composites. Creep resistances of EPR-CH are much improved compared for EPR-MA. Degree of swelling in hexadecane is remarkably restricted. Improvement of these properties is caused because dispersed silicate layers have much larger interface with the EPR matrix and are thought to strongly restrain the EPR polymer chains. Nanocomposite technology using small amount of silicate layers is useful to improve properties of thermoplastic elastomer. Various kinds of thermoplastic elastomers are expected to be produced by loading of silicate layers or without conventional fillers.

10:30 AM EE7.2

Complexing ligands are often used to slow down the reactivity of metal alkoxides in sol-gel processes. Substitution by appropriate organic groups allows, in principle, to introduce organic functionalities in metal oxide-based sol-gel materials. However, there are some chemical problems associated with the preparation of organofunctional metal alkoxides, which are mainly caused by the Lewis-acidic character of the metal alkoxides. This will mainly be discussed for single-source precursors of the type (RO)3Si(CH2)xM(OR)(n) (M = Al, Ti, etc.), where n is a coordinating ligand.

10:45 AM EE7.3
Controlling Morphological Behavior in Polymer-Clay Hybrids using Very Low Surfactant Loadings. Rick Beyer1, Mary Kurian1, Arnab Dasgupta4 and Mary E. Galvin2, Army Research Laboratory, Aberdeen Proving Ground, Maryland; 1Materials Science & Engineering, University of Delaware, Newark, Delaware; 2Air Products & Chemicals, Inc., Allentown, Pennsylvania; 3Indium Corporation of America, Utica, New York.

The promise of lightweight yet very strong and tough hybrid materials based on simple combinations of polymer matrices and layered silicate clay fillers has not come to fruition as once hoped. A significant reason for this continues to be difficulty controlling dispersion of individual silicate layers during fabrication of the hybrid material. Typically, immisibility between hydrophilic clays with hydrophobic organic materials limits formation of exfoliated nanocomposites by in situ synthetic processes, solution-processing, or melt blending. In cases where in situ synthesis is possible, the addition of clay to the reaction mixture affects the molecular weight distribution and reaction kinetics, leading to the formation of a potentially undesirable product. Where melt processing is used to form0 nanocomposites, dispersion of the individual silicate layers, the matrix polymer is also at risk of damage. Clays are typically modified using surfactants to compatibilize them with their polymer matrices prior to
processing; if this process could be used to facilitate dispersion, hybrid materials would be more likely to become a reality. It has been predicted that under certain conditions the exfoliation of the silicate layers may be induced by the enthalpic interactions between the silicate, surfactant, and homopolymer. These same models also found an effect of surfactant length on equilibrium morphology. This project has examined these predictions using a novel technique, forming poly(ethylene/montmorillonite (PS-MMT) system. Low polydispersity, quaternary amine terminated PS surfactants were synthesized with a variety of molecular weights and used to modify MMT in different ways. The results showed that a low loading of silicate modified PS, around 17%, helped the surfactate naturally disorder in a PS matrix \( (\chi = 0) \) with simple annealing (direct melt intercalation). The identical experiment with much higher surfactant loadings resulted in no change in silicate morphology. Surprisingly, using poly(vinylmethylether) \( (\chi < 0) \) did not cause an increase in dispersion under those conditions, but samples made with poly(methylmethacrylate) \( (\chi > 0) \) did not show a change in silicate dispersion. The experiments showed that the shortest surfactant provided the most change in morphology upon annealing. Although longer surfactants might enhance the disruption of the clay tactoids through their entropic benefit to any intercalating polymer molecule, this is only observed experimentally for short surfactants. Several situations provide reasonable explanations for this observation; to distinguish between surfactant molecular weight and surfactant coverage as control behavior, a set of samples have been fabricated at only 5% surfactant loading and characterized. These results and their implications will be presented here.

11:00 AM EE7.4 Inorganic-Organic Hybrid Materials From Layered Double Hydroxide Structure and Their Subsequent Carbonaceous Replication, Fabrice Leroux1, El M. Mouradi2, C. Roland1, L. Vieille1, C. Taviot-Guebo1, J. P. Bese1, E. Raymundo-Pinero2 and F. Beguin1. 1Mines ParisTech, Université Blaise Pascal, Aubiere, Auvergne, France; 2CRM, Orleans, France. Under specific conditions, some organic molecules and polymers once confined into a host structure give rise to carbonaceous materials associated to a large microporosity. It has been illustrated by several examples such as clay materials, but also with 3D host structures such as MCM-48. In this idea, various monomers and/or polymers have been incorporated into the sheets of intercalated double hydroxide (LDH) (hydrotalcite and hydrocalumite-type) materials. In this contribution, we will focus on a biopolymer (alginic and two monomers, sulfopropylmethacrylate (SPMA) and vinylbenzenesulfonate (VBS), as the organic moiety. In a first step, the synthesis of the inorganic-organic hybrid materials will be described, and the interaction between the host structure and the guest molecule will be discussed according to the preparation pathway. For vinyl and acrylate-based intercalated monomers, the reaction in situ polymerization will be characterized, and the behavior in temperature will be presented. In a second step, the textural properties of the carbonaceous materials obtained after a charring process in the polymer hybrid materials will be described in terms of porosity and specific surface area and related to the preparation mode. Specific surface area up to 2800 m²/g may be reached for samples prepared initially via the monomer polymerization and their subsequent melt intercalation. In addition, the carbonaceous materials have been tested as electrochemical supercapacitors in sulfuric acid medium (1M) by means of galvanostatic and potentiostatic techniques and also by complex impedance spectroscopy. Some of the studied materials present interesting capacitances (up to 100 F/g) associated to a good behavior upon cycling.

11:30 AM EE7.5 Graphite Nanoplatelets: A Nanoreinforcement Capable of Modifying Mechanical, Thermal and Electrical Properties of Polymer Composites, Lawrence T. Drael1, Hicryuki Fukushima2, and Kiriki Kusaka-Taidou1. Lawrence T. Drael, 1Composite Materials and Structures Center, Michigan State University, East Lansing, Michigan; 2Dept of Chemical Engineering and Materials Science, Michigan State University, East Lansing, Michigan. Nanocomposites composed of polymers reinforced with exfoliated clays and carbon nanotubes are being considered for applications such as interior and exterior accessories for automobiles, structural composites for inflatable electronic devices, and films for food packaging. While most nanoinservative research has focused on exfoliated clay platelets and carbon nanotubes, the same nanoreinforcement concept can be applied to another layered material, graphite. Graphite can produce nanolayers and nanocomposites. Graphite is the stiffest material found in nature (Youngs Modulus = 1060 GPa), having a modulius several times that of clay, but also having excellent electrical and thermal conductivity. With the appropriate surfactant treatment, exfoliation and dispersion in a meso- or thermoplastic polymer matrix results in a composite with excellent mechanical, electrical and thermal properties, opening up many new structural applications as well as non-structural ones with high and thermal high requirements as well. In this presentation, the mechanical, thermal and electrical properties of exfoliated nanographite platelet reinforced polymer composites (epoxy, polypropylene and nylon) will be presented, including mechanical strength, coefficient of thermal expansion, as well as electrical and thermal properties. The results will be compared and contrasted with the same polymer matrices reinforced with nanoclay, vapor grown carbon fibers and particulate graphite. The results show that exfoliated graphitic nanoplatelets can be added to a polymer, the resulting composite can have three times the modulus of nanoclay platelet reinforced composites. With the proper surface treatment of the nanoplate, little reduction in composite tensile strength was detected to the next generation. Impedance measurements have shown that these platelets percolate at below 3% volume percent and exhibit a 10 order of magnitude reduction in impedance at these concentrations.

SESSION E8: Hybrid Polymers

1:30 PM E8.1 Kinetic Stability of the Well-Dispersed or Exfoliated State of Polymer Nanocomposites Made by a Novel Process Method, Kosmas Katsimatid1 and John M. Torkelson1,2. 1Chemical & Biological Engineering, Northwestern University, Evanston, Illinois; 2Graduate School of Engineering, Northwestern University, Evanston, Illinois. Polymer nanocomposites have the potential to yield materials that are "lighter, stronger, and harder" or that possess enhanced barrier, electrical, thermal, and dimensional stability. These enhancements rely on the achievement of exfoliation or dispersion of the nanofiller. Unfortunately, the production of well-exfoliated or well-dispersed polymer nanocomposites has proven challenging, especially when the polymer is nonpolar, or has a high melt temperature or a limited thermal stability. While there has been some success in producing well-dispersed nanocomposites by in situ polymerization in the presence of nanofiller, this is less desirable from a technological standpoint than an approach allowing for direct mixing of polymer and nanofiller. However, melt mixing, e.g. twin-screw extrusion (TSE), has proven unable to yield substantial dispersion or exfoliation for many polymer-nanofiller hybrids. Here we report both on the use of a novel process method that yields well-exfoliated or well-dispersed polymer nanocomposites and on the long-term kinetic stability of the dispersion or exfoliation during subsequent melt processing into a final product. The process is called solid-state shear pulverization (SSSP) and has the virtue, as does TSE, of being a solventless, continuous process that is well suited for commercial application. However, unlike TSE, SSSP produces well-exfoliated nonpolar/organoclay nanocomposites, whereas well-exfoliated polypropylene (PP)/clay nanocomposites result without using male anhydride-modified PP as the matrix. SSSP uses a twin-screw extruder that is specially modified so that processing occurs in the solid state, yielding a powder or particulate that can be subsequently melt processed into a final product. During SSSP, the system undergoes many fragmentation and fusion steps, resulting in intimate mixing and excellent dispersion. The achievement of the exfoliated state of PP/organoclay nanocomposites made by SSSP is evidenced by several methods: transmission electron microscopy (TEM), x-ray diffraction (XRD), and differential scanning calorimetry (DSC). The TEM, XRD, and DSC results contrast sharply with similar characterization done on PP/organoclay hybrids made by twin-screw extrusion which exhibit little exfoliation. Furthermore, the well-exfoliated state is maintained after 2 hr of annealing above the melt transition of PP. Thus, even though the PP/organoclay system is thermodynamically incompatible, the exfoliated state achieved via SSSP is apparently kinetically stable in the melt state over times that are long in comparison to melt processing times. This indicates that SSSP can yield a variety of polymer nanocomposites that cannot be made in a well-dispersed state by melt mixing. Further examples of this will be detailed including nanocomposites involving other polymers with organoclay as nanofiller and nanocomposites involving other fillers, such as carbon nanotubes.

1:45 PM E8.2 Fabrication of Nanocomposite Thin Film of Hydroxyapatite and Polyvinylalcohol and its Ionic Conductive Properties, Toshihiko Takaki1, Kazuyuki Fukuda1 and Yoshiro Tajitsu2. Toshihiko Takaki1,2, Hiroyuki 1Interfacial Science group, Material Science Laboratory, Mitsui Chemicals, Sodegaura-shi, Chiba, Japan; 2Graduate School of Engineering, Kansai University, Suita-shi, Osaka, Japan. Polymer nanocomposites have the potential to yield materials that are "lighter, stronger, and harder" or that possess enhanced barrier, electrical, thermal, and dimensional stability. These enhancements rely on the achievement of exfoliation or dispersion of the nanofiller. Unfortunately, the production of well-exfoliated or well-dispersed polymer nanocomposites has proven challenging, especially when the polymer is nonpolar, or has a high melt temperature or a limited thermal stability. While there has been some success in producing well-dispersed nanocomposites by in situ polymerization in the presence of nanofiller, this is less desirable from a technological standpoint than an approach allowing for direct mixing of polymer and nanofiller. However, melt mixing, e.g. twin-screw extrusion (TSE), has proven unable to yield substantial dispersion or exfoliation for many polymer-nanofiller hybrids. Here we report both on the use of a novel process method that yields well-exfoliated or well-dispersed polymer nanocomposites and on the long-term kinetic stability of the dispersion or exfoliation during subsequent melt processing into a final product. The process is called solid-state shear pulverization (SSSP) and has the virtue, as does TSE, of being a solventless, continuous process that is well suited for commercial application. However, unlike TSE, SSSP produces well-exfoliated nonpolar/organoclay nanocomposites, whereas well-exfoliated polypropylene (PP)/clay nanocomposites result without using male anhydride-modified PP as the matrix. SSSP uses a twin-screw extruder that is specially modified so that processing occurs in the solid state, yielding a powder or particulate that can be subsequently melt processed into a final product. During SSSP, the system undergoes many fragmentation and fusion steps, resulting in intimate mixing and excellent dispersion. The achievement of the exfoliated state of PP/organoclay nanocomposites made by SSSP is evidenced by several methods: transmission electron microscopy (TEM), x-ray diffraction (XRD), and differential scanning calorimetry (DSC). The TEM, XRD, and DSC results contrast sharply with similar characterization done on PP/organoclay hybrids made by twin-screw extrusion which exhibit little exfoliation. Furthermore, the well-exfoliated state is maintained after 2 hr of annealing above the melt transition of PP. Thus, even though the PP/organoclay system is thermodynamically incompatible, the exfoliated state achieved via SSSP is apparently kinetically stable in the melt state over times that are long in comparison to melt processing times. This indicates that SSSP can yield a variety of polymer nanocomposites that cannot be made in a well-dispersed state by melt mixing. Further examples of this will be detailed including nanocomposites involving other polymers with organoclay as nanofiller and nanocomposites involving other fillers, such as carbon nanotubes.
A great deal of research interest is being invested in the fabrication and characterization of nanocomposites because they may be of particular significance both as well as of the application to the new optical and electrical devices. The interface between the polymer and inorganic particle has the different property from the bulk material. Inorganic particle size decreased to nanometer size, so the increase of surface-to-bulk ratio enhances the unique property. We investigated the preparations and characterizations of hydroxyapatite (HAp) polymer nanocomposites because HAp has unique chemical and physical properties. The HAp-PVA nanocomposite was prepared by reacting Ca(OH)2 with H3PO4 in the presence of polyvinylalcohol (PVA) having ca. 20000 molecular weight and HAp particles were uniformly dispersed in the PVA matrix. The transparent and formed transparent films by casting method. The cross-sectional TEM image of the films revealed that the HAp particles with nanometer size were uniformly dispersed in PVA matrix. The transparent and flexible films were obtained. Besides, it is possible to draw the nanoscale features on the surface of the inorganic nanoparticles. Finally, the high conductivity silica-PYA nanocomposite. Now, we speculate that, the realization of silica particles, and as a result, the free lithium ions increase at the solid polymer electrolyte. The HAp colloidal solution was stable when the Linc(CF3SO2)2aqueous solution was poured. The PVA nanocomposite films containing lithium salt were casting from the HAp colloidal solution with Linc(CF3SO2)2. The transparent and flexible films were obtained. Besides, it is possible to draw the nanoscale features on the surface of the inorganic nanoparticles. The conductivity of the film (PVA:HAP = 1:1) with the 35wt % content of Linc(CF3SO2)2 is about 10^-2 S/m at room temperature. The ionic conductivity of the drawn film increased. Its value reached to 10^-3 S/m. In order to investigate the effect of HAp particles on the enhancement of ionic conductivity, we prepared the silica-PVA nanocomposite films and measured the ionic conductivity. The value of ionic conductivity of anionic silica-PVA nanocomposite was lower than that of anionic silica-PVA nanocomposite. Now, we speculate that, the realization of the high ionic conductivity of this films is because, the union of lithium ion at the surface of the inorganic nanoparticles such as HAp or silica particles, and as a result, the free lithium ions increase at the surface of the inorganic nanoparticles. Finally, the high conductivity in the HAp-PVA composite film might be realized.

2:00 PM EE8.3 Nanostructured Organosilicates from Mixtures of Amphiphilic Copolymers and Polyorganosilicates. He-Chieng King, James L. Hedrick, Eric Drockenmuller, Teddie Magbitang, Victor Lee, Philip Rice and Robert D. Miller; IBM Almaden Research Center, San Jose, California.

Self-assembled periodic structures of organic copolymers have been used to direct inorganic nanostructures. Selective chemical reaction using precursors or preferential interaction with specific domains is commonly used to localize inorganic materials, hence to create controlled nanoparticle generation, structure-property correlations of thin films of organosilicates containing nanoscopic structures. Binary mixtures of amphiphilic copolymers and organosilicates were used to create the nanostructured organosilicates. A variety of molecular architectures of amphiphilic block copolymers including linear, radial and linear-dendritic block copolymers were used to direct the nanostructures. Ordered spherical, cylindrical and lamellar morphologies were characterized using atomic force microscopy (AFM), electron microscopy (TEM), and small angle x-ray scattering (SAXS). A laser excited surface acoustic wave spectroscopy (SAWS) was used to determine mechanical properties of the nanostructured organosilicates, which will be discussed in correlation with morphologies of the thin films.


Composites comprised of a polymer matrix and inorganic fillers are one of the most important and significant materials in today’s society. Examples include the use of glass fibers dispersed throughout a polymer matrix. Such materials are of great interest because they usually display significant improvements in mechanical properties, and often other properties such as barrier and fire retardancy, over and above that of the pure polymer. One of the most significant developments in the past decade or so has been nanocomposite materials in which at least one component has nano-scale dimensions. Perhaps the best examples of such nanocomposite materials are layered silicate nanocomposites (PLSNs) that consist of well-dispersed silicate (clay) layers within the polymer matrix. In these materials the large surface to volume ratios of the inorganic component, inter alia, leads to significant improvements in properties, and perhaps most importantly, the tradeoffs in physical properties often observed in macroscopic filled composites may be avoided in the nanocomposites. The work presented in this paper examines the use of in situ living radical polymerization to prepare layered silicate nanocomposites. The study involves the design of new copolymers and organosilicates, which will be characterized using solution synthesis, X-ray diffraction (XRD), TEM, AFM, SAXS, and DSC. The mesoporous materials with pore sizes ranging from 5-50 nm for separation technology and catalysis, solid hybrid polymer electrolytes for battery applications, the syntheses of nanocomposites, and as well as thin film materials with potential applications in microelectronics and nanobiotechnology.

3:30 PM EE8.6 Inorganic-Organic Hybrid Materials with Surface-Modified Metal Oxide Cluster as the Inorganic Component. Yu Gao, Franz Rene Kogler, Myhedin Japs, Michael Puschelberger and Ulrich Schubert; Institute of Materials Chemistry, Vienna University of Technology, Vienna, Austria.

Inorganic-organic hybrid materials have extraordinary properties due to the synergism between properties typical of both components. Pre-formed transition metal oxide clusters having suitable organic groups bonded to their surface are prepared by carefully controlled hydrolysis and condensation of carboxy-substituted transition metal alkoxide. The clusters are then polymerized in the presence of organic co-monomers by various polymerization techniques to form inorganic cluster-reinforced polymers. The properties of the cluster-crosslinked hybrid polymers drastically differ from those of the parent polymers.

3:45 PM EE8.7 Structural Control and Characterization of Organic-Inorganic Hybrid Materials. Plinio Innocenzi1, Giovanna Brusatin2, Florence Babonneau2, Bruno Alonso3, Dominique Massiot4 and Tongji Kidob1; 1Architecture and Planning, University of Sassari, Alghero (Italy); 2Chemistry of Coordination Systems, Poly-Com, 6, Paris, France; 3Dipartimento di Ingegneria Meccanica, setto
Microcellular Organic/Inorganic Hybrid Polymers from High Internal Phase Emulsions and Their Use in Inorganic/organic Hybrid Materials I

SESSION EE9: Poster Session: Organic/Inorganic Hybrid Materials I
Wednesday, December 1, 2004
8:00 PM
Exhibition Hall D (Hynes)
have recently developed a new fabrication process for printable organic TFTs called “self-aligned self-assembly process (SALSA)”, where soluble molecules such as metallo-supramolecular organic molecules are self-assembled into a device structure with micrometer resolution and the components of TFT such as semiconductor, source, drain and gate are substantially self-aligned to each other. SALSA is especially used for TFT arrays mainly used as an active-matrix backplane to drive liquid crystal displays. An ordinary bottom-gate and bottom-contact TFT structure is used in which the gate electrode, gate insulator, self-assembled monolayers (SAM) and source/drain electrodes are stacked on a transparent substrate, and finally semiconductor film is formed to complete the device. A key point of this process is patterning the hydrophobic SAM by a back-substrate exposure technique using the dry-gate metal mask [1]. The optically patterned SAM not only defines the self-aligned positions of the solution-processed pixel electrode and drain lines, but it also selectively orders the structure of the semiconductor molecules deposited on it. Moreover, both the gate and the semiconductor are substantially self-aligned to each other. In order to fabricate TFT arrays, where gate lines and drain lines are crossed and TFTs at the cross points are electrically isolated each other, we design a specific gate pattern which defines boundaries of these electrodes fabricated using solution materials. We demonstrated to fabricate 3 x 9 arrays using SALSA process and now are trying to fabricate 64 x 64 arrays. SALSA process with a specific design of TFT-array patterns will become one of the powerful methods fabricating high-resolution self-aligned electronic components manufactured using inexpensive solution processing and direct printing processes without using any physical patterning tools with small materials [1].

Three-Dimensional Structure and Liquid Transport Behavior of Siloxane Gels with Co-continuous Macropores

Haruka Saito1, Kazuki Nakashima1, Kazuyo Hiro1, Hiroshi Jinnai2, Kei Morisato3 and Hiroyoshi Minakuchi1

1Material Chemistry, Kyoto University, Graduate School of Engineering, Kyoto, Kyoto, Japan; 2Polymer Science and Engineering, Kyoto Institute of Technology, Kyoto, Kyoto, Japan; 3Kyoto Monotech Co., Kyoto, Japan.

Sol-gel process of alkoxide-derived silica accompanied by phase separation leads to macroporous silica with interconnected skeletons and well-defined cylindrical pores. Co-continuous macroporous silica thus obtained has been attracting separation media for a decade because of its numbers of advantages over conventional packed beds column: improved liquid transportation behavior and higher efficiency, which have successfully matured into commercial high performance liquid chromatography (HPLC) column. In spite of numerous reports on the performance of this column, the behavior of co-continuous silica gel is still poorly understood. Traditionally, the flow behavior has been described by pressure drop using Kozeny-Carman equation with porosity and pore diameter as principal geometrical parameters of the flow. The pore space is made up of small materials [1].

The mechanism of formation of ordered mesoporous silica synthesized by in situ XRD. Niki

On the mechanism of formation of SBA-1, SBA-2 and SBA-3 mesostructured silicas as studied by in situ XRD. Niki Bascile1, Andrew Riley1, Heinz Anetschit1, Sarah Tolbert1, Mika Linden2 and Georg Kossenkov1

1Centre for Materials Science and Engineering, University Pierre et Marie Curie, Paris, France; 2Dept of Chemistry and Biochemistry, UCLA, Los Angeles, California; 3Institute of Biophysics and X-ray Structure Research, Austrian Academy of Sciences, Graz, Austria.

