SYMPOSIUM CC
Hybrid Organic/Inorganic Materials
April 24 – 28, 2000

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*Invited paper
SESSION CC1. CHEMICAL STRATEGIES FOR THE DESIGN OF NEW HYBRIDS

Chair: Richard M. Laine, Clement Sanchez, C. Jeffrey Brinker and Emmanuel P. Giannelis
Monday Morning, April 24, 2000
Metropolitan III (Argent)

8:30 AM *CC1.1
BRIDGED POLYSILSESQUIXANES: A MOLECULAR-BASED APPROACH TO THE SYNTHESIS OF FUNCTIONAL HYBRID MATERIALS. Kenneth J. Shea, Dept of Chemistry, University of California, Irvine, CA; Douglas Loy, Sandia National Laboratory, Albuquerque, NM.

Bridged polysilsesquioxanes (BPS) are a family of hybrid organic-inorganic materials prepared by solgel polymerization of monomers that contain a variable organic component and at least two trivalent metallic elements. The resulting materials have physical and mechanical properties that are strongly influenced by the organic bridging group. The talk will focus on functional bridged polysilsesquioxanes. These materials are prepared by solgel polymerization of monomers that incorporate functionality in the variable organic bridging group. The functional groups, which include carbonates, mercaptans, disulfides, and amine, can provide handles for modifying bulk morphology and for provide function to the sorbents. The applications of these materials include ion exchangers, stationary phases for chromatography, protosilicas and high capacity chromatographic adsorbents.

9:00 AM *CC1.2
FUNCTIONAL ORGANOTIN ALKYLIDES AS PRECURSORS OF TIN-BASED HYBRID MATERIALS. Pascal Jaunier, Bernard Joussenme, Manon Toupane, Univ Bordeaux 1, Laboratory of Chimie Organique et Organometallique, Talence, FRANCE; Mohamed Labcinii, Univ Cadi Ayyad, Dept de Chimie, Marrakech, MAROCCO.

Triorganotin and diorganotin oxides and alkoxides have been the subject of numerous studies and many different preparations of these compounds have been proposed in the literature. However, only a few simple trinioxides are known and their preparations are more limited. Difficulties have been experienced in trying to introduce functional or polymerizable groups in the chain linked to the tin of such compounds. Either the corresponding organotin trichlorides are not stable or the functionality is not compatible with the introduction of alkox group at the terminal. That is why new functional organotin trialkoxides have been prepared to solve this problem and thus allow an easy and general access to functional organotin trioxides and oxides. In this study, organotin trialkoxides were obtained either by classical alklylation of the corresponding trichlorides, when they are available, or by a novel alkylation reaction of tetralkyltinyl with Grignard reagents[1], when the trichlorides are not stable. In contrast to the use of lithium reagents, this transmethylation reaction is very selective and leads to monomeric tin trialkoxides in high yield. Then, organotin trialkoxides were hydrolyzed to the corresponding oxides leading to the same clusters as organotin trialkoxides. They could also be alkylated with alcohols[2] giving the corresponding trialkoxides and transformed with organic acids into organotin carboxylates[3]. Functional oxides and organotin carboxylates are co-polymerized in the presence of suitable monomers to give tin-based organic-inorganic hybrids.


9:30 AM CC1.3
SOL-GEL CHEMISTRY OF TRIALKOXY SILANES. Diane A. Schneider, Douglas A. Levy, Karnataka Rahimian, Catalysts and Chemical Technologies Department, Sandia National Laboratories, Albuquerque, NM.