The mechanism of formation of ordered mesoporous silica synthesized in the presence of surfactant molecules at high surfactant-to-silica ratio has been already studied in some detail. It is now fairly well established that the formation process is co-operative in nature and is crucially dependent on the balance between the relative strengths of the surfactant-silicate, silicate-surfactant, and silicate-silicate interactions. Furthermore, in many cases the reaction is under kinetic control and can be chemically frozen into non-equilibrium states as a consequence of inorganic condensation reactions. Most mechanistic studies cover the alkaline synthesis route, which usually involves negatively charged silicate species and a positively charged surfactant. The acidic synthesis route has attracted much less attention from a mechanistic point of view, despite the fact that morphology control can be much more readily achieved under acidic rather than basic conditions. Here, the silicate species carry a slight positive charge, and the interaction with the surfactant is thought to be mediated through counter-ions present in solution. In this communication we report on the in situ synchrontron X-ray diffraction, XRD, data obtained during the first stages of the formation of SBA-1 (cubic Pm3m), SBA-2 (hexagonal P63/mmc) and SBA-3 (hexagonal p6m) silicas. They have been prepared from TEOS in acidic medium (HCl) using respectively cetyltrimethylammonium bromide (CTAB), cetyl(dimethylammonium)propyltrimethylammonium dibromide (MMG) and cetyltrimethylammonium bromide (CTAB), as surfactants. The three final phases form directly after an induction period of few minutes, with no intermediate mesophase. However one difference can be noticed: while sharp XRD peaks appear in the case of SBA-2 and SBA-3 phases, the presence of a diffuse scattering peak precedes the appearance of the XRD peaks due to the cubic SBA-1 phase. This suggests different interaction mechanisms that will be discussed with respect to the nature of the surfactants.

Sila Monoliths Hierarchically Textured via Concentrated Direct Emulsion and Miscellar Templates, Renai Bachov1, Florent Carn1 and Annie Colin2; 1Chemistry, CRPP-CNRS UPR8641, Pessac, Gironde, France; 2Physical-Chemistry, OF-UMR-CNRS Rhodia FRE2771, Pessac, 33607, France.

In a general context of bio-inspired materials researches aim to generate highly organized materials with emphasis toward obtained a certain degree of hierarchy and complexity. Generating this class of materials is not such an easy task to reach. One way is to promote inorganic condensation at macroscopic metastable thermodynamic interfaces. In this route we make the use of concentrated direct emulsion to tune silica macroscopic void spaces while micellar templates is used at the mesoscale to create mesoporosity. In order to control the size of the monolith macropores we varied the starting emulsion viscosity by increasing the amount of emulsifier. Increasing the emulsion viscosity we increase the shear stress applied to the oil droplets during the oil phase emulsification process minimizing thus both the droplet sizes and the sizes of the windows that connect two adjacent cells. Beyond the oil water interface we used the pH conditions to tune the wall textures that connect two adjacent cells providing either only internal cell junctions (windows that connect two adjacent cells) or both internal and external cell junctions (knots connecting four adjacent cells). Those materials show interconnected macroporosity associated to vermicular-type mesostructure. They possess and average mesoporosity of around 800 m2g-1 associated to bulk density as low as 0.08 g cm-3 which is comparable to values obtained for silica aerogel. 1- Inorganic monoliths hierarchically textured via concentrated direct emulsion and miscellar templates. Florent Carn, Annie Colin, Marie-France Achard, Elisabeth Sellier, Marc Birot, Herve deLeau and Renal Backov. J. Mater. Chem. 2004, 14, 1367.

Rational Design of Macromolecular Metal Oxide Monoliths Obtained by Combining Soft Chemistry and Air-Liquid Foams, Renai Bachov1, Florent Carn1 and Annie Colin2; 1Chemistry, CRPP-CNRS UPR8641, Pessac, Gironde, France; 2Physical-Chemistry, UMR-CNRS Rhodia FRE2771, Pessac, 33607, France.

Recently new concepts of "chemistry of shapes" or synthesis over "all length scales" have enhanced the generation of hierarchically organized materials associated to complex textures. To constitute such high organization, patterns or templates at different length scales have to be used while processing growth of inorganic scaffolds or particles. One way of shaping solid state materials is to combine soft matter and hard chemistry. In this general framework, we propose the synthesis and characterization of mesoporous macromolecular scaffolds
of different metal oxide scaffolds with emphasis toward rational design over the macroscopic void sizes and shapes. By using air-liquid foams as macroscopic templates, we were able to prepare mesoporous metal oxide scaffolds where both Plateau-borderer lengths and widths as cell morphologies (i.e. spherical or polygonal shapes) can be tuned on demand while avoiding vermicular mesoporosity. This dynamic approach on the control of macroscopic foams during the mineralization process has been first applied to the synthesis of SiO2 amorphous macrocellular foams that depicts internal porosity of 1.470 mg/L. In a second approach we succeed in extending this strategy towards preparation of 0.1 N NaOH or HCl catalyst, THF, and 6 equiv H2O) either as a homopolymer or as a copolymer. Gas sorption can be tuned on demand while offering vermicular mesoporosity. This during the mineralization process has been first applied to the challenging task. In particular, the synthesis of well-defined dynamic approach based on the control of foam’s liquid fraction over the macroscopic void spaces sizes and shapes. By using air-liquid deleuze, Zoubida Saadi and Renal Backov. Adv. Mater. 2004, 16, 140.

**EEO.6**

**Monolithic Periodic: Mesoporous Silica with Well-defined Macropores, Tomohiko Amami, Kazuaki Nakahishi, Kazuyuki Hirao**

The first synthesis of oxides with highly ordered mesopores templated by structure-directing agent was reported in the early 1990s. They have attracted considerable attention due to their fascinating structures and wide potential applications in the fields of separation, photonics, optics, drug delivery and supports for catalysts. Mesoporous materials are now available in the forms of the powder, rods, thin film and controlled-size particles, and even in monolith. In spite of a drastic progress in the synthesis of mesoporous materials, the preparation of materials with a simultaneous control of morphology and pore size on different length scales still remains as a challenging task. In particular, the synthesis of well-defined macroporous monoliths with highly ordered mesopores is difficult to achieve. If these monoliths with well-defined pore structures on different scales can be synthesized, a lot of benefits are expected from the integrated pore systems. Here, we present the successful preparation and characterization of pure silica monoliths having hierarchical porosity (macroporous and mesoporous). Monolithic silica gels with spontaneous hierarchical pore structure have been synthesized via sol-gel process from silicon alkoxide in the presence of structure-directing agent and micelle-swelling agent. Monolithic bodies with well-defined co-continuous macropores are results of concurrent phase separation and sol-gel transition induced by the polymerization reaction, whereas the mesopores are templated by the supramolecular assembly of the structure-directing agent. These biphasic polymeric gels polymerize spontaneously and simultaneously in a closed condition at a constant temperature. The following removal of surfactants by calcination gives silica gels with hierarchical and fully accessible pores in discrete size ranges of micrometer and nanometer. The well-ordered 2D-hexagonal arrays of mesopores have been confirmed by XRD measurements and FE-SEM images. Furthermore, by additions of larger amounts of micelle-swelling agent, the macroporous structure was induced without altering the 2D-hexagonal mesoporous structure. The microporous mesostructured arrays of mesoporous silica monoliths are non-porous while the pentylene-bridged polysilsesquioxane gels, prepared under the same conditions, are porous. We also discovered that the more reactive 1,6-bis(trimethoxysilyl)hexane could polymerize under acidic conditions to afford porous xerogels. In this study we have extended our study of bis(trimethoxysilyl)alkanes to the hexene-bridged polysilsesquioxane xerogels prepared from 1,6-bis(trimethoxysilyl)hexane under acidic conditions. The morphology of the resulting xerogels was characterized by nitrogen sorption porosimetry and electron microscopy. Solid state NMR was utilized to structurally characterize the materials.

**EEO.7**


We wish to present here a systematic study of the fundamental interactions associated with the formation of co-polysilsesquioxane xerogels, a unique family of hybrid organic-inorganic materials. These materials were prepared by the sol-gel polymerization of the corresponding alkylene- or arylene-bridged hexene-bridged polysilsesquioxane under relatively mild conditions (0.1 N NaOH or HCl catalyst, THF, and 6 equiv H2O) either as a homopolymer or as a copolymer. Gas sorption porosimetry, in conjunction with electron microscopy, will be used to graphically depict such dramatic effects as may manifest by alteration of the sol-gel catalyst. The focus of this presentation, however, will showcase the use of various solid-state NMR techniques to investigate the hydrocarbon spacer homogeneity, the structural identity of primary and secondary building blocks, and how these are affected by building block assembly to ultimately afford macromolecular andheteronuclear (FLS-GHETCOR) experiments were used to correlate all nuclei via the magic angle spinning chemical shift information in the direct dimension of 13C or 29Si and the isotropic CRAMPS information in the indirect dimension. Systematic variation of the contact time gave both temporal and spatial information concerning both spacer homogeneity and mobility. These results will be presented using Lee-Goldburg build-up curves and subsequent comparison with expected cross-polarization distance values. Cross-polarization correlation times will be discussed as pertinent to the differences in morphology of the gels. The two-dimensional 1H-1H Lee-Goldburg Combined Rotation and Multiple Pulse Spectroscopy (LG-CRAMPS) experiments were used to correlate 1H isotropic chemical shift information and 1H magic angle spinning information. And finally, selective deuteration incorporation into one spacer and subsequent analysis by the techniques just discussed will afford further insight into spacer homogeneity and overall spatial information of the hydrocarbon and silicate functionalities present within the xerogel.

**EEO.8**

**Polyfunctional phenylsilsesquioxane by modification of bromoaliphatics, Novel Nanoconstruction Sites, Mark Roll**, Richard M. Laine, Chad Brick and Michael Asuncion; *MSE, University of Michigan, Ann Arbor, Michigan,* Chemistry, University of Michigan, Ann Arbor, Michigan.

The introduction of organic substituents into sol-gel materials can often result in the networks that collapse during drying to afford non-porous xerogels. This can be useful if non-porous coatings or membranes are the ultimate objective. Collapse of porosity is also manifested in bridged polysilsesquioxane with flexible bridging groups. Alkylene-bridged polysilsesquioxane xerogels whose organic bridging group is an integral constituent of the network polymer can be systematically varied in length to probe its influence on the xerogels porosity and morphology. Our previous studies have shown that hexylene-bridged polysilsesquioxane xerogels prepared from 1,6-bis(trimethoxysilyl)hexane under acidic conditions are non-porous while the pentylylene-bridged polysilsesquioxane xerogels, prepared under the same conditions, are porous. We also discovered that the more reactive 1,6-bis(trimethoxysilyl)hexane could polymerize under acidic conditions to afford porous xerogels. In this study we have extended our study of bis(trimethoxysilyl)alkanes to the include the heptylene, octylene, nonylene, and decylene-bridges so as to examine at what bridging group length the polymer will collapse. The morphology of the resulting xerogels was characterized by nitrogen sorption porosimetry and electron microscopy. Solid state NMR was utilized to structurally characterize the materials.

**EEO.10**

**Alkylene and Arylene Bridged Polysilsesquioxane Aerogels**, Kimberly Ann DeFriend, Douglas A. Loy and James H. Small; Los Alamos National Laboratory, Los Alamos, New Mexico.

The introduction of organic substituents into sol-gel materials can often result in the networks that collapse during drying to afford non-porous xerogels. This can be useful if non-porous coatings or membranes are the ultimate objective. Collapse of porosity is also manifested in bridged polysilsesquioxane with flexible bridging groups. Alkylene-bridged polysilsesquioxane xerogels are hybrid xerogels, whose organic bridging group is an integral constituent of the network polymer that can be systematically varied in length to probe its influence on the xerogels porosity and morphology. Our previous studies have shown that hexylene-bridged polysilsesquioxane xerogels prepared from 1,6-bis(trimethoxysilyl)hexane under acidic conditions are non-porous while the pentylylene-bridged polysilsesquioxane xerogels, prepared under the same conditions, are porous. We also discovered that the more reactive 1,6-bis(trimethoxysilyl)hexane could polymerize under acidic conditions to afford porous xerogels. In this study we have extended our study of bis(trimethoxysilyl)alkanes to the include the heptylene, octylene, nonylene, and decylene-bridges so as to examine at what bridging group length the polymer will collapse. The morphology of the resulting xerogels was characterized by nitrogen sorption porosimetry and electron microscopy. Solid state NMR was utilized to structurally characterize the materials.
Bridged polysilsesquioxanes are an organic-inorganic hybrid siliceous-based material that offers the unique combination of silica-based gel to possess inorganic and organic characteristics. The composition of the bridging group, an arylene or alkylene group, affects the physical structure of the gel, whether the gel behaves more elastically or more robust, respectively. Super critically drying the gels with CO₂ affords organically bridged polysilsesquioxane aerogels. We will describe our efforts to synthesize arylene and alkylene bridged polysilsesquioxane aerogels. The aerogels will be synthesized through sol-gel polymerization of the bridge containing monomers and solvents, followed by super-critical CO₂ drying to afford the hybrid monolithic aerogels. Properties and characteristics of the resulting aerogels will be investigated.

CVD Modification of Low-Density Silica and Bridged Polysilsesquioxane Aerogels, Kimberly Ana DeFriend, Douglas A. Loy and James H. Small, Los Alamos National Laboratory, Los Alamos, New Mexico.

Silica and bridged polysilsesquioxane aerogels are transparent, low-density materials used in a wide range of applications, such as thermal insulation, porous separation media or catalyst supports, sorbents, and cometary dust capture agents. Silica aerogels can be composed a second metal, forming a mixed-metal oxide. Forming the mixed-metal oxide enhances the characteristics of the aerogels and broadens their ability to be used in additional applications. Here, we will describe our efforts to chemically modify and enhance the characteristics of inorganic/organic hybrid aerogels using chemical vapor techniques without sacrificing their characteristic low densities. Monolithic silica and organic-bridged polysilsesquioxane aerogels were prepared by sol-gel polymerization of the respective methoxysilane monomers followed by supercritical CO₂ drying of the gels. The gels were reactively modified with silylating agents or transition metal metal compounds to demonstrate the viability of CVD modification of aerogels, and to investigate the morphology, surface area, and mechanical properties of the modified aerogels.

Hierarchically Structured Silica Monoliths Carrying Organic Functions, Nicola Karola Huesing and Doris Brandhuber; Institute of Materials Chemistry, Vienna University of Technology, Vienna, Austria.

In the synthesis of mesostructured monoliths, diol- or polyol-modified silanes, such as tetrakis(2-hydroxyethyl)silane, have some distinct advantages compared to commercially available tetraalkoxysilanes, such as tetraethoxysilane, since they can be condensed without a co-solvent, under neutral conditions (no catalyst is required to start the sol-gel reactions), and the diols/polyols released upon hydrolysis show a very good compatibility with lyotropic phases of surfactant molecules. The materials obtained from polyol-modified silanes are characterized by a distinct ordering in the mesoscopic regime and a very unique microstructure. In this work, we present three different approaches towards the modification of the material prepared from polyol-modified groups: a) co-condensation reactions of polyol-modified tetraalkoxysilanes with the corresponding polyol-modified trialkoxysilanes e.g. phenyl- or methylsilanes, b) reaction of polyol-modified bridged silanes, e.g. bis(2-hydroxyethyl)silyl, and c) the posttreatment of materials prepared from polyol-modified silanes with organofunctional silanes, e.g. trimethoxy- or methacryloxy- or methacryloxyethylaminosilane, etc. For route a) the focus is on investigations of the reaction rates of the different precursors and the differences in the structure compared to an unmodified material. With respect to route b) the structural features of the material will be compared to one prepared from the corresponding ethoxy- or methoxyderivatives. Pathway c) not only allows to modify the monoliths with functional units, but in addition, offers an alternative to supercritical drying. The material is not only silylated, but the template is extracted simultaneously from the monolith and drying can be performed easily by heating. The final porous structure is interconnected with respect to its organic functions by elemental analyses, spectroscopic techniques such as IR and solid state NMR spectroscopy, and thermal analyses (TGA, DSC). Structural characterization is carried out by small angle X-ray scattering; electron microscopy (SEM, TEM), sorption techniques, and metal porosimetry.
tissues like wood or bone, artificial "bio-inspired" ceramic composites were fabricated. The goal of this work was to merge different approaches to tackle on the particular hierarchical levels (nanometer to micrometer range). On the one hand, nanostructured silica was synthesized using the sol-gel method with different precursors, such as tetramethyloxysilicate (TEOS), tetramethoxysilane (TMOS), diethoxysilane (DGEOS), and surfactants (Brij56, P23, CTAB) leading to mesoporous materials with or without implemented organic network. External fields were applied to influence the orientation of surfactant/surfactant systems while still in the liquid crystalline state. The macroscopic structure of the material was designed using organic moulds built by rapid prototyping (RP). This method provides enormous flexibility in realizing different nanostructured shapes. The precursor/surfactant mixtures are infiltrated into these sacrificial cellular RP moulds and polycondensation of silica was allowed to take place inside the template. Position resolved small-angle X-ray scattering (scanning SAXS) was used to investigate the nanostructured properties of the cellular nanostructured ceramics and tested and compared to those of cellular ceramics with different structures on the nanometer scale.

**EE9.10**

**A Novel Method for Rapid Formation of High-ordered Self-Assembled Monolayer. Yoshihisa Fujita**, Norifumi Nakamoto1, Hiroaki Takeda1, Tomoya Hidaka1, Nobuo Kimura1, Hiroshi Suzuki1, Nobuyuki Yoshimoto1 and Satoshi Ogawa1; 1Laboratory for High-Performance Sensors, Matsui Soda Co., Ltd., Ichihara, Japan; 2Graduate School of Engineering, Iwate University, Morioka, Japan; 3Faculty of Engineering, Iwate University, Morioka, Japan.

Self-assembled monolayers (SAMs) spontaneously form molecular films on certain materials surface and homogeneously covered a wide area. On the other hand, SAMs are rapidly and homogeneously formed on various inorganic surfaces with a high-order. ODMS was dissolved in toluene (10mM/kg) and the solution was saturated with water at about 500 ppm. One wa% toluene solution was prepared and stirred for 24 hours. (The initiator for the formation of the SAM was introduced in some metal oxides, M(Ti, Zr, Si ...)/ODMS = 0.1 mol/mol)) with stirring. Two hours later, the solution was filtered (1 μm glass filter) and saturated with water; then a clear ODMS-SAM solution was prepared. The washed Si substrate was cleaned with UV/ozone irradiation and immersed in the solution. After immersion, the substrate was washed by super-sonic waves in toluene and then dried. The process was done on other substrates such as, alkylamine, non-alkylamine, quartz and indium-tin oxide (ITO). All processes were done in air at room temperature. The water contact angle of all the substrate surfaces in the experiments was up to 105±1° after a minute immersion. The thickness estimated by super-sonic waves in toluene and then dried. The thickness estimated by super-sonic waves in toluene and then dried. The thickness estimated by super-sonic waves in toluene and then dried. The thickness estimated by super-sonic waves in toluene and then dried. The thickness estimated by super-sonic waves in toluene and then dried. The thickness estimated by super-sonic waves in toluene and then dried. The thickness estimated by super-sonic waves in toluene and then dried. The thickness estimated by super-sonic waves in toluene and then dried. The thickness estimated by super-sonic waves in toluene and then dried. The thickness estimated by super-sonic waves in toluene and then dried. The thickness estimated by super-sonic waves in toluene and then dried. The thickness estimated by super-sonic waves in toluene and then dried. The thickness estimated by super-sonic waves in toluene and then dried. The thickness estimated by super-sonic waves in toluene and then dried.

**EE9.17**

**Layer-by-Layer Surface Modification and Patterned Electrostatic Deposition of Quantum Dots. Saeeda Jaffar**, Ki Tae Nam1, Ali Khademhosseini1, Jia Xing1, Robert S. Langer1 and Angela M. Belcher1; 1Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2Bio Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 3Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Modification of quantum dot (QD) surfaces with polyelectrolyte coatings, and subsequent layer-by-layer deposition to build hierarchical structures is presented. Mercaptoacetic acid (MAA) treated QDs were adsorbed onto a polystyrene-coated amine (PAA) and polyvinylsulfonic acid (PVSA), and their properties were analyzed using zeta potentials, absorbance spectra and transmission electron microscopy. The modified QDs were deposited on patterned hyaluronic acid (HA) glass substrates to produce self-assembled heterostructures (QDs-MAA/QDs-PAA/HA/glass), as revealed by fluorescence and atomic force microscopy.

**EE9.18**

**LDH-DNA Nanohybrids: A Complete Biophysical Characterization. Fabrice Leroux**, M. Benbelhassen, G. Goutard, L. Desinge4, L. Dietrich1, P. Jachimiak2, C. Bellet1, G. Pitor1, C. Pitard1; 1Faculty of Chemistry, Universite Blaise Pascal, Aubiere, France; 2Laboratoire des Materiaux Inorganiques UMR 6002, Universite Blaise Pascal (Clermont-Ferrand II), Aubiere, France; 3Institut des Materiaux Jean Rouxel, Nantes, France; 4US335, Inserm, Nantes, France.

The successful intercalation of biological and drug molecules such as DNA, ATP or ibuprofen into layered double hydroxides (LDH) has led to consider their potential as drug or gene delivery carriers (1,2,3). In one approach developed by Chou(3), DNA-LDH hybrid can be obtained by simple ion-exchange upon substituting NO3 anions incorporated between hydronium layers. Alternatively, and to be demonstrated here, immobilization of DNA within LDH can be achieved by coprecipitation reaction in which the layered inorganic lattice and the intercalate of DNA are simultaneously formed. Well defined LDH-DNA nanohybrids were obtained by the coprecipitation method which allows to fine-tune the design of this new kind of inorganic delivery vector. In this work, we report a complete biophysical characterization of DNA-LDH hybrids obtained from magnesium-aluminium, magnesium-iron and magnesium-gallium LDH with double-stranded DNA fragments of various length and plasmid. The effect of LDH physico-chemical properties i.e. hydroxide layer composition and charge density on the DNA/LDH interaction was examined at the molecular level through the molecular orientation, size, and binding affinity. Many experiments have been performed to one end: ethidium bromide exclusion and gel retardation experiments, x-potential measurements, dynamic light scattering, circular dichroism, 31P NMR, IR spectroscopy and transmission electron microscopy. The main results of this study are that the colloidal stability and the morphology of DNA-LDH nanohybrids depend on the DNA/M3+ molar ratio (M3+ = Mg2+, Zn2+, Cd2+). On the other hand, it is strongly affected by the synthesis temperature as well as Mg2+/M3+ molar ratio leading to values ranging from 16 to 24 angstroms. FTIR and NMR spectroscopies suggest that DNA binding is mainly through the phosphate group, yet small spectral changes in the region of 1700-1500 cm⁻¹ may also indicate a participation of the carboxyl group of the DNA in the stabilization. References: (1) J.-H. CHOY, S.Y. KWAK, J.S. PARK, Y.J. JEONG, J. PORTIER J. Am. Chem Soc 121 (1999) 1386-1400; (2) V. AMBROGI, G. FARDIELLA, G. GRANDOLINI, L. PERIOLI Int. J. Pharm. 229 (2001) 29-32; (3) J.-H. CHOY J Phys Chem B 109 (2005) 273-283 and references therein.
organic radicals, whereas a contribution composed of several lines is present for (IV), which was refined by the presence of super hyperfine interactions between unpaired spins of neighboring oxygen nuclei. For the former, it is explained by a polymerization, for the latter by a dimerization occurring between monomer molecules. Additionally, electrochemical measurements were performed under potentiostatic mode in aprotic medium. The correlation between the different findings (electrochemistry vs ESR) will be presented. The thermal behavior of the hybrid materials are studied. Organic molecules are found to provide a clear enhancement of the structural stability in inorganic and organic assemblies, whereas a contribution composed of several lines is present for (IV), which was refined by a super hyperfine interaction between unpaired spins of neighboring oxygen nuclei.