Hydrolysis and condensation of trialkoxysilanes, HS(OEt)3 and HS(OEt)2, has been used to prepare polyhydroxosilanes for dielectric applications. In this study we examined the ability of trimethoxysilane and triethoxysilane to undergo solgel polymerization to afford gels. Solgel polymerization experiments were conducted under acidic (HCl), basic (NaOH), and neutral conditions in methanol or ethanol. Polymerizations with basic catalysts were exothermic with the evolution of hydrogen gas. Gels from all experiments were worked up under aqueous conditions to afford xerogels. Surface area analyses by nitrogen sorption porosimetry revealed that the materials were mostly mesoporous materials with surface areas up to 2000 m2 g-1 under different conditions. The Si 29 CP MAS NMR was used to determine the level of retention of the hydrido group in the xerogels. Gels prepared under acidic conditions were essentially polysilanesquioxanes with very little loss of hydroxyl functionalities. In gels prepared under basic conditions the hydrido groups were completely gone leaving siloxen gels. Gels prepared with neutral water lost approximately two thirds of the hydrido groups.

9:45 AM *CC1.4
ORGANOPHOSPHORUS-BASED ORGANIC/INORGANIC HYBRIDS. A. Vieux, P.H. Mutin, J. Le Bideau, D. Ledercq, Univ Montpellier 2, FRANCE.

The aim of this talk is to highlight the interest of organophosphorus precursors, especially phosphonate and phosphite derivatives, in the field of organic/inorganic hybrid materials. A wide range of applications are illustrated by examples focused on two typical metals, titanium and aluminum. In particular the synthesis of organosoluble molecular precursors with cage structures, the hydrothermal synthesis of crystalline (two or three-dimensional) phases, the introduction of organic moieties into metal oxide matrices by solgel processing, and the grafting of metal oxide surfaces are discussed. The last two applications are stressed as a general alternative to carbon and silicon coupling agents in the bonding of organic groups to metal oxides.

10:45 AM *CC1.5
NEW PREPARATIVE METHODS FOR ORGANIC-INORGANIC POLYMER HYBRIDS. Ryo Tanaki, Yoshiko Chiaja, Kyoto Univ, Dept of Polymer Chemistry, Kyoto, JAPAN.

This paper describes new methods for the preparation of organic-inorganic hybrid materials. [1] In-situ polymerization method: the radical polymerization of N,N-dimethylacrylamide or styrene was carried out simultaneously together with the solgel reaction (hydrolysis and condensation of alkoxysilanes) to produce homogeneous and transparent polymer hybrids. IPN (Interpenetrating polymer network) hybrids were prepared by this method using bifunctional vinyl monomers (methacryloxyethyl or divinylbenzene). The IPN polymer hybrids obtained showed excellent solvent-resistant properties. [2] In-situ hydrolysis method: the solgel reaction of tetramethoxysilane in the presence of poly(vinyl alcohol) produced only phase-separated materials due to the aggregation of alcohol groups within organic polymer segments. Thus, the acid-catalyzed solgel reaction of tetramethoxysilane was carried out in the presence of poly(vinyl acetate) instead. During the formation of silica matrix, the acid-catalyzed hydrolysis of poly(vinyl acetate) took place. As a result, the homogeneous polymer hybrid consisting of silica gel and poly(vinyl alcohol) were successfully obtained. [3] Aromatic interaction between organic and inorganic matrix: The combination of polystyrene and tetramethoxysilane produced only turbid materials. On the other hand, in the presence of polystyrene, the solgel reaction of phenyltrimethoxysilane gave homogeneous polymer hybrids. In this reaction, the interaction of phenyl groups of polystyrene and phenyl groups of silica gel matrix was found to play an important role for the preparation of homogeneous polymer hybrids. By using this idea, the polymer hybrids based on polycarbonate or poly(dialkyl phthalate) were also prepared starting from phenyltrimethoxysilane.

11:15 AM *CC1.6
HYBRID SILICA-BASED MATERIALS AS NEW SOLID PHASE EXTRACTION ACTANTS. Jean-Charles Broide, Olivier Concour, Joel-JE Moreau, Daniel Meyer, Michel Wong Chi Man, Laboratoire de Chimie Organometallique, CNRS UMR 5076, Ecole Nationale Superiéure de Chimie, Rue de l'Ecole Normale, Montpellier, FRANCE.