Polymer/clay nanocomposites are of interest to both industry and academia, because these materials often have superior properties and are ideal systems for understanding polymer dynamics in nanometer-confined spaces. In this work, phase morphology and its relationship with polymerized composites (organic and inorganic), the assembly may appear as a mutual benefit.

**EE0.20**

**Influence of TiO2 on the Pore Structure and Texture of SIO2-PDMS Hybrid Materials**

Lucia Tellez1, Juan Rubio1, Miguel Valenzuela1, F. Rubio1, E. Morales1 and Jose Luis Otero1,

1Lab. Catalysis y Materiales, Instituto Politecnico Nacional, Mexico City, Mexico; 2Dpt. Ing. Metalurgica y Materiales, Instituto Politecnico Nacional (IPT), Mexico City, Mexico; 3Instituto de Ceramica y Vitrific, CSIC, Madrid, Spain.

SIO2-PDMS-TiO2 hybrid materials have been prepared by the Sol-Gel method using tetraethylorthosilicate (TEOS), silanol terminated (PDMS) and tetraethylortosilicate (TBT) as precursors. In this work, the influence of the TBT concentration in the final pore structure and texture of SIO2-PDMS-TiO2 hybrid materials was studied. These materials were characterized by means of nitrogen adsorption, mercury porosimetry and helium pycnometry. All samples show micro, meso and macroporosity. The microporosity is constituted by ultra and supermicropores. Meso and macroporosity are predominant in all studied samples. The increase in TBT concentration decreases the pore volume of micropores, mesopores and macropores and promotes the decreasing of specific surface area of all samples. However, it is also observed that at the specific surface area of meso and macropores decreases but increasing of specific surface of micropores. This is attributed to the formation of ultramicropores. Surface roughness increases with the increase of TBT concentration due to the creation of oxide-based nanoparticles. The presence of TiO2 also changes the connectivity between poros and their average linear dimensions.

**EE0.21**

**Wear Properties of Carbon Nanotube-Filled Ultra High Molecular Weight Polyethylene Prepared by in-situ Ziegler-Natta Polymerization. Hong-Jo Park1, Seung-Youp Kwak1 and Soongjong Kwak1,**

1Material Science & Engineering, Seoul National University, Seoul, South Korea; 2Polymer Hybrid Research Center, Korea Institute of Science and Technology, Seoul, South Korea.

Ultra high molecular weight polyethylene (UHMWPE) has been recognized as a most suitable bearing material for artificial joints implanted in human body. Chief operation of artificial joints is a sliding action between soft UHMWPE and hard femoral material that is metal or ceramic. Therefore, wear behavior of UHMWPE, which is one of the most important factors determining the durability of artificial joints. UHMWPE filled with ceramic or metal filler has displayed improved wear properties where a dispersion state of the filler in the UHMWPE matrix is of great importance for proper wear performance of the composites. In this study, we have polymerized UHMWPE/carbon nanotube (CNT) composites through in-situ Ziegler-Natta polymerization method and investigated their wear behaviors. Fixation of catalyst on the surface of CNT and polymerization of ethylene were consecutively carried out in a pressure reactor. When compared at the same CNT content, polymerized composite displayed higher tensile modulus and yield strength than traditionally blended composites. Load test was performed on a ring-on-block type apparatus without lubrication. Wear rate of the polymerized composites was significantly lower than unfilled UHMWPE and mechanically blended composites. Scanning electron microscopy (SEM) observations of fractal surfaces of wear specimens showed that the wear mechanisms of the polymerized composites are totally different from those of unfilled UHMWPE. The neat UHMWPE showed a ploughing wear, which is well known to result from the abrasive removal of soft UHMWPE. The ploughing wear was greatly suppressed for the CNT-filled composites, which is supposed to result from the increase in surface hardness and subsequent suppression in abrasive wear. It is believed that uniform dispersion of CNT and improved interfacial properties produced in the in-situ polymerization are the main factors leading to the superior mechanical and tribological properties of the polymerized composites.

**EE0.22**

**Two-step De-intercalation and Intercalation Induced by Polymer Crystallization and Melting in Poly(ethylene oxide)/Organo clay Nanocomposites. La Sun1, Lei Zhu1, Jianjun Miao1, Carlos A. Avilla-Orta2, Igos Sics2 and Benjamin S. Hsiao2,**

1Institute of Materials Science and Department of Chemical Engineering, University of Connecticut; 2Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York.

Polymer/clay nanocomposites are of interest to both industry and academia, because these materials often have superior properties and are ideal systems for understanding polymer dynamics in nanometer-confined spaces. In this work, phase morphology and its relationship with polymerized composites (organic and inorganic), the assembly may appear as a mutual benefit.

**EE0.23**

**Coordination Compound Molecular Sieve Membranes. Jonguk Won, of Applied Chemistry, Seoul University, Seoul, South Korea.**

Highly selective coordination compound molecular sieve composite membranes have been prepared using well dispersions of porous transition metal complexes confined within amorphous glassy polysulfone. The new approach reported here is a promising method for constructing organic sieve molecular sieve membranes, which have an extremely high selectivity for the molecular sieve composite membranes. Therefore, the membrane has a high potential to contribute to produce a renewable energy source, hydrogen from the hydrogen plant, in which hydrogen is produced by reforming hydrocarbon feedstock, such as CH4.

**EE0.24**

**Vanadium oxide nanotubes: new synthesis routes and mechanisms of formation. Maria C. Cassaignon; Thieary Azais, Jean-Pierre Jolivet and Jacques Livage; Chimie de la Materie Condensee, University Paris 6, Ile de France, France.**

Vanadium oxide based materials have been extensively studied during the past decades due to their electrical, magnetic, catalytic and electrochemical properties. Hybrid organic-inorganic vanadium oxides have been synthesized by the sol-gel process, which are stable under mild hydrothermal conditions. Depending on the nature of the species present in the reaction medium, they may exhibit a wide range of structures and morphologies that are crucial to the performance of the materials in applications. In particular, vanadium oxide based phases are interesting materials for the mild oxidation of light alkanes.
Recently, mesostructured vanadium oxides with a tubular morphology have been synthesized in the presence of long alky1 chain amines [1]. These vanadium oxides nanotubes and nanoscrolls with thick walls composed of sheets packs of several vanadium oxide layers.[2] The anisotropic tubular shape is expected to lead to unusual physical and chemical properties. This communication deals with the synthesis of nanotube-like vanadium oxides from V2O5-nH2O gels and hexadecylamine. V2O5-nH2O gels are synthesized via the reaction of crystalline V2O5 with H2O2. Another synthesis route is also proposed and is based on the incorporation of phosphate groups into the network of the vanadium oxide nanotube. The different V2O5 nanotubes were characterized by X-ray diffraction, scanning and transmission electron microscopy and 23V (or 31P) solid state NMR. In-situ experiments were performed in order to get a better understanding of the mechanism of these nanotubes formation. References [1] Krumeich, F., Muhr, H.-J., Niederberger, M., Bieri, F., Schnyder, B., Nesper, R. J. Am. Chem. Soc., 121 (1999) 8824 Niederberger, M., Muhr, H.-J., Krumeich, F., Bieri, F., Gunther, D., Nesper, R. Chem. Mater., 12 (2000) 1995 Muhr, H.-J., Krumeich, F., Schnorholtzer, U.P., Bieri, F., Niederberger M., Gauckler, L.J., Nesper, R. Adv. Mater. 12 (2000) 261

**EE9.26**

*Synthesis of molecular building blocks containing 2,6-dicarboxypyridine units for the design of porous crystalline solids, Kasim Biyikli, Joseph C. Busch and John C. MacDonald, Chemistry & Biochemistry, Worcester Polytechnic Institute, Worcester, Massachusetts.*

We are investigating a family of supramolecular building blocks to construct solid porous microporous materials. We have shown previously that complexes between mono- and bis-2,6-dicarboxypyridines and transition or lanthanide metals assemble through metal-ligand coordination and hydrogen bonding into two-dimentional, three-dimentional scaffolds several of which show modest porosity. Current efforts in our laboratory focus on the synthesis of large tetrahedral building blocks that self-assemble via metal-ligand coordination. Molecular building blocks that we are pursuing consist of two different 2,6-dicarboxypyridine units linked covalently to acetylene units in a symmetrical arrangement around a tetrahedral core. We currently are using several different approaches to synthesize tetrahedral molecules that utilize Sonogashira coupling to acetylene units to acyclic compounds which are characterized by NMR and IR spectroscopy. These compounds will provide large tetrahedral building blocks that bind transition metals at each of the four 2,6-dicarboxypyridine units. Metal-ligand coordination in this manner will permit the molecular assembly in three dimensions. We expect the resulting metal-organic frameworks to have a diamondoid structure that features large channels.

**Abstract Withdrawn**

**EE9.30**

*Comparison of the Electrical and Mechanical and Morphological Properties of Polymer Nanocomposites Made from Multiwall Carbon Nanotubes (MWN) and Nickel Nanostrands (NS), Max D. Alexander, George Hansen 2, Heather J. Petry 1, Brandon Black 1, and Darrin J. Pochan 1,2. Materials Science and Engineering, University of Dayton Research Institute, Dayton, Ohio; 2Polymer Branch, Air Force Research Laboratory, Dayton, Ohio.*

Here we explore polymer / inorganic nanocomposites based on a new high aspect ratio nano-material, nickel Nanostrands and compare the electrical, and mechanical behavior to that of multiwall nanotube composites. The nanostrands have a large aspect ratio but are made of solid nickel and can be readily produced in large quantities. The volume content of the nanostrands in a polyurethane matrix was varied from 0.1% to 20% to characterize the percolation behavior of the system. DC electrical characterization was performed at room and elevated temperatures as a function of polymer elongation. Identical loadings and dispersion technique were used for the multiwall nanotubes allowing for one to one performance characterization. The nanostrands were found to produce
conductivities substantially higher than the corresponding carbon nanotube composites and had the added advantage easily imparting a tailored orientation of the nano-element by the use of magnetically assisted processing.

**EF0.31**  
Layered Tungsten Oxide-Based Hybrid Materials  
Incorporating Transition Metal Ions. B. Ingham, Shen Yun Chong and J. L. Tallon; 1 Victoria University of Wellington, Wellington, New Zealand; 2 Industrial Research Limited, Lower Hutt, New Zealand.

A number of transition metal tungsates, M₂WO₄, are known to exist; many of which occur naturally as pure or mixed tungsate ores (e.g. wolframite, ferberite, stolite). The M₂WO₄ species primarily form either in the wolframite or the scheelite structure, depending on the size of the M²⁺ ion. Recent work by our group on tungsten oxide-based hybrid materials - consisting of layers of corner-shared WO₄-octahedra separated by organic amine/aminomonomer spacer molecules - has led us to explore the possible incorporation of transition metal ions within the hybrid structure, and/or the formation of new layered structures altogether. The materials were produced by a solution-based method and characterised by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), infrared and Raman spectroscopy, and magnetisation measurements. Preliminary results of manganese tungstate oxide-diaminoalkane hybrids show that this system has interesting properties. XRD and SEM of these new hybrids strongly indicate the presence of a layered structure, and magnetisation results show an antiferromagnetic transition at low temperatures. The transition temperature decreases with increasing chain length, which corresponds to the inter-inorganic layer spacing. This indicates a crossover from 2-dimensional to 3-dimensional magnetic behaviour, which is frustrated as the distance between the layers is increased.

**EF0.32**  
Intercalation of n-Alkylamines in the Vapor Phase into Vanadium Pentoxide Xerogel Dispersed into Silica Matrix.  
Reinaldo Paulo Oliveira and Maria Alves Figueiredo; Quimica, Universidade de Sao Paulo/EFCLIP, Ribeirao Preto, Sao Paulo, Brazil.

Over the past twenty years, the interest in the host-guest chemistry has mushroomed, mainly due to the large number of applications in energy storage, catalysts, adsorbents, optical devices, etc. In this work, we report a new intercalation reaction: three different n-alkylamines (n-butylanine, n-hexylamine and n-octylamine), in vapor phase, were intercalated into free vanadium pentoxide xerogel and into this lamellar material homogeneously dispersed into Si-O-Si network (obtained by polycrystallization of the silicon alkoxide) vapormorphinated with V-O-V and V-OH-V polymeric chains previously formed by oxidation and alation reactions. The reaction with non-dispersed xerogel leads to the increase of interlamellar distance for low time of reaction (up to 2 hours) and after 24 hours we observed a new phase. In contrast, for the reaction with xerogel dispersed in silica, it was observed only the increase of the basal distance retaining the original bi-dimensional structure (001 diffractions lines were observed); suggesting that the silica matrix stabilizes the vanadium pentoxide xerogel intercalation due to the cross-linking and entanglement of both components. The reactions were monitored using powder X-ray diffraction, infrared and electronic spectroscopy, electron paramagnetic resonance and scanning electron microscopy. Electrochemical properties were also investigated. Acknowledgment: Fundacao de Amparo a Pesquisa do Estado de Sao Paulo (fellowship no 02/12378-8 and grant no 01/1527-5).

**EF0.33**  
Control of the Morphology of the Layered-Silicate Epoxy Nanocomposite. Chenggang Chen and Tia Benson-Tolle; 1 University of Dayton Research Institute, Dayton, Ohio; 2 Air Force Research laboratory, Wright-Patterson Air Force Base, Ohio.

Polymer-layered-silicate nanocomposite has attracted great attention due to its unique nanostructure and properties. The property of the nanocomposite is determined by the morphology of the nanocomposite. The typical morphologies of the nanocomposite are the intercalated and exfoliated nanostructure. In this study, the layered-silicate epoxy nanocomposite with different morphology can be controlled. The different morphology could include the intercalated nanostructure with the 15 A-increase of the interplanar spacing, the intercalated one with 150 A-increase of the gallery and fully exfoliated nanostructure.

**EF0.34**  
The Structure of a Molybdenum Disulfide Intercalation Compound. Ralph Bruning, Kristopher Bulmer, Rabin Bissessur, Pravin Varma and Stephen Emeneau; 1 Physics Department, Alliston Allison University, Sackville, New Brunswick, Canada; 2 Department of Chemistry, University of Prince Edward Island, Charlottetown, Prince Edward Island, Canada.

The x-ray powder diffraction spectrum of molybdenum disulfide with intercalated tetrazamocrocycle molecule was simulated. The measured spectrum shows well-defined peaks and broad scattering. Model crystallites were generated using a computer program, and the x-ray spectra corresponding to these trial structures were calculated by Fourier transforming the Debye sum. The match between the experimental and simulated spectra was improved by a trial-and-error procedure. Matching the peak widths shows that the crystallites contain typically 6500 MoS₂ units in about nine layers. While in the layers in the best model structure are oriented in the same direction (unidirectional), they are translated randomly in the plane perpendicular to the stacking direction. In contrast to prior work on intercalation compounds, which suggests various types of periodic reconstruction within the MoS₂ layer, we obtained the best match with a non-periodic reconstruction. It involves triangular and hexagonal groupings of the molybdenum atoms with a random choice of centers. This type of reconstruction reproduces the experimentally observed broad scattering in detail.

**EF0.35**  
Effects of Surface Modification of Mg(OH)₂ with Polysiloxane Oil and Silica Additive on the Flame Retardancy and Mechanical Properties of LDPE-Mg(OH)₂ Composites. Koji Kodama, Makoto Egashira, Yasuhiro Shimizu and Takeo Hyodo; 1 Faculty of Engineering, Nagasaki University, Nagasaki, Nagasaki, Japan; 2 Material R&D Center, Yanaki Parts Co., Ltd, Susono, Shizuoka, Japan.

Magnesium hydroxide is considered to be a promising filler for polymer-based composites from the viewpoints of no generation of corrosive and toxic gases upon firing. To achieve sufficient flame retardancy, however, a high loading level of Mg(OH)₂ is requested, and this results in degradation of mechanical properties of the composites, such as elongation and impact strength, due to poor affinity between nonpolar polymeric matrix and Mg(OH)₂ powder. Therefore, special attention is being paid on the surface modification of Mg(OH)₂ powder which enables us to realize a high loading level along with sufficient mechanical properties. Our recent studies have revealed that the addition of anhydrous silica treated with methyl grope (M-silica) to the composites of low-density polyethylene (LDPE) and commercial magnesium hydroxide powder treated with stearylic acid (Magnifin HSC, Allemane Corporation) could improve flame retardancy, and that the surface treatment of Mg(OH)₂ with methylhydrogen polysiloxane (MHS) was effective for improving flame retardancy without any degradation of mechanical properties (LDPE-Mg(OH)₂ composites. In the present study, therefore, synergistic effects of the surface modification with MHS and the M-silica addition on the properties of LDPE-based composites have been investigated. For comparative purpose, another series of composites was also prepared with Magnifin HSC. When comparison was made at the addition of 40 wt% Mg(OH)₂ only, the composite with MHS-treated Mg(OH)₂ was superior to that with Magnifin HSC from the viewpoints of oxygen index and large elongation with yield strength which were comparable to each other. With increasing the additive amount of M-silica at a fixed total filler content of 40 wt%, oxygen index and yield strength increased accordingly in both the composite series. However, elongation tended to decrease beyond 3 wt% M-silica in the case of the MHS-treated Mg(OH)₂ composite, whereas it increased up to 2 wt% M-silica and beyond that reached a saturated value for the Magnifin HSC composite. As a result, the MHS-treated Mg(OH)₂ composite showed a smaller elongation value than the Magnifin HSC composite at 5 wt% M-silica. In the next step, therefore, the effect of the total filler content on the composite properties was tested, while maintaining the additive amount of M-silica to be 12.5 wt% of the total filler content. Elongation could be improved, while maintaining a high oxygen index value of 24.6%, by the decrease in the total filler content from 40 to 35 wt% in the case of the MHS-treated Mg(OH)₂ composite. Thus, the MHS-treated Mg(OH)₂ composite showed higher oxygen index than the Magnifin HSC composite and comparative elongation and yield strength at the total filler content of 35 wt%. This result enabled us to reduce the total filler content with maintaining improved oxygen index and suppressing the degradation of elongation by the synergistic effect.
in a sodium exchanged Montmorillonite clay aerogel. Encapsulation of the aerogel with polymer leads to a slight change in the d-spacing from 12.5 to 12.8 Å. The composite shows reversible swelling behavior in water and demonstrates thermo-responsive properties of the polymer which undergoes a phase change at LCST (30-32°C). The interpenetrating structure of the polymer network through the low density access provides the aerogel a higher internal surface area even submerged under water for extended periods; without the polymer, the aerogel loses its structure in water. Composites of various copolymer compositions are reported. Such aerogels-hydrogel composites may be used as air-pore imprints, trapping slow neutrals with the use of Cd clay, as insulating materials and for chromatography.

**EE9.27**

**Self-Directed Assembly of Mesoscopically Ordered Polydiacetylene/Silica Nanocomposites from Bridged Silsesquioxanes.** Huisheng Peng, Jiebin Pang and Yunfeng Lu; Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana.

Sol-gel chemistry opens new routes for designing hybrid organic-inorganic materials with novel properties. Recently, in an effort to better control structure and function, surfactant-directed co-assembly or self-directed assembly has been used to synthesize hierarchical organo-bridged polysilsesquioxanes that exhibit order over multiple length scales. In this work, we report the preparation of highly ordered polydiacetylene/silica nanocomposites with reversible or irreversible color changes by self-assembly of diacetylenic bridged silsesquioxanes without or using surfactants. The bridged silsesquioxanes were prepared by the reaction of diacetylenic diol (or acids) with 1H,2H,3H-trimethylsilylpropyne. After the bridged silsesquioxanes were subjected to acid hydrolysis with HCl in a 3:2 volume mixture of THF and water, the self-assembled supramolecular products were obtained by casting the resulting solutions on glass slides followed by evaporation of solvent. The PDA/silica nanocomposites were characterized by powder X-ray diffraction (XRD), transmission electron microscope (TEM) and ultra violet-visible (UV-vis) spectrophotometer. The XRD patterns exhibit sharp peaks that indicate the materials with highly ordered lamellar or hexagonal structures. TEM analysis further confirms the lamellar or hexagonal structure of the diacetylene/silica nanocomposites. The reversible or irreversible thermochromatic transition was investigated by UV spectroscopy. The results showed the adsorption maximum at about 652 nm for films with blue color and 541 nm for those with red color. Subsequent heating of the samples caused a reversible or irreversible blue to red thermochromic transition. The PDA/silica nanocomposites were characterized by powder X-ray diffraction (XRD), transmission electron microscope (TEM) and ultra violet-visible (UV-vis) spectrophotometer. The XRD patterns exhibit sharp peaks that indicate the materials with highly ordered lamellar or hexagonal structures. TEM analysis further confirms the lamellar or hexagonal structure of the diacetylene/silica nanocomposites. The reversible or irreversible thermochromatic transition was investigated by UV spectroscopy. The results showed the adsorption maximum at about 652 nm for films with blue color and 541 nm for those with red color. Subsequent heating of the samples caused a reversible or irreversible blue to red thermochromic transition.

**EE9.38**

**Control on the Morphology and Polymorph Selectivity in Carbonate Mineralization.** Suresh Valiyaveetil1,2,3, Sindhu Swaminathan2 and Parayil Kumaran Ajikumar2; 1Chemistry, National University of Singapore, Singapore, Singapore; 2Singapore National Research Foundation and NUS Nanoscience and Nanotechnology Initiative (NUSNNI), National University of Singapore, Singapore, Singapore; 3Singapore - MIT Alliance (SMA), National University of Singapore, Singapore, Singapore.

Understanding the process of biomineralization of calcium salts is an interesting theme owing to its perceived importance in restorative surgeries. Recently, we have investigated a few systems involving both soluble and insoluble templates for the nucleation of calcium salt crystals. In this presentation, we will describe our recent results from our lab in which polypeptides are used for the mineralization and morphology control of crystalline calcium carbonate. The present talk will focus on detailed account of the crystallization conditions and the influence of various additives on morphology as well as full crystallization of the crystals nucleated.

**EE9.39**

**Pyridine on Si(100) and H-Si(100) - STM observation of dative bonded adducts.** Jill Minn1, Brian Eves1, Federico Rosei1, Gregory Lopinski2,3; 1INRS-EMT, University of Quebec, Varennes, Quebec, Canada; 2Stacie Institute of Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada.

The potential of fabricating nanoscale hybrid organic/silicon molecular devices has stimulated considerable interest in understanding the interaction of organic molecules with silicon surfaces [1]. Unsatuated species react readily with the dimers of the Si(100)-2×1 surface, forming Si-C bonds. Nitrogen containing species can additionally form dative bonded adducts, which involve donation of the N lone pair electrons to the silicon surface [2,3]. In this work we present scanning tunneling studies of pyridine (or pyridine-derivatives) on Si(100). On the clean surface, low coverage images clearly show that pyridine binds primarily via formation of a dative bond. The resulting charge transfer complex, imaged as paired protrusions on the single dimer, gradually turns to a species similar to the 'light-bridge' binding motif, reported previously for benzene adsorption on this surface [4]. The bridge structure is distinguished by its characteristic two dimer footprint. Back conversions to the dative species are observed when the sample is exposed to air. Such highly ordered polydiacetylene/silica nanocomposites with reversible or irreversible thermochromatic transition were investigated by UV spectroscopy. The results showed the adsorption maximum at about 652 nm for films with blue color and 541 nm for those with red color. Subsequent heating of the samples caused a reversible or irreversible blue to red thermochromic transition. The PDA/silica nanocomposites were characterized by powder X-ray diffraction (XRD), transmission electron microscope (TEM) and ultra violet-visible (UV-vis) spectrophotometer. The XRD patterns exhibit sharp peaks that indicate the materials with highly ordered lamellar or hexagonal structures. TEM analysis further confirms the lamellar or hexagonal structure of the diacetylene/silica nanocomposites. The reversible or irreversible thermochromatic transition was investigated by UV spectroscopy. The results showed the adsorption maximum at about 652 nm for films with blue color and 541 nm for those with red color. In conclusion, this work demonstrates a powerful and clean way of producing highly ordered and mechanically robust conducting polymer-based optoelectronic materials with applications ranging from light-emitting diodes to biomolecular sensors.

**EE9.40**

**Structure and Nanomechanical Properties of Electrosynthesized Polystyrene/Clay Nanofibers.** Yuan Ji1, Shouren Ge1, Bingquan Li1, Tohru Araki2, Harald Ade2, Jonathan Sokolov3 and Miriam Rafaelovich1; 1Materials Science and Engineering, SUNY at Stony Brook, Stony Brook, New York; 2Physics, North Carolina State University, Raleigh, North Carolina.

Poly(styrene)/clay nanofibers can be fabricated successfully using an electrosprinning technique. Polystyrene/clay nanocomposites with different clay concentrations (4, 8, 12 wt%) were synthesized by mixing solution of tetrahydrofuran and N, N-dimethylformamide and then electrosynthesized to form fibers with diameters ranging from 150nm to 10um by selectively controlling the solution concentration and solvent composition. The structure and morphology of electrosynthesized PS/clay fibers were investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning transmission x-ray microscopy (STXM) and atomic force microscopy (AFM). SEM and AFM pictures showed that the surface morphology changes from ridge like structure (with clay) to a ridge like structure (with clay). STXM and TEM pictures showed that electrosprinning can induce chain orientation in electrosynthesized fibers and clay exfoliation can be found in electrosynthesized fibers at a concentration of 4 wt%. Shear modulation force microscopy (SMFM) was used to investigate the relative modulus of electrosynthesized fibers as a function of fiber diameter and temperature. Results indicated that modulus of fibers increases relative to bulk fibers with decreasing fiber diameter when temperature is lower than glass transition temperature (Tg). Modulus of fibers can be restored to bulk value when temperature is higher than Tg due to the change from polystyrene to polystyrene/Ca clay composite. This was consistent with STXM results. Tg measurement by SMFM showed that electrosynthesized fibers had a higher Tg than the bulk film when clay exfoliated at a concentration of 4%. Supported by NSF MRSEC 1037 (1998).

**EE9.41**

**Synthesis and Characterization of Mesoscopic Silica/ Hydrogel Composites.** Donghai Wang, Nurettin Sahiner, Lynn Rice, Vijay John and Yunfeng Lu; Chemical Engineering, Tulane University, New Orleans, Louisiana.

It is known that organic/inorganic hybrid nanomaterials can be synthesized by incorporating the polymer into a performed nanostructured material or vice versa, which possesses synergistic properties for wide applications. Hydrogel can respond to some external stimuli such as temperature, pH, electric field, etc. For example, hydrogels can swell to form superporous networks with the response of pH changes. Calcium silicate nanofibers spontaneously constructs highly ordered mesostructured liquid crystal phase and thus form ordered mesoporous silicil after removal of surfactants. Here we present synthesis and characterization of mesoscopic silica/hydrogel hybrid nanocomposites. Hydrogel have been prepared via redox and/or UV irradiation polymerization from cationic, anionic, and neutral monomers. Mesoscopic silica can be introduced into hydrogel superporous networks when the hydrogel swell at the appropriate conditions such as pH, solvent, and hydrogel types. Cooperative assembly of silica/surfactant nucleates at the liquid/polymer interface within hydrogel superporous networks and form hybrid nanocomposites after hydrogel shrinks. For mesoscopic silica/hydrogel nanocomposites characterization, swelling and pH responses behaviors were investigated, and SEM, TEM and BET measurement were employed to elucidate the mesoscopic silica/hydrogel nanocomposite structure. The nanocomposite morphology can be controlled from mesoporous films, to monoliths

Functionalization often (adversely!) affects the synthesis, order, spectra to compare and contrast the ordering and surfaces. We are also using similar functionalization in exploring the use of CVD treatments of silica aerogels with carbon dioxide. The nanocomposites were characterized by SEM, TEM, X-ray Diffraction (XRD), TGA, and DMA, and showed this general route allows for clean synthesis of nanocomposites with inorganic filler, but also an effective stabilizer for PMMA growth in pseudo-dispersion polymerization in Supercritical carbon dioxide. Jet is subsequently stretched to form a continuous fiber. Before it reaches the collecting screen the solvent evaporates or solidifies, and the fibers are collected on a conductor surface. They form nonwoven mats characterized by high surface area and pore sizes. This method has been utilized in creating metal oxide semiconductor, and biological composite nanofibers. Differently proportioned mixtures of metal oxide sol gel solutions (MoO3,WO3) with Polyvinylpyrrolidone (PVP) solution were electrospun. Metal oxide composite nanowires of both molybdenum and tungsten were created. The process of electrospinning can be controlled through different parameters such as solute composition, flow rate, voltage, and needle to collector distance. The as received samples obtained were compared in terms of average diameter when concentration, and flow rate were varied, while other parameters kept constant. The Scanning Electron Microscopy and Transmission Electron Microscopy studies proved the diameter of as received composite samples is inversely proportional to the metal oxide concentration. It was also concluded that it is directly proportional to the flow rate. Self-supported one-dimensional metal oxide nanomaterials were obtained through heat treatment of as received samples deposited on Silicon Nitride grids. The TEM images of post heat treatment confirmed both Tungsten and Molybdenum Oxide one-dimensional nanowires were achieved through this process.


Silica aerogels are prepared by the supercritical drying of gels obtained from the sol-gel polymerization of alkoxysilane monomers under critical condition. These materials, which possess surface areas over 1000 meters squared per gram and densities as low as 3 milligrams per cubic centimeter, have been used as insulation, radiation detectors and as a component in targets used in inertially confined fusion experiments. The low density of silica aerogels also makes these materials fragile and difficult to handle, with shapes having to be molded in place rather than machined. We have been exploring the use of CVD treatments of silica aerogels with polymeric organic monomers to create nanocomposite structures with improved mechanical properties. Surface area (nitrogen porosity), density, and compression strength measurements were performed on the samples to determine before and after properties. Polypropylene and carbon NMI monomers were used to characterize the structure of the coating as well as serve to compare treated and untreated materials. Changes to the samples were also observed by optical microscopy. The ultimate aim of this research is to produce machinable, low density aerogels.
Vinyl ester resins are used as a thermoset matrix for glass fiber reinforced composites. These composites are used for a variety of uses, especially in civil engineering and for industrial applications. In this presentation, we will describe the modification of vinyl ester resins with nanoclays. We have investigated the effects of clay type, synthesis routes and the type of vinyl ester on the morphology, thermal, tensile and fracture properties of vinyl ester/clay nanocomposites. We obtained an intercalated morphology with d-spacings expanded to twice that of pristine clay. The nanocomposites made by adding clay before casting clay after the esterification step during vinyl ester synthesis had slightly better intercalation than those made by adding clay before esterification. However, the difference did not lead to a significant impact on the properties. All nanocomposites had a higher glassy and plateau modulus than the unmodified resin. The nanocomposites had a similar Tg and higher fracture toughness compared to the unmodified resin. The analysis of the fracture surface also suggested that nanocomposites has a higher fracture toughness than the unmodified resin. All nanocomposites had a lower elongation to break than the unmodified resin. The clay clusters found in the nanocomposites may act as stress concentrators and may be responsible for the low elongation to break.

**EE0.49 Abstract Withdrawn**

SESSION EE10: Organosilicon-based Polymers
Chairs: Clement Sanchez and Ulrich Wiesner
Thursday Morning, December 2, 2004
Room 302 (Hynes)

8:30 AM *EE10.1

Polysilane is a well-known functional organosilicon polymer with a high quantum efficiency of photoluminescence (PL), a high hole drift mobility, a significant photobreaching property, etc., which are associated with σ-conjugation along the Si-Si main chain. On the other hand, polysilanes in hybrid sol-gel matrices, such as polysilane/polymer hybrids (PMPS) is molecularly dispersed in inorganic matrix, might be an attractive material. For the preparation of polysilane/inorganic hybrid materials, a chemical modification of PMPS is essential to interaction or reaction with metal alkoxides in a sol-gel reaction. Polysilane block copolymers with reactive groups were synthesized by the photoinitiated polymerization of functional vinyl monomers using PMPS as a macro-photo-initiator. The polysilane/silica hybrid thin films were prepared from the PMPS-trialkoxysilylpropylmethacrylate copolymer and tetraethoxysilane via sol-gel reaction, in which PMPS segments are homogeneously embedded in silica matrix. These exhibited unique and interesting photodegradable properties: refractive indices and the energy migration became lower and PMPS segments protected the PMPS concentration in the hybrid thin films. The photo-decomposition of PMPS segments in polysilane/inorganic hybrid caused the significant changes for the optical, chemical, and morphological characteristics. It was found that a refractive index of the hybrid thin films changed due to the photo-decomposition of PMPS segments. The fixation of high refractive index difference (ca. 3.5%) on the polysilane/silica hybrid thin films was also investigated. This reactive index change seems to be effective for important applications, such as periodic optical waveguides, distributed feedback lasers, etc. Furthermore, as the PMPS copolymers had a photo-reducing characteristics, Au (III) ions in hydrogen chloroaurate were reduced to gold nano particles (5nm diameter) by using polysilane-acrylamide copolymer under UV irradiation. In this reaction, polyacrylamide segments acted as the protecting groups for gold nano-particles. The color changed to reddish purple resulted from the plasmon resonance of gold nanoparticles. During photo-reduction of Au ions, the silanol derived from photolysis of PMPS segments functioned as reactive components in the sol-gel reaction and provided the gold nano particles thin films. And, the negative pattern of gold nanoparticles was successfully fabricated by UV irradiation through a photomask.

9:00 AM EE10.2
Crystallization of POSS in a PEO-Based Multiblock Polyurethane Architecture. Jian Wu1, Qing Ge2, Kelly A. Burkel1 and Patrick T. Mather2,1, 1Chemical Engineering Department, University of Connecticut, Storrs, Connecticut; 2Institute of Materials Science, University of Connecticut, Storrs, Connecticut.

To date, polyhedral oligosilsesquioxanes (POSS) have been incorporated into a wide range of polymeric systems, either as a molecular-level filler or as a comonomer, but usually without ordering of the POSS moieties as evidenced by x-ray diffraction analysis. Building upon earlier success in forming materials with crystalline ordering of POSS via the telechelic architecture with Polyethylene Oxide (PEO) end-capping polyethylene glycols, here we report similar ordering in PEO-POSS thermostable polyurethanes. Thus, a unique series of thermostable polyurethanes (TPU) were synthesized using polyethylene glycol (PEG) and incorporating an iso-butyl-functionalized POSS diol (TIP POSS diol) in the hard segment. The molecular weight of PEG was systematically varied to include 10, 20, and 35 kDa while the mole ratio of PEG to TIP POSS diol (PEG/POSS) was held constant. The disocyanate employed for TPU polymerization was 4,4’-methylenebis(phenyl-isocyanate) (MDI). Wide-angle x-ray diffraction (WAXD) studies revealed that both the hydrophilic soft segments (PEG) and hydrophobic hard segments (POSS) can form crystalline structures driven by micro-phase separation, itself due to thermodynamic incompatibility. As molecular reinforcements, the presence of nanoscale POSS crystals remarkably improves the mechanical properties of the new TPUs. To be consistent with common stress-strain behaviors, stress-strain curves of the new POSS-based TPUs show a clear necking-based yield and large strain-to-failure. During deformation, reflection peaks attributed to PEG crystals unusually features two kinds of orientation of the POSS crystallization and postulate other polymeric architectures that might favor POSS organization.

9:15 AM *EE10.3
Evolution of Porosity and Morphology in Alkylene-Bridged Polysilsesquioxane Xerogels as a Function of Gel Aging Time. Douglas Aman Log1, James H. Small1, Kimberly A. Defriend2, McKenzie Mink3, Colleen R. Baugher2, Brigitta M. Baugher2, Duane A. Schneider2 and Kenneth J. Shees1, 1Polymers and Coatings Department, Los Alamos National Laboratory, Los Alamos, New Mexico; 2Sandin National Laboratories, Albuquerque, New Mexico; 3Department of Chemistry, University of California, Irvine, California.

Aging of silica gels before drying is known to result in significant changes in xerogel morphology, porosity and properties. In this study, the influence of aging gels on the porosity and morphology of alkylene-bridged polysilsesquioxane xerogels was examined. Gels of hexylene-, heptylene, octylene, nonylene, and decylene-bridged polysilsesquioxane xerogels were synthesized using the respective bis(trimethoxysilyl)alkane monomers under acidic or basic conditions in methanol and in tetrahydrofuran. The gels aged 3.7, 14, 21, 28, 35, 42, and 49, and 56 days before drying to afford xerogels. The xerogels were characterized by nitrogen sorption porosimetry and scanning electron microscopy. Those prepared in methanol were non-porous. Those prepared and aged under basic conditions in methanol or tetrahydrofuran exhibited coarsening of porosity with aging time. With the exception of the hexylene-bridged gels, those prepared and aged in acidic methanol showed little change with aging. The surface area of the hexylene-bridged xerogels nearly tripled with aging times of up to several weeks, then decreased, for the gels aged for more than two weeks, to around 100 meters squared per gram.

10:15 AM *EE10.4

Polyhedral oligomeric silsesquioxanes (POSS) consist of an inorganic core that can be functionalized with various organic or inorganic groups to produce a wide gamut of nano-sized building blocks. Today, such POSS-based building blocks can be synthesized reliably and cost-effectively. A great variety of molecular designs have already been reported and possibilities for the formation of new POSS-based materials is still lacking. To advance this knowledge, we are developing a computational framework for the simulation of structural assembly in POSS nanoparticles by combining computational techniques ranging from ab initio quantum mechanical calculations to molecular dynamics simulations to coarse-grained mesoscale modeling methods.
Using 

on initial conclusions, we can predict the inherent properties of molecular building blocks. Using large-scale molecular dynamics simulations we can predict the transverse and longitudinal evolution processes that occur during nano-assembly, and thereby generate realistic models that serve to establish structure-property-processing relationships for these materials. In this presentation the general approach taken with our computational framework will be outlined and results from two representative materials simulation studies will be discussed. One example details the strategies pursued for the design of materials with photonic applications. The other one describes the peculiar amphoteric behavior of mono-tethered POSS that causes nano-phase separation and can be exploited for pattern formation at this scale. This work is supported by the National Science Foundation (DMR-0103399).

Reactive molecular dynamics based on a three-body potential with dynamic charge transfer is used to study the effect of precursor functionalization on the nature of nanosized silicas structures produced by sol-gel condensation reactions. We have simulated different precursor systems - pure silicic acid monomers and dimers, dimers functionalized with hydrolytically-stable dimers for crosslinked with cyclohexyl groups - covering a range of functional groups from pure silanols to silanol-organic hybrids. With monomer precursors, the sol-gel condensation process produces fractal 3-D network structures. As we alter the precursor from silanol-functionalized dimers to hybrids - we observe closed cage-like structures in the network, followed by the emergence of isolated silica clusters. In this presentation we illustrate the mechanisms that control structural developments in these systems, as well as the structure-property relationships of the resulting configurations.

The Aminopropylsiloxane-based inorganic/organic hybrids have a high sensitivity and irreversible detection. We investigated the affinity control of the aminopropylsiloxane-based inorganic/organic hybrid toward nitrogen dioxide gas. The aminopropylsiloxane-based inorganic/organic hybrids have a high sensitivity and irreversible detection. We investigated the affinity control of the aminopropylsiloxane-based inorganic/organic hybrid toward nitrogen dioxide gas. The aminopropylsiloxane-based inorganic/organic hybrid containing an Nb inorganic component resulted in a detectable change in the optical properties and acted as a reversible sensitive material toward nitrogen dioxide gas. 1) A. Barnard, et al., Sensors and Actuators B, 11, 361(1998), 2) Y. Xu, et al., Chemical Sensors 18, 145(2002).

Photoluminescence study of organic/inorganic hybrids for integrated optic devices. Luis Dias Carlos, Rute Sa Ferreira, Verónica de Ren Brandao, Silvia Nunes, Celsa Molina, José Abreu, Joaquim Legendziewicz, Ana Barilla, University of Aveiro, Aveiro, Portugal; 2Chemistry, University of Tras-os-Montes e Alto Douro, Vila Real, Portugal; 3Chemistry, University of Aveiro, Aveiro, Portugal.

Sol-gel processing offers a low temperature route for the development of organic-inorganic hybrid materials potentially suitable for the production of optical waveguides and functional integrated optic devices at low cost. Urea cross-linked poly(ethylene)/silica and new amido cross-linked poly(ethylene)/silica nanohybrids, classed as di-ureasils and di-amidosils, respectively, have been shown to simultaneously achieve acceptable transmittance and mechanical flexibility leading to easier processing of thick films. These hybrids are also versatile hosts able to incorporate high concentrations of lanthanide ions (up to 15 % w/w) and, therefore, to achieve high luminescence intensity (desirable for optical devices). Another type of attractive hybrid matrix is that derived from methacryloxypropyltrimethoxysilane (MAPTMS) which contains a photopolymerizable organic group and thus can be easily patterned using ultraviolet light radiation and lithographic techniques. Control over the refractive index of the films produced with this hybrid precursor can be achieved through the use of a stable sol containing nanoparticles of zirconium oxide. The hybrid hosts are room-temperature (RT) efficient white light emitters lacking metal activator ions with RT emission quantum yields as high as 20 % [1,2]. In spite of the potential technological relevance of such materials, the origin of their efficient white-light intrinsic photoluminescence (PL) is not yet completely clarified. With the goal of investigating further the nature of such emission and to develop innovative hybrid systems with a wide range of useful and tailored properties, the influence of the incorporation of nanoparticles of zirconium oxide (ZrO) and MAPTMS into the di-ureasil and di-amidosil was studied by photoluminescence in steady state and time-resolved modes. Preliminary results and di-amidosil incorporating nanoparticles of ZrO and MAPTMS are efficient RT white-light emitters due to the convolution of donor acceptor pairs recombination that occur in the NH groups of the urea/amidoxyl linkages and in the siliceous nanodomains, similarly to the situation found in the undoped di-ureasil [1,2]. However, changes are observed in the peak energy of zirconium and MAPTMS-based hybrids. Moreover, these new hybrids present smaller recombination time-scale mechanisms than the undoped di-ureasil, for instance for a zirconium doping concentration around 25 % lifetime values of ca. 75 and 3.3 ms were detected for the NH and siliceous nanodomains related emissions, respectively. These values are smaller than those previously reported for di-ureasil, ca. 195 and 3.5 ms, respectively [2].

SESSION EE11: Chemical Strategies for the Design of New Hybrid Materials Chair: Francois Fajula Thursday Afternoon, December 2, 2004 Room 302 (Hynes)

1:30 PM EE11.1 Synthesis of nanomaterials in Highly Swollen Liquid Crystals. Miriam Tokumoto, Eduardo Pena dos Santos, Geetaranji Surdon, Hynd Remita, Laurence Ramos, Eric P. Prouzet, I.E.M., C.N.R.S., Montpellier Cedex 05, France; 2L.C.P., C.N.R.S., Montpellier Cedex, France; 3G.D.P.C., C.N.R.S., Montpellier Cedex, France. Highly Swollen Liquid Crystals (SLC) that exhibit hexagonal, cubic
iono-covalent as well as trialkoxysilanes have been used to prepare iono-covalent formation of M-O-P and M-O-Si bonds, respectively (M stabilities of the M-O-P or M-O-Si interfacial bonds can also be quite surface modification of an oxide support. However, the reactivity shows a Young modulus at 63 MPa. For characterization necessity, the series of chemical reactions, as liquid electrolytes, as extractant confinement of ionic liquid within the pores of the inorganic skeleton is expressed by several specific behaviour, like for instance that seen liquid is nanoconfined in a highly stable oxide framework. The magnitude of the ionic liquid itself. Moreover, this one-pot process enabled network porous volume and pore radius to be tailored. The changements in the SLC structure can modify the structure of the composite as related to their mechanical properties. In addition, for their complete performance, these materials require to illustrate the differences between organophosphorus and organosilane coupling molecules with several recent results and examples of application in our group. - study of the behaviour of phosphate units in titania/phosphate hybrid solids by 17O MAS-NMR spectroscopy; - simultaneous phase transfer and surface modification of titania nanoparticles - selective surface modification of particles doped with silica and mixed oxides - self-assembly of dipolar phosphoric acid self-assembled monolayers on titania for applications under strongly basic conditions: extraction of heavy metals using thiol-terminated SAMs and octadecylphosphonic acid SAMs as ultrasound coatings. A. J. G. F. G. Leclercq, J. P. Mutin, P. H. Leclercq, D. Topics in Current Chemistry 2004, 232, 145.