Organic-inorganic hybrids exhibiting specific properties are easily prepared by incorporation of organic fragments in an inorganic network. Increasing attention is being paid to hybrid siloxenoxanes, which are prepared by solgel hydrolysis and condensation of organic molecules containing two or more trilinkoxylsulitate substituents. These hybrids consist of a mixed three-dimensional network, where the organic fragment, cross-linking chains in part the inorganic framework. Owing to the presence of a strong Si-O bond between the organic and the inorganic fragments, highly stable hybrid network are produced in this way. A variety of materials can be produced according to the intrinsic properties of the organic fragment and according to the nature of the bonding interaction between the organic and the inorganic components. The incorporation of Lewis bases or ligands has for example allowed the preparation of materials containing metal complexes. These heterogenized metallic species proved to be of interest as catalytic materials. We report the preparation of hybrid materials with complexing properties upon hydrolysis condensation of ligands functionalized by Si-OH groups. New hybrid silica-based materials containing molybdenum ligands have been prepared by solgel hydrolysis of functionalized precursors and have been used as solid phase extractants for the complexation of actinomic elements. This approach for the immobilization procedure of complexing agents. The solgel approach allows one to adjust the ligand loading and to achieve some control.
and tuning of the ligand environment since the oxide matrix is built around the complexing moieties. These hybrids proved to be highly efficient extracting solids which compare favorably to related silica materials.

11:45 AM CC1.7
STRUCTURAL MODIFICATION OF SOL-GEL MATERIALS THROUGH RETRO DIELS-ALDER REACTION. Ralf Shaksht, Douglas Loy, Mark McChinn, Sandia National Laboratories, Albuquerque, NM; Shinmuyan in Pohakular, University of New Mexico, Albuquerque, NM; John Green, Kenneth Shen, University of California, Irvine, CA.

Novel bridged polysiloxanes, whose organic bridging group was designed to undergo a retro Diels-Alder reaction, were prepared. The retro-Diels-Alder reaction results in loss of an organic diene from the organic bridging group (without depolymerization) resulting in modified hybrid material's architecture. These monomers were polymerized by hydrolysis and condensation under standard sol-gel conditions and dried as aerogels. The dry gels were thermally treated to induce the retro Diels-Alder (Retro-DA) process. The retro-DA reaction of the cyclopentadienyl Diels-Alder adducts was confirmed by 13C NMR and the nitrogen sorption isotherm.

SESSION C22 WELL-DEFINED NANOBUILDING BLOCKS PRECURSORS FOR HYBRIDS
Chairs: Joseph D. Lichtenstein, Douglas A. Loy
Monday, April 30, 2000
130 PM *CC2.1
MAJOR ADVANCES IN THE SYNTHESIS OF POSS MONOMERS.

Polyhedral oligosilsesquioxanes (POSS) are an interesting class of three-dimensional Si/O clusters derived from the hydrolytic condensation of functional organosilicon M. At this (temperature of POSS N. Since their discovery in 1986, many stoichiometrically well-defined POSS frameworks have been reported, but it was only recently that POSS frameworks suitable for use as monomers or di-functional molecules have been synthesized. Over the past few years we have been exploring the fundamental reaction chemistry of fully condensed [RSiO3]n clusters, n = 6, 8, 10, 12 frameworks with an eye toward developing practical, low-cost methods for manufacturing POSS monomers on a large scale. Our work since the MRS Meeting in Spring 1999 has been particularly successful, and it is now possible to prepare a very large number of useful POSS monomers. This talk will outline several new methods for preparing POSS monomers from inexpensive silane and silicate feedstocks.

2:00 PM CC2.2
HYBRID MATERIALS BASED ON ASSEMBLING ORGANOMETALLIC CARBOXYLATE CLUSTERS. François Q. Billot, Delphine Minoux, Clément Sanchez, Chimie de la Matière Condensée, Université Pierre et Marie Curie, Paris, FRANCE.