2:00 PM EE11.2 Iono-Tic Liquids Confined in Silica Membranes, a new Class of Solid State Electrolytes. Marie-Alexandra Nceur1, Jean Le Bideau1, Fabrice Leroux2, and Andre Viois1. 1CMOS UMR CNRS 5957, Universite Montpellier, Montpellier, CEDEX 5, France; 2LMI UMR CNRS 6602, Universite Blaise Pascal - CNRS, Clermont-Ferrand, France.

In the course of our studies on hydrolytic and non-hydrolytic sol-gel processes, the use of ionic liquids for their own properties as well as reactant medium appeared to be a promising field. Indeed, ionic liquids have been proposed as a new reactive solvent for series of chemical reactions, as liquid electrolytes, as extractant liquids. Their potential is enhanced by their very low volatility, their reusable and recoverable feature. Moreover their chemical and physical properties may be tune by the choice of cation / anion content. We have carried out a typical one-pot sol-gel reaction (tetramethoxysilane with formic acid) in some ionic liquids among which the 1-butyl,3-methylimidazolium [BMI] bis(trifluoromethylsulfonyl)imide [TFSI]. This results in a transparent solid material that we have named Ionogel. This material exhibits high ionic conductivity, up to 2.10-2 S.cm-1 around 470 K. Mechanical characterization of this solid shows a Young modulus at 63 MPa. For characterization necessity, the ionic liquid can be washed off. The resulting compound is the inorganic skeleton alone and presents an adsorption isotherm which permits to deduce a BET area at 900 m2.g-1 with a quasi-monodisperse pore size around 120Å. In Ionogel, the ionic liquid is nanocoagulized in a highly stable oxide framework. The confinement of ionic liquid within the pores of the inorganic skeleton is expressed by several specific behaviour, like for instance that seen on 1H NMR spectra. The spectrum of the solid state Ionogel recorded without spin-polarization is comparable to the liquid phase and even with a low spinning (400 Hz). This evidences the peculiar state of the ionic liquid within the Ionogel. Studies are in progress in order to identify the origin of the ionic liquid conductivity in such a low spinning condition. It is noteworthy that we have observed here ionic conductivity for our solid state material in the order of magnitude of the ionic liquid itself. Moreover, this one-pot process yield a material which is still a gel, the reactant medium, bringing also the desired property, being preserved in the final compound.

2:15 PM *EE11.3 Hybrid Materials Based on Organophosphorus and Organosilane Coupling Molecules: what is the Difference. P. Hubert Mutin1 and Gilles Guerresi,2 1Chemistry, CNRS, Montpellier, France; 2Chemistry, University Montpellier 2, Montpellier, France.

Organosilanes [1] and organosilane [2] coupling molecules can both be used to tether organic groups to an oxide network through the formation of M-O-P and M-O-Si bonds, respectively (M = Ti, Al, Zr, Si, etc.). Thus, phosphonic acids (RP(O)(OH)2) or phosphonic esters (RP(O)(OEt)2) as well as trialkylsilyl oxides (RSi(O)Me3), R(OEt)2, and trichlorosilanes (RSiCl3) have been used to prepare iono-covalent organic-inorganic hybrid solids, either by sol-gel processing or by surface modification of an oxide support. However, the reactivity of organophosphorus and organosilane coupling molecules are quite different. For instance, the hydrolysis of P-O-Et groups and the hydrolysis of Si-O-Et groups proceed easily hydrolyzed whereas Ti-O-P bonds show exceptional hydrolytic stability. For instance, the hydrolysis of P-O-Et groups and the hydrolysis of Si-O-Et groups proceed

3:00 PM EE12.1 Bioactive Aerogels. Luis Maria Esquivel1, Manuel Pinoz2, Nicolas Daniel De la Ross-Fox3, Jose Gonzalez-Calbet4, Antonio Salinas5 and Maria Vallet-Regi3. 1Fisico de la Materia Condensada, Universidad de Cadiz, Puerto Real, Cadiz, Spain; 2Fisica Aplicada, Universidad de Cadiz, Puerto Real, Cadiz, Spain; 3Quimica Inorganica, Facultad de Farmacia. Universidad Complutense, Madrid, Madrid, Spain.

One of the sol-gel routes to organic-inorganic hybrid materials (OIHMs), incorporates an organic phase in the inorganic precursor sol in combination with the asasted high power ultrasound. When both phases are chemically bonded a sono-organic, also called hard organic results after gelation. These hybrid materials combine the advantages of the sol-gel process regarding the use of metallo-organic precursors, organic solvents and low processing temperature, with the specific characteristics of the organic polymers as hydrophobic/hydrophilic parts. These materials are being used for implants since they are tolerated by the human organism that creates a fibrous tissue when they are embedded in the body. However, they do not become bonded to the bone unless they are bioactive. In such case, a layer of hydroxycarbonateapatite (HCA) grows wrapping the material when it is immersed in blood plasma. HCA layer is also formed when bioactive materials are soaked in solutions mimicking the features of plasma. These are so-called in vitro assays of bioactivity, a common tool in the development of new biomaterials, where HCA formation is monitored. In addition, for their complete performance, these materials require to approach their mechanical behavior to that of the bones. Two alternative and biocompatible hard organic rubbers are currently under investigation. Recently, several materials obtained by ultrasonic agitation of colloidal silica with a sol solution containing tetraethoxysilane (TEOS) were used to form crack-free monoliths. The addition of colloidal silica particles to TEOS-based aerogels has enabled network porous volume and pore radius to be tailored. The porous structure also features the performance and applications of these materials because it permits the specimens to get infiltrated and vascularized. Specimens of these hybrid colloid-polymer gels exhibited a strain, followed by yield and plastic hardening. Bulk modulus was significantly reduced as the content of silica particles in the gel was increased. We have used this combination colloid-polymer as precursor of the inorganic part of the OIHMs with the aim of tailoring the porosity to control the density and mechanical strength in the range of those of human bones. Finally, in vitro bioactivity of this material has been promoted by adding calcium to the initial sol. In inorganic materials, it has been shown that Ca cations together with unreacted -OH groups form a bioactive hydroxyapatite layer in a simulated body fluid. The effect of calcium addition in the microstructure of the OIHMs was studied by High Resolution Transmission Electron Microscopy (HREM). An increase in the distances between [SiO4-] units as a consequence of the presence of calcium ions was shown. In this paper we also present some results on the structure on this composite as well as related to their mechanical properties.

3:15 PM EE12.2 Recent Developments in the Synthesis and Use of Highly Porous Hybrid Colloid-Polymer Gel Particles as Reversed-Phase HPLC Packing Materials. Kevin Daniel Wyndham, John O’Gara, Ken Gloe, Nicole Lawrence, Bonnie Alden, Cheryl Boisell, Tom Walter and Pamela Ianra; Waters Corporation, Milford, Massachusetts.
A wide variety of applications for hybrid organic/inorganic materials have emerged over the last ten years including their use as polymer additives, catalyst supports, monolithic materials, bioconjugates, and photonics materials. Siloxane-based hybrid organic/inorganic materials are a unique group of hybrid materials that are comprised of organofunctionalized siloxane networks. As part of our ongoing exploration into the new field of hybrid organic/inorganic particles as chromatographic packing materials, we have recently evaluated the preparation of porous, highly spherical ethyl-bridged and methyl hybrid particles for use in reversed-phase high-performance liquid chromatography (RP-HPLC). The reversed-phase chromatographic properties of these hybrid materials proved to be a combination of properties that are often observed for both silica-based materials (i.e., high separation efficiencies, mechanical stability, large surface area) and organic polymeric materials (i.e., large usable pH range of 1-12). In this report, we will compare mechanical and physical properties of hybrid particles with conventional silica particles, and describe the implications regarding the elementary step reaction time in RP-HPLC applications - having a focus on the material attributes of porous hybrid particles before and after surface modification. For example, the presence of surface organofunctional groups of most hybrid particles results in less surface silanol groups compared with silica particles. This decrease in surface silanol groups results in a lower concentration of unreacted silanol groups after surface bonding reactions, and drastically reduced peak tailing of basic analytes that are caused by residual silanol groups in reversed-phase HPLC applications.

**Hierarchical Porous Silica for Chromatographic Applications Obtained by Pseudomorphic Synthesis**
Anne Galarmeau, Julien Lapichelli, Carolina Pettitto, Francesco Di Renzo and Francesco Pajula, UMR 5018, ENSCM/CNRS, Montpellier, France.

Pseudomorphic transformation of pre-shaped silica beads into MCM-41 and MCM-48 is introduced as a new versatile procedure to independently control and finely tune the textural characteristics of advanced high-performance chromatographic supports at nanometer- and micrometer-scale. The reaction takes place in the intergranular porosity of the parent silica-gel particle which acts as a nanoreactor. Because the resulting hybrid mesophase is metastable in its synthesis medium, the kinetics of each of the elementary steps (diffusion of hydroxide and surfactant dissolution of parent silica, self assembly, condensation of the new silica network) must be precisely controlled. In the lecture examples will be given of the preparation of discrete homodisperse spherical particles of MCM-48 and MCM-41, with mesopore sizes in the range 4 to 9 nm, form different silica sources.

**Hybrid Materials Approach in the Design of Electrodes and Electrolytes for Energy Storage and Conversion**
Pedro Gomez-Romero, Materials Science Institute of Barcelona, CSIC, Bellaterra, Spain.

The integration of electrochemically active inorganic species in polymer matrices allows for the design of either electrode or electrolyte materials depending on the conducting or insulating properties of the polymer used. Conducting polymers can be used as the basis for a variety of hybrid electrode systems, whereas other polymers such as polybenzimidazoles have been used as electrolyte membranes by themselves or in combination with inorganic solid acids. We will discuss the general approach of hybrid design with this in mind and specifically we will describe our recent results on the use of polyelectrolyte-containing hybrids in energy storage conversion devices. In this respect we have worked in our laboratory on electrochemical supercapacitors and fuel cells but emphasis should be made on the broader potential fields of application of this type of materials.

**Electrochemical Characterization of Phosphosilicate-modified Nafion Membranes**
Lisa C. Klein and Mario Aparicio; 1Rutgers University, Piscataway, New Jersey; 2Electrochemical Materials, Polymer Electrolytes and Fuel Cells. Itaru Honma and Je-Doek Kim; EEI, AIST, Tsukuba, Ibaraki, Japan.

Polymer electrolyte membrane fuel cells (PEFC) using hydrated perfluorosulfonic polymers such as NAFION have been developed in the past years. However, the high materials cost and complicated water managements are major obstacles for practical applications of PEFC. Also, CO poisoning of Pt alloy electrodes reduces the efficiency of the complicated reforming system, which purifies the hydrogen rich gas down to the CO contamination level of few ppm. One of the technological challenges is to develop an electrolyte membrane that can be operated at higher temperatures (150-200°C) and lower humidity level, which drastically improve the Coloradence performance and the cell efficiency. In this paper, we have investigated the structure and proton conductivities of organic/inorganic hybrid membranes synthesized by sol-gel processing with polydimethylsiloxane (PDMS) or polytetramethylenoxide oxide (PTMO) and metal (zirconium, titanium) alkoxydes. The hybrid membranes have been found to be temperature tolerant and stable even at higher temperature with acidic condition. The membranes become a proton conducting electrolytes by the soaking of phosphoric solution or adding heteropolycacids such as 12-phosphotungstic acid (PWA). Various polymer membranes by incorporated acids afford the conductivity of the membrane. The hybrid membranes showed good protonic conductivities at intermediate temperatures up to 150°C.

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**Hybrid Materials II**
Thursday Evening, December 2, 2004
Exhibition Hall D (Hynes)

**Di-Urethane Cross-Linked Poly(Alcohol) Siloxane Nanohybrids Doped with Eu(CF3SO3)3**
Maria Cristina Alvares Pereira Goncalves, V. de Zea Bermudez, D. Ostrovskii, R. A. Sa Ferreira and L. D. Carlos; 1Departamento de Quimica and CQ-VR, Universidade de Tras-os-Montes e Alto Douro, 5000-111 Vila Real, Portugal; 2Department of Applied Physics, Chalmers University of Technology, Göteborg, Sweden; 3Departamento de Fisica and CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal.

In many scientific areas the sol-gel method is considered to be one of the best ways of synthesizing organic/inorganic hybrid systems with tunable design and a wide scope of technological applications. In particular, the hybrid concept has been extensively used to produce room-temperature efficient white-light photoluminescent materials [1]. With the goal of developing materials with high quantum efficiency for application in optics, sol-gel derived poly(oxyethylene) (POE)/siloxane frameworks, designated as di-urethanesils, containing POE chains with 6 OCH2CH2 repeat units (average molecular weight, MW = 300 gmol-1) and incorporating a wide concentration range of Eu(CF3SO3)3 (0-20 mol%) were investigated [2-5]. In these materials the organic and inorganic components are bonded through urethane linkages (-N=O(-O)-). In the present work Eu(CF3SO3)3-doped di-urethaneils analog xerogels including longer POE chains (13 OCH2CH2 repeat units (MW = 600 gmol-1)) were analyzed. Fourier Transform mid-infrared and Raman spectroscopies and Photoluminescence (PL) were used to determine the local cationic and anionic environments as a function of salt concentration. The Eu3+-coordination in these materials depends markedly on the amount of Eu3+ incorporated, inducing changes in the PL features of the xerogels, namely in the emission color coordinates (determined according to the Commission International de Eclairage procedure).

The atomic force microscopic technique is utilized to study the spatial distribution of silica nanoparticles embedded in poly(tetramethylene glycol diacrylate) matrix. The casting samples of these hybrid materials show distinct mechanical property change as the weight ratio (SiO2/PMMA) reaches 40%. The morphological observation from spin-coated films on silicon substrates shows pronounced nanoparticle network formation correlated to the elasticity transition. The percolating particles reduce the local strain field, i.e., inhibit the deformation of the stratum, and cause the dramatic increase in the Young's modulus. Our experimental result is consistent with recent theoretical predictions.[1] [1] G. A. Buxton and Anna C. Balazs, Phys. Rev. E 67, 031802 (2003). Funding source: Department of Industrial Technology in the Ministry of Economic Affairs, R.O.C, contract number 92-EC-17-A-08-S1-0015

EE13.3
Comparison of Different Reversed-Phase Packing Materials Based on Ethyl Bridged Hybrid Particles, Nicole Lawrence, Kevin Daniel Wyndham, John O’Gara, Ken Glose, Pamela Iraneta, Boston Alden, Cheryl Boisvert, Warda Water Corporation, Milford, Massachusetts.

As part of our ongoing exploration into the new field of hybrid organic/inorganic particles as HPLC packing materials, we have recently evaluated the use of ethyl bridged alkoxysilanes as particle precursors. By employing a 4:1 molar ratio of inorganic (SiO2) to organic substituent groups (SiO1.5CH2CH2SiO1.5), novel hybrid nanoparticles have been shown to be excellent base particles for the preparation of efficient and resilient reversed-phase (C18, C4, phenyl, embedded pores) packing materials. In this report, we take a close look at the synthesis and characterization of different reversed-phase packings on these ethyl bridged particles and report the results of the reversed-phase chromatographic performance of these new packing materials, and compare these results with conventional silica-based materials under similar chromatographic conditions.

EE13.4
Synthesis of Daisy-Shaped and Multipod-Like Silica/Polystyrene Nanocomposites, Stephane Reculua, Elodie Bourgoin-Lami, Christophe Mingotaud, Serge Ravaine and Etienne Duguet, 1) ICMB, CNRS & University of Science and Technology of Bordeaux, Pessac, France; 2) CRC, CNRS & University of Science and Technology of Bordeaux, Pessac, France; 3) LCPP, CNRS & CPE, Villeurbanne, France; 4) LIMRCP, CNRS & University Paul Sabatier, Toulouse, France.

Colloidal nanocomposites have attracted a great attention in recent years as new multifunctional materials with unusual properties that originate from their organic and inorganic counterparts. Among their important features are the interface characteristics between both components. In that work, we report the synthesis and morphology characterization of original multipod-like and daisy-shaped hybrid nanoparticles consisting of spherical silica beads (in the diameter of range of 100 nm) supporting smaller polystyrene ones. Their synthesis was derived from the seeded heterophase styrene polymerization. In a first step, silica particles of various sizes were synthesized according to procedures inspired from the literature. In a second step, they were functionalized by adding organotrialkoxysilanes molecules. Finally, they were used as seeds during the polymerization of styrene in water using a non-ionic surfactant as emulsifying agent and sodium persulfate as initiator. Scanning and transmission electron microscopy experiments showed that nanocomposite morphologies are strongly dependent on (i) the organosilane nature, (ii) its surface density onto silica beads and (iii) the styrene conversion.

EE13.5

Reaction of zirconium butoxide with methacrylic acid in different molar ratios results in the formation of ZrO2(methacrylate)12 or ZrO2(OH)(methacrylate)12. These clusters are structurally well defined nanosized building blocks and can be used as co-monomers in polymerization reactions. Adding carboxylic acids, like propionic acid or iso-butyric acid, to a cluster-containing solution results in exchange reactions between the methacrylic acids and the zirconium oxide surface and the carboxylic acids. Hence it is possible to partially or completely exchange methacrylate ligands to other carboxylate ligands. By changing the chemical properties of the cluster surface it is possible to lower the density of functional groups on the cluster surface, to adjust solubilities, as well as bringing in new functionalities.

EE13.6
Electro-Spraying of Polymer-Inorganic Mixture Solution for Microparticles in Electrophoretic Display, June Whan Choi, Young Chul Kim, Ji Kyung Kim, Ji Seon Kim, Ho Gyu Yoon and Young-Won Yu, Division of Materials Science and Engineering, Korea University, Seoul, South Korea; 2) Materials Research Center, Kyung Hee University, Yongin, South Korea; 3) Optoelectronic Materials Research Center, Korea Institute of Science and Technology, Seoul, South Korea.

The present work focuses on the preparation of polymer-inorganic composite particle by electro-spraying and the characterization of resultant composite particles. These composite particles were utilized for Electrophoretic Display (EPD). EPD is a reflective type display using the electrophoretic phenomena of charged particles suspended in a liquid medium and displayed with the migration of charged particles as Electric Field [1]. The basic requirements for EPD microparticle materials are high refractive index, high surface charge and specific-gravity-match to the liquid medium [2]. To obtain suitable microparticles, the feasibility of electro-spraying method was investigated. Rutile TiO2 (mean size: 0.2 μm) and polystyrene (Mn: 7,700) were used to prepare composite reaction medium. The homogeneity of stock solution prepared by dissolving TiO2, polystyrene and polyisobutene succinimide (OLOA 1200) in tetrahydrofuran was maintained with rod type sinter. OLOA 1200 was utilized as a dispersant and the charge control agent. The electro-spraying was performed with the range of 0.5-2.9 ml/hr in flow rates and 6-10 kV DC voltage for applied electric field. The counter electrode was located in insulation bottle filled with nonpolar-nonsolvent oil (hexacarbon 0.8 cSt, polychlorotrifluoroethylene), such that resultant composite particles were retrieved from this oil. The analyses of sprayed particles were performed with electrospraying spectrophotometer, TEM and thermogravimetric analyzer. The mean size of produced particles was maintained from 0.8 to 3.0 μm by controlling the solution concentration. OLOA 1200 concentration, the flow rate and the electric field. The zeta potential of produced particles was controlled from 50 to 90 mV with the OLOA 1290 concentration. Density of particle was controlled from 1.3 to 1.7 g/cm3 with the polystyrene concentration. The actual electrophoretic driving test of microparticles was proceeded in a device formed by two patterned ITO cell with 70 μm spacer at 100 V external field. The result proved that electro-sprayed composite particles were suitable for EPD in the requirements of the size, high surface charge and density. [1] S. Inoue et al., IEEE Trans Electronic Devices 49, 1502(2002). [2] B. Comiskey et al., Nature 394, 253(1998).

EE13.7
Abstract Withdrawn

EE13.8

There has been a growing research effort in organic electronics to improve the semiconductor, conducting, and gate insulating properties of organic thin films formed by sol-gel process. Hey Jin Myoung, In-Joo Chih, Chul Am Kim, Gi Heon Kim, Seong Deok Ahn, Seung Youl Kang, In-Kyu You, Kyu-Ha Baek and Kyung Soo Suh, 1) Polymer Science and Engineering, Inha University, Incheon, South Korea; 2) Basic Semiconductor Research Lab., Electronics and Telecommunications Research Institute, Daejeon, South Korea.

There has been a growing research effort in organic electronics to improve the semiconductor, conducting, and gate insulating properties of organic thin films formed by sol-gel process. Hey Jin Myoung, In-Joo Chih, Chul Am Kim, Gi Heon Kim, Seong Deok Ahn, Seung Youl Kang, In-Kyu You, Kyu-Ha Baek and Kyung Soo Suh, 1) Polymer Science and Engineering, Inha University, Incheon, South Korea; 2) Basic Semiconductor Research Lab., Electronics and Telecommunications Research Institute, Daejeon, South Korea.
and has adhesive properties with glass, metals, and other plastics, organic/inorganic nanocomposites are shown to have both process advantages over the materials building excellent dielectric characteristics of the inorganic materials.

**EE13.9** Photoresponsive Hybrid Organic-Inorganic Polysilesquioxane Materials Containing Functionalized Coumarin Dimer.
Lihua Zhao1, Douglas A. Loy2 and Kenneth J. Shea3; 1Department of Chemistry, University of California, Irvine, Irvine, California; 2Ploymer Science and Engineering Group, Los Alamos National Laboratories, Los Alamos, New Mexico.

Creation of siloxane networks by sol-gel polymerization has been widely used to prepare thermally and chemically robust, hybrid organic-inorganic materials for numerous applications including membranes for gas separations, electro-optic systems and catalyst supports. Detailed structure information of these macromolecular architectures is invaluable for designing and synthesizing nanoscale structures with improved properties. The focus of our research is to develop a "photochemical" dissection process that would render the intractable, hybrid organic-inorganic networks into more readily characterizable, soluble fragments. We describe the synthesis and characterization of monomers containing coumarins and their dimers. The sol-gel derived polysilesquioxane networks or co-polymer networks are built from the coumarin containing monomer and bis-trialkoxysilane co-monomers. The photochemical dissection has been used in both solution and in thin films to provide detailed structural information on the developing bridged polysilesquioxane network.

**EE13.10** Oligo(2-acetylenylphenyl)siloxanes. Highly Polyfunctional Coumarin Dimer Construction. M. Asuncion, Richard M. Laine, Chad Brick and Mark Roll. 1,2,3 Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; 2Macromolecular Science and Engineering Center, University of Michigan, Ann Arbor, Michigan; 3Chemistry, University of Michigan, Ann Arbor, Michigan.

Oligo(2-acetylenylphenyl)siloxanes, whose photo- and electroluminescent properties are readily tailored, offers the rigidity and heat capacity of silica. This leads to thermally and oxidative stability without crystallization (high Tg) are also available for designing and synthesizing nanoscale structures with improved properties. Recent experiments have demonstrated that self-assembly of tethered POSS nanocubes is a promising route to synthesis of novel materials with highly ordered complex nanostructures. Using a coarse-grained model developed for tethered POSS [1], we present the results of molecular dynamics simulations of organic-inorganic POSS molecules, to investigate how the architecture of these hybrid building blocks can be exploited to achieve useful structures via self-assembly [2-4]. We systematically explore the parameters that control the assembly process and the resulting equilibrium structures, including concentration, temperature, tethered POSS molecule topology, and solvent composition. We report conventional lamellar and cylindrical structures as typically found in block copolymer and surfactant systems, but with interesting modifications of the phase diagram caused by the bulkiness and cubic geometry of the POSS molecules. [1] T. Ionescu, X. Zhang, E.R. Chan, C-Y. Lee, H.C. Li, P. Cummings, J. Kieffer, C. McCabe, M. Neurck and S.C. Glotzer, preprint. [2] X. Zhang and S.C. Glotzer, preprint. [3] E.R. Chan, X. Zhang, A.S. Keyes, C.Y. Lee, M. Neurck and S.C. Glotzer, preprint. [4] H. Lo, E.R. Chan, X. Zhang and S.C. Glotzer, preprint. This work is supported by the National Science Foundation under grant no. DMR-0103399.

**EE13.11** Highly Luminous Stibenoacetalsilsequioxanes, Chad Brick1, Michael Asuncion2, Mark Roll3, Ryo Tamaki3, Richard Laine2,3, Matthew Neurck4 and Jean-Sebastien Filhol4; 1Chemistry, University of Michigan, Ann Arbor, Michigan; 2Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; 3Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan; 4Chemical Engineering and Chemistry, University of Virginia, Charlottesville, Virginia.

The field of molecular electronics now covers diverse subject areas perhaps best epitomized by work directed towards the development of organic light emitting diodes (OLEDs). Despite extensive efforts to optimize materials for light emitting devices many synthesis and processing problems remain to be resolved. Among these are the need for simple synthetic routes to easily purified and processed materials whose photo- and electro-luminescent properties are readily tailored. Still other needs include methods of avoiding aggregate and exciplex effects on surfaces have been more extensively investigated in recent years, the self-assembly of molecules from solution to two-dimensional layered compounds still plays an important part in the development of novel materials. Tungsten oxide has been a much-studied compound due to its electronic and structural properties. An example of the former is the amazing colour range displayed in the various tungsten bronze series; while the latter can be seen in the complex arrangement of tungsten oxide octahedra (WO6) through a combination of edge or corner sharing to form 1-, 2- or 3-dimensional network structures. In this paper we report the synthesis of two-dimensional layered hybrid compounds with alternating organic ammes and tungsten oxide layers. The synthesis of these tungsten oxide hybrids via homogenous and heterogeneous routes were explored and compared. In the former case, tungstic acid (H2WO4) and an appropriate diamine were dissolved in ammonia solution under nitrogen atmosphere, and the product was precipitated out via evaporation of the solvent and subsequent heating in an oven, a non-aqueous approach was employed in which H2WO4 powder was aged in a solution consisting of the diamine dissolved in an appropriate organic solvent (for example hexamethylenediamine in toluene); XRD and FTIR showed that the hybrid materials obtained from the two different methods are identical. This has enabled us to prepare films/coatings of the hybrid materials by dip-coating tungstic acid films prepared by sol-gel technique, in a non-aqueous diamine solution. The XRD spectra of the films exhibit multiple peaks, indexed as [004], which correspond to the Bragg peaks for the hybrid compounds. SEM shows the morphology of the platelets changes from the irregularly shaped ("cornflakes"-like) tungstic acid to a needle-like structure of the hybrids and resulted in a loosely
Packed (open multistructure) coating.

**EE13.15**
Abstact Withdrawn

**EE13.16**
Refraction index measurements of thin films using both Brewster and m-line technique: a combined experimental setup. Mauro Casalboni, Fabio De Matteis, Paolo Prospisitio, and Stefano Schutzmann. Dipartimento di Fisica e Istituto Nazionale per la Fisica della Materia, University of Rome Tor Vergata, Rome, Italy; Dipartimento di Fisica e Istituto Nazionale per la Fisica della Materia, University of Rome Tor Vergata, Rome, Italy; Dipartimento di Scienze e Tecnologie Chimiche e Istituto Nazionale per la Fisica della Materia, University of Rome Tor Vergata, Rome, Italy.

We report on the refractive index measurements of guiding and non-guiding films synthesized by sol-gel technique. An experimental setup has been developed in our laboratory based on both m-line and Brewster angle methods. The main feature of the setup is the possibility to perform both m-line and Brewster angle measurements on the same sample. This allows a more careful evaluation of the refractive index. The combined method, based on the application of both m-line and Brewster angle techniques, represents a completely non-destructive, inexpensive (compared to traditional ellipsometric techniques) and, in addition, very simple method. Moreover, using different laser sources at different wavelengths, we are able to measure refractive index as a function of wavelengths in the visible and near infrared spectral range. We have tested our experimental setup performing measurements on many systems, both on non-guiding or guiding sol-gel films deposited by spin-coating technique on glass substrate. We have synthesized both purely inorganic and hybrid organic/inorganic sol-gel-based films. The purely inorganic samples were based on zirconium(IV)-propoxide as inorganic modifier and trimethylolpropanetriacrylate as organic modifier. The neutral longest lifetime was for samples with the highest concentration of 3-[(trimethoxysilyl)propyl methacrylate (TMSPM) as inorganic components. Estimation of refractive index values for non absorbing thin films has an accuracy of about 1% and very good reproducibility in a wide spectral region have been achieved.

**EE13.17**

Electrochromism is defined as the ability of redox active species to develop electronic absorption bands upon oxidation or reduction. Typical electrochromic devices can function as self-darkening or "smart" windows and mirrors and have the potential to be used in large area displays. Sol gel matrices are often used to immobilize electrochromophores on electrode surfaces to afford air stable devices with an accuracy of about 1% and very good reproducibility in a wide spectral region have been achieved.

**EE13.18**

Pulsed laser ablation in gas phase has been widely used for the preparation of variety of nanostructures such as nanoparticles, nanotubes, nanotubes. Reactions of gold, silver and platinum, and oxide nanoparticles of TiO2 and SnO2 have been performed by the pulsed laser ablation of the metallic target in water. This technique can be also apply for the preparation of organic/inorganic nanocomposites, because ablated metallic species with high energy can be easily oxidized with water to form oxides and/or hydroxides, and these nuclei can react with the organic molecules in aqueous solution. In this paper we report that the fabrication of organic/inorganic nanocomposites via pulsed laser ablation of Zinc in aqueous solutions of various surfactants. Zn plate was ablated by a pulsed Nd:YAG laser in four types of surfactant solutions (cationic, anionic, amphoteric and nonionic) with different concentrations. Zinc oxide nanoparticles with average diameter of 10-40 nm were obtained in cationic, amphoteric and nonionic surfactant solutions. In contrast unique organic/inorganic nanocomposites with the thickness of 20-30 nm were obtained in anionic surfactant solutions. The nanocrystalline octagonal shaped form of the solution of the anionic surfactant, sodium dodecyl sulfate (SDS) has a layered structured compound of zinc hydroxide layer and surfactant molecules. In this presentation, the detailed structure and the formation process of the layered organic/inorganic nanocomposite will be also discussed.

**EE13.19**
Femtosecond Fluorescence Studies of Auramine O in Hybrid Sol-Gel Derived Films. Paolo Prospisitio, Hong Zhang, and Max Glasbeek. Physics Department and Istituto Nazionale per la Fisica della Materia (INFN), University of Rome Tor Vergata, Rome, Italy; Laboratory for Physical Chemistry, University of Amsterdam, Amsterdam, Netherlands.

Femtosecond fluorescence upconversion experiments have been performed on Auramine O (a diphenylmethane dye) in polymethylmethacrylate (PMMA) and in hybrid organic/inorganic sol-gel based films. Tetramethyl orthosilicate (TMOS) and 3-(trimethoxysilyl)propyl methacrylate (TMSPM) were used as inorganic and organic modifier, respectively. Different films were studied with relative molar concentrations of TMOS/TMSPM from 70/30 to 30/70. Two experimental set-ups have been employed for the optical characterization of the samples. The first one is a picosecond time-correlated single photon counting fluorescence detection setup (characterization in time windows up to 10 ns) and the second one is a femtosecond fluorescence upconversion equipment (for characterization in time windows up to 13 ps). Fluorescence transients of Auramine O were measured for a series of different detection wavelengths in the emission band in order to trace the excited state dynamics. The averaged decay time was found to be dependent on the detection wavelength: the longer the detection wavelength the slower the kinetics. All the investigated samples showed an instantaneous rise followed by a fast decay (few picoseconds) and long decay (hundreds of picoseconds). The fast components are representative of the rapid cooling of the excitation energy excess to the matrix. We found a weak dependence of the fast components on the matrix composition. The long components are representative of the excited-state lifetime of the probed molecules. Auramine O in solid matrices showed lifetimes longer than in liquid solutions. The longest lifetime was for samples with the highest concentration of TMSPM (70%). This behaviour indicates a higher hindering of the torsional motions of the phenyl groups in films characterized by a higher organic content in the matrix. A strong concentration effect on the dynamics Stokes shift has been observed for all samples. The lack of a rise time when detection was on the red side is explained in terms of an adiabatic coupling between emissive and nonemissive excited states, as is the case of liquid solutions [1]. The different spectral data fit best measured for PMMA and hybrid glasses. This is attributed to a different coupling between the emissive and nonemissive excited states for the two types of matrices considered. [1] M. J. van der Meer, H. Zhang and M. Glasbeek J. Chem. Phys. 112, 2878 (2000). [2] P. Changneg, H. Zhang, M. J. van der Meer, M. Glasbeek P. Plaza and M. M. Martin J. Phys. Chem. A 102, 6716 (1998). [3] M. Glasbeek and H. Zhang, Chemical Reviews 104, 1929(2004).

**EE13.20**

In the context of materials development for optical applications, such as waveguides, organic/inorganic hybrid materials offer new and exciting opportunities. The development of multi-functional organo-silanes, such as acrylate and methacrylate alkoxysilanes, has enabled increased control over chemical composition, cross-linking and phase stability. This has led to the production of new materials that have the optical transparency of polymers, but also have inorganic characteristics, such as the thermo-mechanical properties of a glass or ceramic. Such tunability of properties is of particular interest in the area of organic waveguide materials. These hybrid organic/inorganic material systems cannot be produced by conventional material processing methods, such as CVD or sputtering and therefore new processing routes are required. In this work, a novel preparation method for epoxy functionalised silica material is described. This material system was chosen for the enhanced mechanical and
thermal stability imparted by epoxy functionality, in comparison to other organic functional groups, such as methacrylate or acrylate. These materials enable the fabrication of silicon-based devices compatible with anion salts, which are efficient as photo-initiator species, and also are sensitive to oxygen-inhibition of cure. The sol-gel material can be easily formulated and deposited by spin or dip coating to form layers of up to 430 nm in thickness. The resulting film were selectively cross-linked using photo-lithography, as part of a UV-thermal curing process. The basic refractive index of untreated layers can be adjusted between 1.48 and 1.51 by modifying the concentration of DPDMDS present. The refractive index of treated layers then ranges from 1.49 to 1.52. The onset of purely thermal cross-linking was found to occur at 260 °C, as determined by DSC analysis. A significant improvement in thermal stability over other inorganic-organic hybrid waveguide materials systems which generally contain acrylate or methacrylate groups that are easily cured by thermal processes. Waveguide structures were fabricated; the near-field image of transmitted radiation (632 nm) showed waveguiding and efficient light confinement within the UV-thermally produced core regions. It is therefore concluded that this material system has the potential for use in waveguiding applications in environments where enhanced thermo-mechanical stability is required.

**EE13.21**

**Effects of Nanoparticle Morphology and Composition on the Physical and Barrier Properties of Natural Rubber Nanocomposites.** Michael Genuet, Elizabeth Walsh, Walter Zukas, Axel Rodrique, Frank Valanis, and Thomas Ziegler; U.S. Army RDECOM Natick Soldier Center, Natick, Massachusetts.

Nanocomposites made by adding nanoparticle reinforcement to polymers have been demonstrated to have significantly enhanced properties at relatively low levels of added reinforcement. The observed properties have in some cases been attributed to the shape of the reinforcing particle. Nanoparticle additives with a variety of particle morphologies and compositions have become commercially available in recent years. A study was carried out to examine the effects of varying nanoparticle morphology and composition on the mechanical and barrier properties of polymer nanocomposites made with natural rubber (NR). NR composites were prepared containing different nanoparticles including smectite clays, exfoliated graphite nanoparticles, carbon nanotubes and conventional carbon black. Barrier testing included permeation of selected organic compounds utilizing different vapor and liquid permeation methods. The relationship between the observed properties of the nanocomposites and the nanoparticle composition and morphology will be discussed.

**EE13.22**


We have proposed intercalative type organic-inorganic hybrid materials as the chemical solvents for selective detection of volatile organic compounds (VOCs). The organic and inorganic constituents take part in molecular recognition and transduction of chemical signals to measurable resistance changes. In this paper, we have prepared intercalative organic/MoO3 hybrid thin films by an ex-situ intercalation process. The host MoO3 films were first deposited on LaAlO3 (LAO) single crystal substrates using CVD method followed by the intercalation of polypropylene (PPy) or t-butyllammonium ions (BuNH3) into the MoO3 films. A semiconductor-like transport is observed for both the (PPy)xMoO3 and (BuNH3)xMoO3 hybrid thin films. These thin films exhibit a distinct response to VOCs by increasing in their electrical resistivity, which could be induced by the VOC. The VOCs were then incorporated through the interlayers. The two types of hybrid films show different gas selectivity to VOCs, indicating that the VOC gas selectivity can be controlled by the organic component.

**EE13.25**

**Ligand Control of Semiconductor Nanocrystals for Efficient Carrier Injection.** Masahide Murayama, Toshitake Naka, Kunihiro Irie, and Noriyuki Suzuki; National Institute of Advanced Industrial Science & Technology, Nagoya, Japan.

Recently, electronic interaction between colloidal semiconductor nanocrystals (NCs) and their organic ligands has been extensively investigated to integrate the NCs into organic/inorganic hybrid devices such as photo-voltaic cells and light-emitting diodes (LEDs).[1,2] For LED application, the ligands require several functions: 1) prevention of NC precipitation and aggregation; 2) no photo luminescence; 3) efficient carrier injection through ligands. In order to realize the functions above, we investigated CdSe/ZnS core/shell NCs covered with two kinds of organic ligands. One is for thermal stability, and the other is for carrier injection. The carrier injection ligand itself shows no fluorescence, and its highest occupied and lowest unoccupied molecular orbitals were adjusted to energy levels of the NCs for the purpose of efficient carrier injection from ligands to the NCs. The NCs were then spin coated on ITO/glass substrates to form thin films that are 20 nm thick without any matrix. The conductivity of these thin films was extremely improved in comparison with that of NCs themselves. The NCs were then spin coated on ITO/glass substrates to form thin films that are 20 nm thick without any matrix. The conductivity of these thin films was extremely improved in comparison with that of NCs themselves.

Mild synthetic conditions provided by sol-gel chemistry allows to incorporate organic components into an inorganic network, leading to organic-inorganic materials. The inorganic component is commonly prepared by hydrolysis-condensation of metal alkoxides precursors and the degree of interpenetration of organic and inorganic components ranges between the sub-micro and the nano scale level. Consequently, the sol-gel route provides an easy method to synthesize nanocomposites with promising applications in different fields (optics, electronics, mechanics, protective coatings...). However, the sol-gel process usually leads to an infinity of microstructures, generally polydispersed in size. Since few years, well-defined nanobuilding blocks (NBB) have been used to assure the control of stereochemistry, reactivity, functionality and properties of hybrid materials. This work presents the modification and the characterization of Si-based nanobuilding blocks composed of cyclic Si oligomers and polyhedral oligomeric siliconoxazaines (POSS) holding functionalizable organic moieties. Three precursors (trimethylsilyldiacetone POSS, isobutyl-dimethylsilane POSS and octasilane POSS) were modified by hydrosilylation to introduce a polymerizable vinyl group. ATR-FTIR and multinuclear NMR spectroscopies have been used to describe the reaction mechanisms and to determine the structure of the modified POSS by hydrosilylation of the available Si bonds with allyl alcohol or 4-penten-1-ol. Firstly, the competition between hydroxylation and vinylsilylation was showed to be governed by the nature of the solvent; when C-silylation occured, the methacrylate group was grafted to the modified POSS by addition of methacryloxychloride. The comparison between reactivities exhibited by cyclic oligomers and POSS will be discussed. The European Community is acknowledged for the financial support (contract Nr. HPRN-CT-2002-00300).


TiO2 is an oxide semiconductor, showing wide range of applications including high-refractive optics, oxide semiconductors, oxygen sensors, photovoltaics, photocatalysts, etc. It shows formation of three different crystalline phases such as brookite, anatase, and rutile, among which anatase shows the highest photocatalytic properties. Poly(ethylene oxide)-TiO2 hybrid films were synthesized using sol-gel chemistry and spin coating. Acetylene (AcAc) was added to enhance the solvents binding between PEO chains and aging time was varied during hybrid synthesis. Hybrid films were heated to fully crystallize to anatase phase and further heated to transform anatase phase to rutile at different temperatures for different time periods. The volume fraction values of anatase-to-rutile phase transformation were obtained using a multi-peak separation program for x-ray diffraction (XRD) patterns and an XRD quantitative analysis method. Hybrids, containing AcAc and aged for long time, showed the lowest phase transformation kinetics, while pure TiO2 films showed the highest phase transformation kinetics. Also, PEO-TiO2 hybrids without AcAc showed intermediate phase transformation kinetics. The volume fraction values were used for Johnson-Mehl-Avrami (JMA) isothermal kinetics analysis and JMA plots were produced for each system with temperature variation. Avrami exponent (n) was determined for each hybrid film using the slopes of the JMA plots. Also Arrhenius plots were produced. The activation values of JMA plots and activation energy values for phase transformation were determined from the slopes of the curves. The hybrids having AcAc and aged for long time period showed the highest activation energy, while the pure TiO2 films showed the lowest one. Long-term aging was in the strong hydrogen bonds between PEO and AcAc, and thus strong molecular networks of (Ti-O-Ti)-AcAc-PEO-AcAc-(Ti-O-Ti) would form, which hinders the fast phase transformation of anatase to rutile. Heat treatment of PEO TiO2 hybrid anatase and nanoporous films, and AcAc addition into the hybrids efficiently delayed phase transformation of anatase to rutile at a high temperature. Thus, this hybrid approach suggests an effective way for the fabrication of nanoporous anatase-films with a high anatase fraction.

EE13.28 Organic-Inorganic Hybrid Materials Based on Organophosphonic Coupling Molecules : 12-Mercaptododecylphosphonic Acid

Self-assembled Monolayers as Lubricant Coatings Stable in Alkaline Media, Jeremie Souiller1,2, P. Hubert Mutin3 and Philippe Tordjeman2, 1Chimie Moleculaire et Organisation du Solide, CNRS-University Montpellier, Montpellier, France; 2Laboratoire d’Analyse des Interfaces et de Nanophysique, CNRS-University Montpellier 2, Montpellier, France.

Organophosphonic coupling molecules such as phosphonic acids (HP(O)OH2)2 can be used to prepare organic-inorganic hybrid solids, either by sol-gel processing[1] or by surface modification of an oxide support[2, 3] Formation of Self-Assembled Monolayers (SAMs) occurs in the case of long-chain allylphosphonic acids [4,5] There has been recently much interest in SAMs as boundary layer lubricants for micro-electro-mechanical devices (MEMS)[6,7] However, most examples concern SAMs of alkanethiols (gold or alkyltrichlorosilanes or trialkoxysilanes on oxidized silicon or glass)[8,9] Here, we report the formation, tribological properties, and chemical stability of octadecylphosphonic acid SAMs on glass substrates coated by a 100 nm layer of titanium, deposited by cathodic sputtering. Friction coefficients were measured with a home-made tribometer equipped with a non-rolling metal ball (hardness: 200 HV, diameter: 2 mm, roughness 0.06 micrometer), using normal forces up to 50 N. The kinetics of SAM formation from solutions of octadecylphosphonic acid in water was investigated using water contact angle measurements, friction coefficient measurements, optical and atomic force microscopies. Octadecylphosphonic acid bound strongly to the native oxide layer of the titanium coating. However, the formation of dense, hydrophobic SAMs required several days. Octadecylphosphonic acid SAMs efficiently decreased the friction coefficient, preventing the formation of cracks even at high normal forces up to 50 N. The friction coefficient did not increase even after treatment in a NaOH solution (pH 14) at 383 K for 10 minutes. This excellent stability was ascribed to the high chemical stability of titania and of the interfacial Ti-O-P bonds. (1) Guerrero, G.; Mutin, P.; Viox, A. Chem. Mater. 1998, 10, 1268. (2) Babonneau, P.; Paterson, R. J. Membrane Sci. 1995, 118, 1268. (3) Guerrero, G.; Mutin, P.; Viox, A. Chem. Mater. 2002, 14, 8924. (4) McDermott, M.T.; Green, J.-B.D.; Porter, M.D. Langmuir 1997, 13, 2504. (5) Zhou, Y. H.; Han, P.; Fong, T.; Lopez, G.P. Langmuir 1998, 14, 600. (6) Labinis, P. E.; Hickman, J. J.; Wrighton, M. S.; Waddles, G. M. Science 1992, 254, 455. (7) Labinis, P. E.; Hickman, J. J.; Wrighton, M. S.; Waddles, G. M. Science 1992, 254, 455. (8) Labinis, P. E.; Hickman, J. J.; Wrighton, M. S.; Waddles, G. M. Science 1992, 254, 455. (9) Labinis, P. E.; Hickman, J. J.; Wrighton, M. S.; Waddles, G. M. Science 1992, 254, 455.

Use of 12-Mercaptododecylphosphonic Acid Modified Titania for the Extraction of Heavy Metals, P. Hubert Mutin1, Gilles Guerrero2, Florence Brodard-Severac2 and Sebastien Antierheus2, 1Chemistry, CNRS, Montpellier, France; 2Chimie Moleculaire et Organisation du Solide, Université Montpellier 2, Montpellier, France.