The nanobuilding block route to hybrid organic-inorganic materials is based on the controlled assembling of well-defined nanoscale objects, the structural features of which are retained through out the process. This approach allows the design of novel materials, in which the inorganic component is perfectly defined and well dispersed. With the aim to follow this route for tin-based hybrid materials, the oxo-cluster Bu2Sn(O(C2H4OH)2 has been prepared and characterized. As several other organic-inorganic clusters, this cluster has a hexagonal prismatic coordination of the organic ligands on the six seven-membered faces, which offers a covalent organic-inorganic interface. The assembling step was performed in two ways: directly by hydrolysis of the bis-tin acetate, or stepwise via the functionalization with inorganic precursors (ICSNESAL, which yields the new cluster Bu2Sn(O(C2H4OH)2H)

The reaction of dysprosium with the tin atoms in the clusters is then evidenced by energy-dispersive X-ray analysis. These results suggest that the clusters may be used as a building block for the preparation of hybrid materials.

2:15 PM *CC2.3
INORGANIC-ORGANIC HYBRID POLYMERS FROM SURFACE-MODIFIED OXOMETALLATE CLUSTERS. Ulrich Schubert, Gregor Flemming, Michael Mauers,(from 13Sn NMR has been used to probe the clusters integrity along the assembling procedures.

2:45 PM CC2.4
TITANIUMALKOXIDES MODIFIED BY PHOSPHONATES AND PHOSPHONATE BUILDING BLOCKS FOR THE SOL-GEL PROCESSING OF NOVEL ORGANIC-INORGANIC HYBRID MATERIALS. M. Meier, C. Guimares, M. Neum, P. Martin, A. Vieu, Université Montpellier, 2, FRANCE.

We are currently exploring the homogeneous incorporation of phosphonic units into transition metal oxide networks, via a 2-step sol-gel process. The first step involves the non-hydrolytic condensation of a metal alkoxide with a phosphonic acid, the second step corresponds to the hydrolysis / condensation of the remaining alkoxo groups. In this work we report the isolation of several molecular intermediates in this process, namely [Ti4(O2)[PbO3][Al4]1, [Ti4(O2)[PbO3][Al4]2, [Ti4(O2)[PbO3][Al4]3, [PbO3](3DSO), [Ti4(O2)[PbO3][Al4]2, [Ti4(O2)[PbO3][Al4]3, JDSO, and [Ti4(O2)[PbO3][Al4]2, [Ti4(O2)[PbO3][Al4]3, which were characterized by single crystal X-ray structure analysis. These compounds are structural models for the hybrid material based on TiO2 and phosphonate (phosphonite) groups, giving information on the bonding of the phosphonate (phosphonite) ligands and the titanium atoms. In all cases the non-hydrolytic condensation of a metal alkoxide with a phosphonic acid is complete, and the phosphonate is coordinated to a titanium atom, leading to (PO)(OT)3 and RPO(OT)3 structural units. In addition, these clusters can be used as a component in a small number of organic solvents and contain hydroxzylation alkoxo groups, which makes them potential building blocks in the sol-gel process. Accordingly, the hydrolysis-condensation of clusters 1 and 2 was studied using non-aqueous solution NMR (1H, 31P). Partial hydrolysis of the titanium-phosphonate 1 in the presence of titanium n-propoxide led to the octameric phosphonate [Ti4(O2)[PbO3][Al4]2], with the same structure as 2 and 3. The use of 2 as a single source precursor in a sol-gel process was investigated. FT-IR, 31P MAS NMR, SEM, and BET analysis were used to characterize the structure and texture of the resulting hybrid material.

3:30 PM *CC2.5
FROM CLUSTERS VIA NANOSIZED RING-SHAPED AND SPHERICAL (ICOSAHEDRAL) CLUSTERS AND SUPRA-MOLECULAR SPECIES TO MATERIALS. Achim Müller, Fukushima, Fachr. für Chemie, Universität Bielefeld, Bielefeld, GERMANY.