Organophosphonic coupling agents are an excellent alternative to organosilane derivatives for the preparation of organic-inorganic hybrid materials based on titania either by sol-gel processing or surface modification[1] An important potential advantage of such materials is their high stability in basic media in comparison with silane-based materials. The formation of SAMs (Self-Assembled Monolayers) with long-chain alkylphosphonic acids has already been reported[2,3] Self-assembly leads to dense monolayers with high grafting densities. In this work, our objective was to prepare hybrid materials functionalized by thiol groups with a large number of reactive functions. The strategy of SAMs formation with 12-mercaptododecylphosphonic acid on titanium dioxide allowed us to introduce the maximum amount of terminal functional groups on the surface of the inorganic support. Investigation of the grafting of 12P MAS NMR indicated the covalent bonding of the organophosphorus derivative on the oxide surface. Infrared spectroscopy and elemental analysis informed us respectively on SAMs formation, long chains organization degree and on surface coverage. Similar results as in the case of SAMs formation with octadecylphosphonic acid on titania have been obtained. As thiol groups have a high affinity for binding heavy metals[3-5] extraction experiments have been realized on 10 ppm mercury(II) alkaline aqueous solutions. Atomic absorption measurements of remaining metal concentrations indicated a nearly quantitative removal of mercury from solutions. 1- Guerrero, G.; Mutin, P.; Viox, A. Chem. Mater. 2002, 14, 8924. 2- Guerrero, G.; Mutin, P. H.; Viox, A. Chem. Mater. 2001, 13, 4367. 3- Guerrero, G.; Mutin, P. H.; Viox, A. Chem. Mater. 2002, 14, 8924. 4- Pawsie, S.; Yuch, K.; Reven, L.; Langmuir 1999, 15, 845. 5- Laibinis, P. E.; Hickman, J. J.; Wrighton, M. S.; Waddles, G. M. Science 1992, 254, 455.
The biocompatibility, biodegradability and permeability of poly(c-caprolactone) (PCL) have been extensively explored in the last few years, as it is the product of the polymerization of lactide, a natural cyclic dimer of glycolic acid, is also considered a suitable material for drug delivery. Recently the suitability of sol-gel derived Class II PCL(MW = 2000 g mol⁻¹)/siloxane hybrid systems as degradable bioglasses, non-toxic for living organisms [1,2]. Applications of these hybrids as coating materials for bone implants, prosthetic devices and as supports for enzyme immobilisation were also suggested [1,2]. In the present work we propose that Class II PCL(MW = 538 g mol⁻¹)/siloxane hybrid structures are good host cages for the entrapment of Eu³⁺ ions and the development of technologically attractive materials for optical devices, as they efficiently protect the cations from quenching effects, leading to high quantum yields. The lanthanide ions were introduced as a calcium/europium (Ca/Eu)-complex and as europium triflate, Eu(CF₃SO₂)₃. The use of the CC ligand is advantageous, since it, not only shields the lanthanide ions from deactivating groups, but also gives rise to the antenna effect. Class II (siloxane/triflate) hybrid/organic networks were used to prepare hybrid materials with high thermal stability and ionic conductivity of the xerogels produced were characterized by X-ray diffraction, thermogravimetric analysis, differential scanning calorimetry and impedance measurements. [1] F.M. Gray, RSC Materials Monographs, Royal Society of Chemistry, London, 1997 [2] M. C. González, V. De Zea Bermudez, D. Ostrovskii and L. D. Carlos, Ionics, 8(1&2) (2002) 62 [3] M. C. González, V. De Zea Bermudez, R. A. Sa Ferreira, L. D. Carlos, D. Ostrovskii and J. Rocha, Chem. Mater., in press

**EE13.30**

**Investigation of Li⁺-Doped Di-Urethanesil Poe/Siloxane BiHybrids with a Calcein-Europium Complex and Europium Triflate. S. C. Nunes¹, V. De Zea Bermudez², L. D. Carlos², R. A. Sa Ferreira², D. Ostrovskii² and J. Rocha³, ¹Departamento de Quimica e CQ-VB, Universidade de Trás-os-Montes e Alto Douro, 5000-911 Vila Real, Portugal; ²Departamento de Fisica, Universidade de Aveiro, Aveiro, Portugal; ³Departamento de Quimica e CICECO, Universidad de Aveiro, 3810-139 Aveiro, Portugal; ⁴Department of Quimica e CICECO, Universidade de Aveiro, 3810-139 Aveiro, Portugal.

Li⁺-based solid polymer electrolytes, produced by the dissolution of a lithium salt in high molecular weight polymers containing suitable coordinating sites, have been of interest in many applications of their important technological applications as electrolytes in electrochemical devices, such as high energy-density batteries and fuel cells [1]. To serve as components in commercial lithium batteries these electrolytes must exhibit high ionic conductivity and good mechanical and electrochemical stability. With the goal of developing highly conducting ormolytes (organically modified silicate electrolytes) for primary and secondary batteries, we used the sol-gel process to prepare a new family of lithium triflate-doped poly(oxyethylene) (POE)/siloxane hybrids (di-urethanesils [2-3]) containing a wide range of salt concentration. In these materials the organic and inorganic components (POE chains with approximately 15 OCH₂CH₂ repeat units and a siliceous backbone, respectively) are bonded through urethane linkages (-NHC(=O)O-). The morphology, structure, thermal stability and ionic conductivity of the xerogels produced were characterized by X-ray diffraction, thermogravimetric analysis, differential scanning calorimetry and impedance measurements. [1] F. M. Gray, RSC Materials Monographs, Royal Society of Chemistry, London, 1997 [2] M. C. González, V. De Zea Bermudez, D. Ostrovskii and L. D. Carlos, Ionics, 8(1&2) (2002) 62 [3] M. C. González, V. De Zea Bermudez, R. A. Sa Ferreira, L. D. Carlos, D. Ostrovskii and J. Rocha, Chem. Mater., in press

**EE13.31**

**Novel Er³⁺-Doped Polymer/Siloxane Hybrid Materials for Optoelectronics. S. C. Nunes, V. De Zea Bermudez, R. A. Sa Ferreira, L. D. Carlos, D. Ostrovskii and J. Rocha, ¹Departamento de Quimica, Universidade de Trás-os-Montes e Alto Douro, Vila Real, Portugal; ²Departamento de Fisica, Universidade de Aveiro, Aveiro, Portugal; ³Department of Applied Physics, Chalmers University of Technology, Goteborg, Sweden; ⁴Departamento de Quimica e CICECO, Universidad de Aveiro, Aveiro, Portugal.

The versatility of the sol-gel chemistry (low-temperature processing and shaping, high sample homogeneity and purity, availability of precursors and possibility of preparation of nanocomposites) has motivated the development of rare earth (RE)-doped organic/inorganic hybrids for optics. One of the drawbacks of this strategy is the fact that the luminescence efficiency of RE ions in most sol-gel-derived structures is limited by quenching processes associated with RE ions from residual water and aliphatic groups of the hybrid matrix itself which markedly reduce the RE emission intensity, due to non-radiative decay pathways of the RE ions. In this context the di-ureasils (urea cross-linked polymers/siloxanes) appear to be extremely promising for several reasons: (1) they are essentially hydrophobic; (2) they act as effective protecting cages capable of encapsulating the luminescent centers, virtually eliminating quenching effects; (3) they may withstand extremely high concentrations of photo active species. The first two of these properties have been extensively characterized by UV-vis spectrometry, fluorescence, transmission electron microscope (TEM), dynamic light scattering (zeta-potential, real time distribution), polyacrylamide gel electrophoresis (PAGE), and capillary electrophoresis. Results show that the size and structure of {Au} nanocomposites are highly dependent on the generation number of dendrimer templates. These nanocomposites have a high specific emission intensity (458 nm) than commercially available Au nanoparticles do. PAGE analysis shows that the dendrimer-gold nanocomposites have an electrophoretic migration pattern, which is similar to the dendrimer template. Three components of the {Au} migration peak can be differentiated in capillary electrophoresis. The combination of different techniques provides new insights into the structure and properties of dendrimer-gold nanocomposite materials.

**EE13.34**

**Evaluation of Polypyrrole Coating on Fe₃O₄ and its Effect on Nanocomposite Properties. Silvia Liongl, Alexa W. Harter, Rick L. Moore and William S. Rees, ¹School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia; ²Signatures Technology Laboratory, Georgia Tech Research Institute, Atlanta, Georgia; ³School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia.

Since the discovery of doped polycrylate by MacDiarmid and his group, it has created new possibilities for novel materials. With the appropriate dopant, polymers like polycrylate and polypyrrole may become alternative conductive materials because their resistivity approaches that of metals. Nanocomposites have also been the focus of much research work because they have applications in biosensors, recording media, and electromagnetic (EM) shields. Incorporating conducting polymers into magnetic nanocomposites would produce a novel hybrid material with multifunctional properties and could extend the applications to batteries and non-linear optics. Magnetite (Fe₃O₄) nanoparticles (average diameter is 10nm) will be coated with polypyrrole, and then embedded in a polymer matrix. The polypyrrole coating can impart surface conductivity on these particles. In addition to having magnetic properties, Fe₃O₄ nanoparticles also can be reinforcing materials. By incorporating magnetite nanoparticles in a polymer matrix, such as epoxy, a hybrid material with controllable magnetic, electrical, and mechanical properties will be fabricated. Two processes will be investigated to coat polypyrrole on the surface of magnetite nanoparticles. The first process is surface polymerization, adapted from coating conductive polymer on textiles. Polymerization of pyrrole takes place on the surface of particles by controlling the ratio of monomer to surface area (of nanoparticles). The second process is based on adimellar
polymerization, which uses surfactant to promote polymerization of pyrrole on the surface of the particles. The morphology of the coating will vary within the composite, and it will ultimately affect the properties of the nanocomposite. For example, surface polymerization is expected to form a thicker coating than amido-carboxyl polymerization, producing particles with higher surface conductivity. However, the thicker coating may interfere with the interfacial strength between the particles and the matrix, causing a reduction in mechanical properties. The scope of this work is to compare the two coating processes in terms of the overall properties of the composite. Firstly, the magnetic nanoparticles will be dispersed in a gas phase to form a monolayer of nanoparticles, which will be coated in the presence of 4,4-dicyano-2,2'-bipyridine to allow for suitable control of light in a variety of different fields and applications. CU dots are silica nanoparticles synthesized from a dye-rich silicate core coated in a silicate shell. This architecture introduces a variety of applications, including enhanced fluorescence efficiency and photostability versus free dye in solution. In addition to the synthesis of novel particle architectures and studies of the fundamental photonic properties of individual dots, these optical elements are incorporated into waveguides prepared by a variety of advanced 2D and 3D lithographic methods. Specifically, two photon lithography offers three-dimensional structure control by localized two photon excitation of a radical initiator at the focal point of a near-IR laser. This facilitates the creation of free-standing three dimensional structures for applications in photonics. This is the first demonstration of an integrated materials platform for three-dimensional structural control of encapsulated fluorophores in a hybrid organic/inorganic matrix.

**EE13.35**

Self-assembled Monolayers of High Silica Zeolites. Wanda Low, Alexander Shormikov and Andrew S. Ichimura; Chemistry and Biochemistry, San Francisco State University, San Francisco, California.

Zeolites are microporous materials that have traditionally found use in catalysis, separations, and exchange processes. However, zeolites with conducting or semi-conducting properties might find use in the development of chemical or optical sensors and detectors. One class of materials that have the potential for such applications are inorganic electrodes, which are formed from the addition of alkali metals to pure silica zeolites (M(2/3)SiO2, NaX-Sil). Inorganic electrodes are similar to their organic components based in that the added alkali metal ionizes to yield a stoichiometric number of trapped electrons, as shown by optical spectroscopy and nuclear magnetic resonance studies. In addition, density functional calculations show that the band structure of the silica lattice is significantly altered by alkali metal addition to silica zeolites and suggests that inorganic electrodes may be good conductors. While much work remains to be done on these materials at a fundamental level, in order to develop applications they must be interfaced with conducting or semi-conducting substrates. To this end, we are pursuing a strategy of self-assembly in which the silica zeolite is tethered to a gold or indium tin oxide (ITO) surface by suitable linker molecules. For example, a zeolite may be functionalized by condensation of the surface hydroxyl groups with 3-chloropropylsilane, which leaves the thiol group available for binding to gold. Zeolite monolayers can be formed by mixing a suspension of the linker-coated zeolite in the presence of gold-coated silica wafers. Uniformly zeolite monolayers can be formed by this strategy. These monolayers are stable to short exposure times and stable to desorption at 120 degrees Celsius for up to 5 minutes. Scanning electron microscopy and FTIR specular reflectance measurements are used to monitor zeolite assembly. We report on our efforts to self-assemble silica zeolites on glass substrates and compare the quality and stability of the resulting monolayers as a function of molecular linker and conditions. Wernette, D.P., Ichimura, A.S., Urban, S.A., Dye, J.L. Chem. Mater., 2003, 15, 1441-1448. 2. Li, Z., Yang, J.; Hou, J. G.; Zhu, Q.; J. Am. Chem. Soc., 2003, 125, 1170-1171.

**EE13.36**


The metal organic framework [Cu(OOC-C6H4-C6H4-COO)]2(C6H12N2) has been shown to have a higher methane absorption capacity than the theoretical maximum for activated carbon. This polymer would be ideal for use in the separation of methane from natural gas. In its as-synthesized form the MOF is a powder, which is difficult to deposit a very thin polymer layer onto a fiber-shaped substrate from solution because the high interfacial energy can lead to dewetting. This difficulty presents itself when attempting to apply a gate dielectric to conductive fiber substrates during the fabrication of fiber transistors for use in applications such as "electrotextiles" and fiber transistors for use in applications such as "electrotextiles" and "electrotextiles". For example, surface polymerization is expected to form a thicker coating than amido-carboxyl polymerization, producing particles with higher surface conductivity. However, the thicker coating may interfere with the interfacial strength between the particles and the matrix, causing a reduction in mechanical properties. The scope of this work is to compare the two coating processes in terms of the overall properties of the composite. Firstly, the magnetic nanoparticles will be dispersed in a gas phase to form a monolayer of nanoparticles, which will be coated in the presence of 4,4-dicyano-2,2'-bipyridine to allow for suitable control of light in a variety of different fields and applications. CU dots are silica nanoparticles synthesized from a dye-rich silicate core coated in a silicate shell. This architecture introduces a variety of applications, including enhanced fluorescence efficiency and photostability versus free dye in solution. In addition to the synthesis of novel particle architectures and studies of the fundamental photonic properties of individual dots, these optical elements are incorporated into waveguides prepared by a variety of advanced 2D and 3D lithographic methods. Specifically, two photon lithography offers three-dimensional structure control by localized two photon excitation of a radical initiator at the focal point of a near-IR laser. This facilitates the creation of free-standing three dimensional structures for applications in photonics. This is the first demonstration of an integrated materials platform for three-dimensional structural control of encapsulated fluorophores in a hybrid organic/inorganic matrix.

**EE13.37**

Active Photonic Structures from Fluorescent Silica Nanoparticles. Andrew A. Burns, Christopher A. Coenjaerts, Christopher K. Ober and Ulrich Wiens; Materials Science & Engineering, Cornell University, Ithaca, New York.

We have developed a novel class of radiative organic/inorganic hybrid nanoparticles referred to as CU dots and investigate their applications to photonics and photonic materials. The aim of this work is to develop enabling technologies through the fabrication of suitable control of light in a variety of different fields and applications. CU dots are silica nanoparticles synthesized from a dye-rich silicate core coated in a silicate shell. This architecture introduces a variety of applications, including enhanced fluorescence efficiency and photostability versus free dye in solution. In addition to the synthesis of novel particle architectures and studies of the fundamental photonic properties of individual dots, these optical elements are incorporated into waveguides prepared by a variety of advanced 2D and 3D lithographic methods. Specifically, two photon lithography offers three-dimensional structure control by localized two photon excitation of a radical initiator at the focal point of a near-IR laser. This facilitates the creation of free-standing three dimensional structures for applications in photonics. This is the first demonstration of an integrated materials platform for three-dimensional structural control of encapsulated fluorophores in a hybrid organic/inorganic matrix.

**EE13.38**


Organosilicon polymers are substantially inorganic in nature and are known for their excellent thermal stability, low flammability, good oxidation/radiation resistance, low dielectric constant and dissipation factor, almost negligible water absorption, and low surface energy, yet they are still easily processable. Most organic polymers, however, do not perform well in applications demanding a combination of these properties. But organic polymers usually are much more robust mechanically than organosilicon polymers which have not found wide use for load bearing applications. In this paper an effective approach to combine the strengths of both types of polymers will be presented. Emphasis will be given to glass and quartz fabric reinforced organosilicon/organic polymer laminates. It is shown that by constructing a hybrid composite of organosilicon resins with some common organic resins, the attractive characteristics of silicone resins are retained, and the mechanical properties can be better than composites of any single type of resin due to a synergistic effect. The effect of composite construction geometry, processing methods and conditions, and compatibilizing co-polymers will be discussed. Meanwhile the mechanisms for the synergistic effect will be elucidated.

**EE13.39**

Femtosecond Laser Direct Writing of Sol-Gel Optical Waveguides. Saurabh Kumar Pamint, Chee Chong Wong, David Kuang Yong Low, and Xiao Zhang; School of Materials Engineering, Nanyang Technological University, Singapore, Singapore; Singapore Institute of Manufacturing Technology, Singapore, Singapore.

Femtosecond laser (FSL) direct writing offers the attractive potential of one-step processing of optical structures. In this study, thick films were prepared on the glass wafers by organic-inorganic hybrid sol-gel materials, in which 3-methacryloylpropyltrimethoxysilane (MEMO) and zirconium n-propoxide were used as precursors, following a modified sol-gel fabrication process. Optical waveguides were directly written into the bulk of this film by using FSL at the wavelength of 775 nm and pulse width of 150 fs at various laser power ranges. Other writing variables such as writing speeds and focus depths were also considered for controlling the dimensions and locations of the waveguides. We shall report on the refractive index changes and waveguide propagation loss characteristics along with the resolution and dimensional control of waveguide structures and their dependencies on FSL processing conditions. *Corresponding author: ph2630010@ntu.edu.sg

**EE13.40**

Organic Transistors with High Mobility on Silicon Fibers: Substrates with Dip-coated Dielectrics. Erik Haakon Synstad and Howard Edan Katz; Materials Research, Bell Labs, Murray Hill, New Jersey.

It is difficult to deposit a very thin polymer layer onto a fiber-shaped substrate from solution because the high interfacial energy can lead to dewetting. This difficulty presents itself when attempting to apply a gate dielectric to conductive fiber substrates during the fabrication of fiber transistors for use in applications such as "electrotextiles" and...
optical switches. We present a dip coating process that applies a gate dielectric to metal-coated optical fibers with high uniformity and reproducibility, resulting in a two-step redox-type thin film transistors with excellent transistor characteristics including mobilities up to 0.3 cm²/Vs and on/off ratios up to 7000. In one case, a memory effect could arise and stabilize the RE trivalent oxidation state. Phospho-
rilicate, due to the decreasing mobility of the particles and their declining size, in phosphate glasses prepared by melting. The phosphate interaction with Ce³⁺ in a less compact glass texture, and should increase the relative hardness by pencil test. The resulting coatings were exposed to UV-A radiation during a time greater than 600 hours. The exposed samples still maintain excellent absorption in the UV range, superior to other coatings available in the market.

EE13.45 Two-Dimensional Crystalline Lattice Templating: A New Approach for the Preparation of Polymer-Covered Metal and Allo-yed Metal Nanocrystals by a Simple Redox Reaction. Alexandru Cesar Pavel, Dwight K. Romanovitz, M. Jorge Yacaman and John T. McDevitt, Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas; 2Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas; 3Center for Nanoscale Molecular Science and Technology, Austin, Texas; 4Chemical Engineering, The University of Texas at Austin, Austin, Texas.

The crystal lattice can be used as a template for the preparation of 1-D metal/alloyed metal nanostructures due to its intrinsic ordering of the constituent metal cations. The method shows great potential towards producing custom-made, compositionally tailored metal or alloyed metal nanocrystals by choosing the appropriate 2-D layered oxide and reacting it with pyrrole at moderate temperatures. Crystal lattice engineering by appropriate substitution/doping of some of the original metal cations can be used to create the appropriate precursor for the compositionally targeted final nanostructure.

EE13.46 Molybdenum Dioxide and Vanadium-Doped Molybdenum Dioxide Microcrystals in a Polymer Container. Alexandru Cesar Pavel, Dwight K. Romanovitz and John T. McDevitt, Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas; 2Texas Materials Institute, The University of Texas at Austin, Austin, Texas; 3Center for Nano- and Molecular Science and Technology, The University of Texas at Austin, Austin, Texas.

Pyrrole can be used as a suitable reducing agent for the formation of novel organic polymer-inorganic metal oxide microstructures with potential applications in areas like selective catalysis and chemical sensing. Orthorhombic and hexagonal molybdenum trioxide and hexagonal vanadium-doped molybdenum trioxide with different grain sizes used were produced polymer-contained monoclinic molybdenum- and vanadium-doped molybdenum dioxide crystals by a two-step redox process. By reducing the size of the precursor’s grain it is possible to obtain polymer-contained nanocrystals of the final oxide. The method can be applied to other binary or ternary transitional metal oxides which contain the cation(s) in their highest oxidation state in order to obtain nano- or microcrystals of lower oxidation state metal oxides.


Microstructure patterning technologies for fabrication of integrated optical components such as planar optical waveguides and devices have received great attention in recent years. Conventional microstructure patterning is achieved by lithographic technologies, which involve two main steps: structure patterning with UV-light or E-beam and structure developing by wet chemical etching or plasma etching. These processes are rather complex and may lead to control over surface profile in the etching process. To achieve a low cost
and simple fabrication process, we explore a TiO2-doped hybrid sol-gel glassy material that enables the fabrication of microstructure on film surface in a single step with focused electron beams. In this paper, we firstly describe an anhydrous sol-gel process based on hydrolysis and condensation of metal alkoxides with boronic acid under non-hydrolytic conditions, and show that this anhydrous sol-gel process is useful for effectively incorporating TiO2 into alkoxide gels, which is difficult for the conventional aqueous sol-gel process because of the great hydrolysis reactivity difference between titanium alkoxide and silica precursors. 3-methacryloxypropyltrimethoxysilane (MPS) was hydrolyzed using a boronic acid, with boronic acid ratio of 1:0.5. The reaction was performed under reflux conditions for 2 hours with methanol as a solvent. Titanium ethoxide was then dripped into the hydrolyzed MPS solution at a molar ratio of 0.1:0.7. After refluxing for another hour, the solvent in the reaction mixture was removed under vacuum evaporation, giving clear transparent viscous resins. The TiO2-doped hybrid polymer resins with varied TiO2 concentrations (up to 40 mol%) were spun coated onto fused silica substrates and silicon wafers. Thin films were UV cross-linked with a mercury lamp (350-380nm) irradiation, and then thermally cured (160 oC for 10 hours under vacuum) conditions. Optical characteristics for the TiO2-doped hybrid glassy thin films were performed. The TiO2-doped hybrid material showed a low OH absorption, low optical losses at telecommunication wavelengths (<0.40 dB/cm at 1550 nm and <0.20 dB/cm at 1310 nm respectively), good thermal-optical linearity and good thermal stability up to 200 oC. In the second part of this paper, we examined single-step direct surface patterning in the TiO2-doped hybrid glassy films with focused electron beams. Results showed that fine structure with resolution higher than 0.4 micron can be fabricated in the films. As the process was developed, it provided a development (etching) pattern, and these profiles of the lines fabricated by the E-beam direct writing showed few distortions. The high precise patterning microstructure with submicron focused on the TiO2 hybrid glassy thin films may provide potentials for fabrication of sub-micron period gratings on E-beam direct writing technology.

**EE13.48** Improvement of Polymer Electret Characteristics by Inclusion of Au Colloids

Myongseob Kim, Yumin N. Shen, Chungho Lee and Edwin C. Kan; School of Electrical and Computer Engineering, Cornell University, Ithaca, New York.


**EE13.49** Improvement in Performance of an Organic Field Effect Transistor by Controlling the Molecular Alignment.

Takuya Kambayashi1, Hideo Takeo1, Ken Ishikawa2, Hiroichi Ohta1, Kenji Nomura1 and Hideo Hoso1; 1Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo, Japan; 2Hosono Transparent ElectroActive Materials Project, Japan Science and Technology Corporation, Kawasaki, Japan.

Organic molecules have attracted much attention toward electronic devices such as thin film transistors, light emitting diodes, photo conductors for xerography, and so on. Performances of these devices are, however, not so good as those of inorganic semiconductors, since the mobility of organic materials is quite low particularly in amorphous and randomly oriented polycrystalline films. Therefore, controlling molecular alignment in active layers is important. In this presentation, we will report on bottom contact field effect transistors (FET's) using metallophthalocyanines (MPCs) as active layers. In order to control molecular alignment in the active layer, we applied molecular beam epitaxy (MBE) growth of MPCs on an amorphous flat transparent conducting and insulating films. These films were grown on Ytrrium stabilized Zirconia substrates by pulsed laser deposition. MPCs were epitaxially grown on amorphally flat Indium-Tin oxide (ITO) conducting films. [1, 2] The stacking axis of MPCs is parallel to the surface both in vanadylphthalocyanin(VPc) and copperphthalocyanine(CuPc). The charge carrier mobility of MPCs is higher along the stacking axis, so that this orientation is favorable for applying them to the active layers of an FET with a lateral channel. To fabricate the bottom contact FET device we had to deposit MPCs not on the conducting layer but on an insulating layer deposited on the conducting layer. We selected Scandium Ytrrium Oxide (Sc:Y) as an insulating layer; the lattice parameter of (Sc0.7Y0.3)2O3 is 1.073 nm, which is almost the same value as CuPc. The (Sc0.7Y0.3)2O3 dielectric layer was fabricated on the single crystalline ITO film by pulsed laser deposition technique. From analysis of (Sc0.7Y0.3)2O3 by high resolution X ray diffraction, (Sc0.7Y0.3)2O3 was heteroatomatically grown on the ITO film. Root mean square roughness of the (Sc0.7Y0.3)2O3 layer was approximately 1 nm. Then VpOc and CuPc layers were deposited on the bi layered film of (Sc0.7Y0.3)2O3 / ITO as active layer. From the analysis of the active layer by atomic-force microscopy and X ray diffraction, active layers (MPCs) had the same molecular alignment of MPc layers grown on ITO films. These MPC transistors have rather large field effect mobility, VOc: ~10-4 cm2/Vs and CuPc: ~10-3 cm2/Vs, and the on/off ratio was obtained. In conclusion, FET characteristics were well improved, by controlling molecular alignment in the MPc layers [3], as compared with the values reported on MPc's. [1] H.Ohta et al., AdvancedMaterials, 16, 312/313 (2004) [2] T.Kambayashi et al., Cryst. GrowthDes. submitted [3] H. Ohta et al., AdvancedMaterials. 15, 1258(2003)


Abdiaziz A. Farah1 and William J. Pietro2; 1National Research Council of Canada, Institute of Microstructural Sciences, Ottawa, Ontario, Canada; 2Department of Chemistry, York University, Toronto, Ontario, Canada.

Multifunctional polymers with covalently attached luminophores promise potential applications for useful and interesting optical materials. In our group, the molecular design and characterization of a single component bifunctional macromolecules was successfully achieved through facile incorporation of Ru(II) (bipyridine) chromophore initiator into poly(N-(7’-alkylcarbazolyl) methacrylates) chains via atom transfer radical polymerization. With these metalloinitiators, multifunctional linear and star type polymers and blocks containing well-defined molecular weight and low molecular distribution. Heteroleptic ruthenium-centered poly(c-caprolactones) of various dimensionality were also obtained via ring-opening polymerization of c-caprolactone by using bpy or quinoline ligand initiators followed by chelation to ruthenium. Electronic absorption and emission spectra for these resultant functional polymers provided evidence of the presence of both chromophores within a single polymeric chain. Their high thermal properties were also investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

**EE13.51** Abstract Withdrawn

**EE13.52** Self-Extinguishing Polymer Nanocomposites.

Mayu S1, Hsinchou Chu1, Mirkam Rafailovich1, Jonathan Sokolov1, Daniel Hefter2, Jonathan Hefter and Ardekly Sokolov1; 1Materials Science and Engineering, Stony Brook University, Stony Brook, New York; 2University of Pennsylvania, Philadelphia, Pennsylvania.

Self-extinguishing and smoke suppression are important properties for many polymer materials. This work reports on a novel self-extinguishing polymer nanocomposite developed by preparing organo-silanes derived from phosphorus and boron containing surfactants. The phosphorus containing surfactants are coupled to the polymer backbone using a thiol-ene click reaction, which is then crosspolymerized with an epoxide. The crosspolymerization is performed in the presence of a metalloorganics initiator that will catalyze the formation of the linear polymer backbone with defined molecular weight and low molecular weight distribution. Crosslinked polymer networks with 10 and 20 wt% metalloorganics (Ru and Cu) were synthesized and characterized. The thermostability of the materials was determined using thermogravimetric analysis and the extent of self-extinguishing properties was determined using cone calorimetry on the crosslinked polymer networks. The results indicate that the addition of metalloorganics does not negatively impact the glass transition temperature of the polymer networks and that the metalloorganics provide self-extinguishing properties, which is very important for the development of smoke suppressing materials. Further experiments will be performed to characterize the catalytic activity of the metalloorganics within the polymer networks.
Very few polymers are currently self-extinguishing when exposed to a flame. Since polymers ignite easily, the combustion process can be retarded through compounding with conventional flame retardant agents such as decabromodiphenyl oxide (DB) and antimony trioxide (AO). The efficiency of these compounds depends on their ability to disperse within the polymer. Since they are generally immiscible with most materials, very few polymers can be rendered self-extinguishing according to the stringent UL-V0 designation. The addition of functionalized clays to polymers is known to improve their rheological properties and in some cases to improve flame retardance. Here we show that when the clays are mixed with the retardant agents excellent dispersion within polymer can be achieved. We have investigated the effect of these compounds on key properties such as thermal stability, dielectric properties, and flame retardance.

EE13.53
Electrical Transport in Multilayers of Au/Ag Nanoparticles Films. Claudiu Hapenciuc1, Ashavani Kumar2, G. Ramanath2 and Theodorian Borca-Tasciuc1; 1Mechanical Aerospace and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York; 2Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York.

Nanoparticles based nanostructured films are of high interest since they offer the potential for applications in various fields such as semiconductors, molecular electronics, photothermal, thermochemical, chemical and biological sensing and catalysis. This work reports electrical transport measurements of Au/Ag multilayers of nanoparticles films. An aqueous solution containing 100nm size nanoparticles copped with 4-Aminothiophenol was used to deposit thin-films on glass substrates pre-patterned with microelectrode arrays. DC electrical transport measurements are performed in the 80-300K temperature range for individual monolayers of Au and Ag nanoparticles and Au/Ag bilayer film. The experimental results are discussed in the context of existing models for electrical charge transport in nanostructures.

EE13.54
New Methods for Synthesis of Mesoporous Carbons Through Inverse Replication and Self-assembly. Michael Knoll1, Bruno Dufour1, Ewn B. Celer1, Krzysztof Matyjaszewski1, Tomasz Kowalczyk1, Jian Zhang1, Jarek Janusczyk1, 1Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania; 2Chemistry, Kent State University, Kent, Ohio.

Mesoporous carbons have recently attracted much attention, because of their usefulness as adsorbents for large molecules, components of electrochemical double-layer capacitors, catalyst supports and so forth. One of important recent achievements in this field was the introduction of novel precursors known to impinge on their rheological properties and in some cases to improve flame retardance. TEM images indicated that the clay was instrumental in dispersing the DB and AO components. DMA results show that the introduction of clay improved PMMA bending modulus by 28% and increased Tg by 8 C. Similar behavior has also been found in EPDM/clay system and the addition of clay can effectively avoid dripping during burning test. Addition of the DB and AO did not have a significant effect on the mechanical properties. Hence the quantities used here were not sufficient to embrittle the polymers. Based on TEM and combustion test, the general mechanism is proposed that the introduction of clay can improve the compatibility between polymer and flame-retardant agents by the synergy between the char formed by the clay and gas phase isolation due to the conventional flame-retardant agents make the material become fire-retardant. Supported by NSF funded MRSEC at Stony Brook University.

EE13.55
Order-Order Transition in a Block Copolymer Induced by Polymer-Coated Gold Nanoparticles. Bumjoon Kim1, Julia J. Chiu1, Gi-Ra Yi1, David J. Pine1,2 and Edward J. Kramer1,2; 1Chemical Engineering, University of California at Santa Barbara, Santa Barbara, California; 2Materials, University of California at Santa Barbara, Santa Barbara, California.

Self assembly of inorganic nanoparticles within a block copolymer offers a way to produce materials with unique optical, electronic and magnetic properties. To reveal some of the fundamentals of this self assembly we have investigated symmetric diblock copolymers consisting of various polystyrene-poly(2-vinylpyridine) (PS-P2VP) with total molecular weight (Mn) ranging from 69 to 113 kg/mol and 4 nm diameter Au nanoparticles whose surfaces are modified by PS chains (Mn=1.5 kg/mol) terminated with thiol groups. Thick (100 μm) films of PS-P2VP with various concentrations of PS coated Au nanoparticles are cast by slow evaporation from toluene. The morphology of these films is determined from cross-sectional transmission electron microscopy. At all concentrations the PS coated Au nanoparticles are preferentially located near the center of the PS domains. While at low particle concentrations the block copolymer morphology is lamellar, it changes to a morphology of hexagonal P2VP cylinders in a PS/PS coated Au particle mixture at higher concentrations. At intermediate concentrations a two-phase morphology is observed with the surface layers of the film being lamellar with low particle concentration and the substrate layers being hexagonal with high particle concentration. The PS-coated Au particle additives thus appear to behave like PS homopolymer, inducing an order-order transition between block copolymer phases as the concentration is increased.

EE13.56
Core-shell Titanium Dioxide-Polystyrene Nanocomposites, an Organic-Inorganic Nanocomposite Which Forms Smooth and Flexible High K Dielectric Films. Ashok Joseph Malinskal1, Howard Katz2 and Pat Cotts3; 1Materials Research, Bell Laboratories, Murray Hill, New Jersey; 2Dupont Central Research, Wilmington, Delaware.

Core-shell Titanium Dioxide-Polystyrene Nanocomposites, an Organic-Inorganic Nanocomposite Which Forms Smooth and Flexible High K Dielectric Films. Ashok Joseph Malinskal1, Howard Katz2 and Pat Cotts3; 1Materials Research, Bell Laboratories, Murray Hill, New Jersey; 2Dupont Central Research, Wilmington, Delaware.

In the field of plastic or flexible electronics, a gate dielectric material that exhibits a high dielectric constant and is also capable of forming smooth and flexible films would be valuable. In pursuit of this goal, it would be desirable to combine the ease of processing of organic polymers with the high dielectric constant of inorganic oxides such as titanium dioxide. To this end, organic/inorganic nanocomposites have been synthesized using high K TiO2 as the core nanoparticle, and polystyrene as the shell. These materials form transparent, continuous thin films which exhibit a dielectric constant enhancement of more than double that of bulk polystyrene.

EE13.57
A Unifying Analogy Between Polymer Nanocomposites and Planar Polymer Films. Amirali Banis1, Hoichang Yang1, Kiyoung Cho2, Sanat Kumar3 and Linda S. Schadler4; 1Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York; 2Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, New York; 3Department of Chemical Engineering, Pohang Institute of Science and Technology, Pohang, Kyungbuk, South Korea.

We unequivocally show that the thermodynamic and dynamic properties of polymers filled with nanoparticles are quantitatively equivalent to the behavior of thin polymer films between two parallel impenetrable planar walls. To provide the underpinnings for this unifying picture we have measured the glass transition temperature (Tg) of polystyrene (PS) when it is blended with 15 nm diameter SiO2 particles over a range of silica loadings. For PS filled with untreated SiO2, the Tg of the polymer is found to decrease with increases in silica loading - qualitatively consistent with depression in glass transition found with decreasing thickness of polymer films sandwiched between planar silica walls. Conversely, the Tg of PS filled with surface modified SiO2 particles shows an increase with increasing silica loading - consistent with increases in glass transition found with decreasing thickness of polymer films coated on substrates with attractive interfaces. The glass transition is controlled by the relative necessary control over the polymer composition and molecular weight. Mesoporous carbons obtained from these novel precursors exhibited high specific surface area (up to 750-1000 m2 g-1), large pore volumes (up to 2.8 cm3 g-1) and pore diameters ranging from about 4 to 25 nm. In contrast with most mesoporous carbons reported to date, they exhibited very low microporosity. The templates, polymers and carbons are extensively characterized using nitrogen adsorption, thermogravimetry, transmission electron microscopy and powder X-ray diffraction.
lengths of grafted vs. matrix PS chains. This analogy is quantified using electron micrograph images of the nanocomposites which yield an approximate nanometer thick analog for the wall-to-wall distance in thin films. In combination with recent results on polymer blend phase transitions, where both filled systems and thin films provide similar results, we conclude that the proposed analogy between nano-filled polymers and thin polymer films helps to provide a unified quantitative understanding of these two apparently disparate physical situations.

**EE13.58**

New High-Dielectric-Constant Polymer-Ceramic Composites.

Milind Arbhatti, Lisa L. Orna and Z.-Y. Cheng; Materials Engineering, Auburn University, Auburn, Alabama.

Capacitors are widely used to store energy and/or to perform specific functions. The development of electronic devices and circuit of reduced size led to a need for significantly smaller capacitors having increased performance. Today's electronic industry utilizes materials that have high dielectric constants and that also flexible, strong, and easy to process. Finding single component materials possessing all these properties is different. Therefore, a great deal of efforts has gone in to developing polymer-ceramic composites that are flexible and easy to process and are of relative high dielectric constant and high breakdown strength. Ferroelectric and relaxor ferroelectric materials are widely used as ceramic filler in the composites. However, these materials exhibit a strong electromechanical effect which is not desirable for developing high performance capacitors. Additionally, the dielectric property of these materials is strongly dependent on the temperature. Recently, it was found that CaCuTiO12 (CCTO) has a dielectric constant of 10,000 to 100,000. More importantly, the CCTO does have the electromechanical effect and its dielectric constant is almost independent of temperature over 100 K to 600 K. Therefore, it is very interesting to develop CCTO-based composites for high-dielectric-constant applications. The dielectric property of the composites of CCTO particles and PVDF-TrFE copolymer was studied and reported in this presentation. The influence of morphology on the property of composites was studied experimentally. The flexible polymer-CCTO composites are developed. It is found that the electric breakdown field (>10 MV/m) of the composites is much higher than the CCTO ceramics and many ceramics. At room temperature, the dielectric constant at 1 kHz reaches more than 250, which presents a new record for the highest reported dielectric constant. At about 70°C, the dielectric constant of the composites can reach about 600 due to the high dielectric constant of polymer matrix at the temperature.

**SESSION EE14: Applications II**

Chair: Pedro Gomez-Romero

Friday Morning, December 3, 2004

Room 302 (Hynes)

**9:30 AM *EE14.4**

Functional Mesostructured Hybrid Materials for Energy Transfer, Electron Transfer and Molecular Machines.

Jeffrey I. Zink, Payam Minoofar, Raquel Hernandez, Paul Sierocki, Thoi Nguyen, Bruce Dunn and Fraser Stoddart; Chemistry and Biochemistry, UCLA, Los Angeles, California.

Functional nanostructured hybrid films are synthesized by incorporating molecules designed to carry out the desired function. A dip-coating method that allows one or more molecules to be deliberately placed in specified spatially separated regions of nanostructured silicate materials in a one step synthesis has been developed. The nanostructured thin films contain three distinct regions: (i) a thin matrix, the outer skin of the micelle, and the ionic interface between the charged surfactant head groups and the silica pore surface. Three strategies, succinctly termed "phillicity", "bonding", and "bifunctionality" have been developed for directing molecules to any one of the regions. Simultaneous placement of two different molecules in two different regions has also been demonstrated. Such placement and the maintenance of long range order requires a delicate balance among film preparation methodology, design of the molecules, and concentrations of all of the species. Details and examples of the induced functionality will be discussed. Energy or electron transfer properties are designed by choosing pairs of molecules (one a donor and the other an acceptor) that are spatially separated in the different regions of the films. Detailed studies of energy transfer by a chelated lanthanide as the donor and a rhodamine derivative as the acceptor. Electron transfer is studied using trisbipyridylruthenium as the electron donor and a substituted viologen as the acceptor. Functional materials involving motion (reciprocating motion, rotary motion, and action as a molecular valve) are described. The design, activation and operation of the first two types will be described briefly. The most developed is a functioning nano-machine in the form of a supramolecular nanovalue that opens and closes the orifices to molecular-sized material on demand. The nanovalue is a pseudorotaxane composed of two components - a long thread containing a 1,5-dioxynaphthalene donor unit that is attached to the solid support, and the other component, the dicyanovinyl cyclophane receptor/receptor, cyclovis(parquat-p-phenylene), which controls access to the interior of the nanopore. Operating the nanovalue involves three steps: (i) filling the container, (ii) closing the valve, and (iii) opening the valve to release any of the contents of the container, as desired. The tubes, which are approximately 2 nm wide, are filled with stable luminescent Ir(ppy)3 molecules by allowing them to diffuse into the open pores. The orifices are then closed by pseudorotaxane formation. An external reducing reagent or light is used to effect the decomplexing of the pseudorotaxane that unloads the tubes and allows the guest molecules to be released. This nanovalue is a supramolecular machine consisting of a solid framework with moving parts capable of doing useful work.

**9:45 AM *EE14.5**

Solution processable nanocomposites based on silsesquioxane cores for use in organic light emitting diodes (OLEDs).

Alan Selinger1, Ryo Tanaka2, and Richard M. Laine3; Kazumori Ueno4, Hiroshi Tanabe4, Evan Williams5 and Ghasan A. Jabbour5;

1Institute of Materials Research and Engineering (IMRE), Singapore, Singapore; 2General Electric Company, Niskayuna, New York; 3Macromolecular Science and Engineering, Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; 4Canon, Inc., Tokyo, Japan; 5Optical Sciences Center, University of Arizona, Tucson, Arizona.

Organic light emitting diodes (OLEDs) have been a highly targeted area of technology since the early 1990’s for their application in flat panel displays. Over the years there has been much debate over which functional materials - small-molecules or polymers - is best suited for OLEDs. Small-molecules can be highly purified and vacuum deposited in multi-layer stacks, both important for display lifetime and efficiency. However, vacuum deposition techniques require costly equipment and a limitation to practical display sizes at much lower costs using solution-based deposition techniques. Here we report nanocomposite materials based on polyhedral oligomeric silsesquioxane (POSS) architecture that could combine the best of both small-molecule and polymer approaches to OLEDs. The materials contain a spherical “silica” core with eight functional sites that can be easily decorated with a plethora of OLED functional groups. The resulting materials offer numerous advantages for OLEDs including: high glass-transition temperatures (Tg), high solubility, and high-purity via column chromatography. Initial OLED device performance data is presented that shows a 30% improvement over their molecular counterparts. For example, simple undoped Alq3-based devices prepared using the nanocomposite material as a hole transport layer have high brightness (>85,000cd/m2), and relatively high quantum efficiency (1.25%).

**9:00 AM *EE14.2**

**9:30 AM *EE14.3**
(lower rims of the thiacalixarenes) with silane groups was therefore investigated in order to prepare class II hybrid materials incorporating the optically active molecule. Both molecular engineering and preparation of solid-state materials will be presented. Interactions between the matrix and the dye will be discussed.

9:45 AM **EE14.4**

ORMOCER®: (Organic-Inorganic Hybrid Polymers) for Telecom Applications: Structure/Property Correlations. Frank Kahlenberg and Michael Popall; Fraunhofer - ISC, Wuerzburg, Germany.

The development and characterization of fluorocarly functionalized inorganic-organic hybrid polymers for optical waveguide applications is presented. The materials are prepared from organoalkoxysilanes in a two-step process. The first step is the establishment of the inorganic polysiloxane network by hydrolysis and polycondensation in order to obtain a soluble resin. This can be mixed with a photo initiator and applied onto a substrate as a photo-sensitive film. Micro patterns (waveguides with core and cladding) are then manufactured in a second step by exposure to UV-light through a mask. The polymers are characterized with respect to application in the fabrication of telecom optical waveguide devices. Thus, special attention is turned to optical losses in the telecom wavelengths at 1310 nm and 1550 nm as well as to refractive indices. During all stages of ORMOCER® preparation, structure-property relations are deduced from presented characterization data. Various spectroscopic tools give an insight into network structures of polycondensate resins and cured hybrid polymer samples. 29Si NMR in particular is used for the quantitative analysis of siloxane species. With the aid of molecular modeling, structural characteristics of oligomeric intermediates as determined by experiment are visualized. ORMOCER® resins with low optical losses of 0.28 dB/cm at 1310 nm and 0.42 dB/cm at 1550 nm, respectively, are prepared. Subsequent micropatterning by means of photolithography results in waveguide and other test patterns. A low optical loss of 0.51 dB/cm at 1550 nm is measured on a waveguide manufactured from a photopatternable fluorocarly functionalized ORMOCER®. The presentation will include an overview on ORMOCER® based prototypes and demonstrators for in telecom applications, Registered Trademark of Fraunhofer Gesellschaft zur Foerderung der angewandten Forschung e.V. in German