In Nature, complex molecular systems like proteins have evolved structures that are well suited to their functions. These proteins are produced in a sequence of steps under distinctive conditions that is, in general, not found in the laboratory. The challenge for the chemist is to synthesize correspondingly complex multi-functional molecules also under non-equilibrium (dissipative) conditions using multi-component on-off reactions without having to separate and purify each individual intermediate product. Relevant model reactions have been discovered in simple solutions of transition metal oxometallates: Novel molecular growth processes with feedback (including a type of induced cascade) are described that differ, for example, from the classical, electron-rich, mixed-valence, gant polyoxometalates with modified architectures. These can be used to enhance the generation of defects or to covalently linked together to form chains or as layered metal-organic products with properties related to materials science. They can also start growing again, and the largest polyoxometallate
cluster obtained on the basis of this growth process to-date has 248 atoms. Remarkably, such giant ring species can also act as hosts for other organic/inorganic hybrids and thus provide a new family of molecular capsules. The lecture will be highlighted with a report on the planned synthesis and structure of different sized spherical clusters withicosahedral symmetry which have similar structures as spherical vesicles and which might be linked in different ways with layers for the first time, discrete molecular species with structures related to some of the Archimedean solids will also be reported.


4:00 PM **C2C.6**

**HYBRID INORGANIC/ORGANIC DIOLLOCK COPOLYMERS**


Our main approach to the synthesis and study of hybrid organic/inorganic materials involves incorporating nano-size inorganic/organic hybrid structures into various polymeric networks. A typical POSS cluster is a discrete silicon and oxygen framework stabilized with organic groups and contains a single reactive site. This lone site of reactivity is used to covalently attach the inorganic material to a polymer backbone without causing any crosslinking. This strategy permits the synthesis of melt processable, linear hybrid polymers containing pendant inorganic clusters, and allows us to study the effect these clusters have on chain motion, polymer properties and morphology. The synthesis of nonboronated-based (POSS) macromers, their ring opening metathesis copolymerizations with varying amounts of boron, and analysis of the effect of the pendant POSS group is presented. Ring opening metathesis polymerization permits the easy synthesis of both random and diollock copolymers. Transmission electron microscopy clearly images POSS-rich domains against the POSS-free regions. Major differences in polymer morphology are observed as the amount of inorganic POSS is varied, between random and diollock copolymers, as well as between polymers that differ only in the solubilizing cycloalkyl groups on the POSS cluster.

4:15 PM **C2C.7**

**ORGANIC/INORGANIC HYBRID PARTICLES BY DENDRIMERIC NONTEMPLATING.** Frazier G. Greacen, Barry J. Bauer, Eric J. Amis, National Institute of Standards and Technology, Polymers Division, Gaithersburg, MD.

Organic-inorganic hybrid nanostructures have generated great interest due to a variety of potential applications as electrical, optical, medical and information storage materials. In order to design such hybrid structures, templating a growing inorganic crystal within a polymeric matrix - initially inspired by nature - has been evaluated as an effective synthetic approach. A variety of composite nanostructures come from a desire to understand the mechanisms of polymer nontemplating with a model system. Dendrimers are monodisperse and well-characterized molecules, the size of which spans the characteristic sizes of low molecular mass molecules, polymers and colloids, thereby offering a unique mesoscopic system. Our approach relies on the attachment of metal ions to poly(amide amine) (PAMAM) dendrimers in aqueous solution via oxidative charge or condensation chemistry. The dendrimer end groups can be modified through the inorganic precursors attached to the dendrimer, producing colloid structures that are controlled by the dendrimer. SANS, SAXS and TEM are used to characterize the resulting nanostructures. Different inorganic colloids like noble metal or cadmium sulfide colloids are studied. With increasing dendrimer generation, we observe a transition from low molecular colloid stabilizing, i.e. the attachment of several dendrimers to one inorganic particle (G2 to G4) to an effective polymer templating in terms of a host-guest nanocapsule synthesis (G6 to G10). For these higher generation dendrimers, inorganic colloids are formed inside dendrimer molecules and the size of the nanocapsule can precisely be controlled by the dendrimer generation, i.e. the dendrimer acts as a true template. Synthetic variations are dendrimers that have been incorporated into a polymeric matrix, leading to solid composite materials which combine special colloidal effects with the mechanical properties of polymers. Fluorescence properties of semiconductor quantum dots inside dendrimers will also be addressed.

4:30 PM **C2C.8**

**CUBEOCTAMERIC SILICATE-DIMETHYLISILOXANE HYBRIDS.** Ino Hasegawa, Gifu Univ, Fac of Engineering, Dept of Chemistry, Gifu, JAPAN.

We have so far studied organic-inorganic hybrids with such network that the dimethylsiloxyl group links the cuboctameric silicate (Si8O24)4+ building block. The hybrids were synthesized by the reaction of SiO208: formed selectively in a methanolic solution of tetraethoxysilane and dimethylsilicon. The content of the dimethyl group in the hybrids could be increased with increasing amount of dimethylsilicon. The increase, however, dimethylsiloxanes formed as by-product, which were difficult to separate from the hybrids. This means that this reaction is not suitable for producing the hybrids with a large dimethylly group content. In this study, we have attempted another reaction to produce the hybrids in which a larger amount of the dimethyl group is introduced. The reaction has been carried out under alkaline conditions using (3-hydroxyethyl)trimethoxysilane as a source of Si8O24 and dimethylsiloxane. The content of carbon present as the methyl group in the hybrids has been increased to over 10%. This talk focuses on the reaction and the dimethyl group-rich hybrids.

SESSION C2C: CHEMICAL ROUTES TO NANO/MESOSTRUCTURED HYBRID MATERIALS

Chairs: Bradley F. Chmelka and Francois O. Ribot

Tuesday Morning, April 25, 2000

**10:00 AM **C2C.1**

**THE INFLUENCE OF NEW BLOCK COPOLYMERS IN THE FORMATION OF MESOSTRUCTURED MATERIALS**

G. Kinkelhak, N. Hinsu, J. Bauer, Dietmar Sturmey and Beate Launay, Institut für Anorganische Chemie, Technische Universität Wien, AUSTRIA.

Hybrid materials, especially organic-inorganic nanocomposites and their porous analogs, have recently attracted much interest because they offer promise for novel properties and therefore new applications. The dendrimer-based approach mentioned above allows for facile and deliberate design of the network and pore structure. However, so far it has mostly limited to commercially available organic templates such as amphotilic ionic molecules or simple organic block copolymers. In this study we present the synthesis of different tailor-made block copolymers with lyotropic properties and their use as structure-directing agents for the synthesis of silica-based mesostructured materials. The ability to design the template molecules offers a huge potential for further functionalization of the final material and an extension of the extension of size, shapes and phases. Controlled polymerization techniques were used to keep the polydispersity low and adjust the polymer properties such as block length, polarity and functionalization. The influence of the different parameters on the structure of the resulting hybrid material were investigated in systematic studies by XRD, solid state NMR and nitrogen sorption.

**9:00 AM **C2C.2**

**ORGANIC/INORGANIC NANOCOMPOSITES WITH COMPLETELY DEFINED INTERFACIAL INTERACTIONS FROM CUBIC SILSESQUIOXANES.** J. Chua, R.O.R. Costa, R.M. Lane, Departments of Materials Science and Eng., Chemistry and the Macromolecular Science and Eng., Center, University of Michigan, Ann Arbor, MI.

Octamersiloxanes [RSiO1.5]8 exhibit potential as rigid nanoparticles to form which various functional groups (R=epoxy, methacrylate, etc) can be attached. Octamersiloxanes can be synthesized, polymerized or copolymerized to form nanocomposites wherein the architecture and length of the organic tether or polymer phase between cubes is completely defined. By manipulating the structure of the organic component, one can probe the effects of changes in organic nanostructure on interfacial interactions at the cube through studies of microscopic properties. We describe here the synthesis, processing and properties characterization of cube nanocomposites. Selected nanocomposites exhibit macroscopic, good-to-excellent mechanical, CTE and thin film properties, and much improved thermal stability (as whole organic composites).

9:15 AM **C2C.3**

**EVAPORATION-INDUCED SELF-ASSEMBLY OF HYBRID BRIDGED SILSESQUIOXANE FILM AND PARTICULATE MESOPHASES WITH INTEGRAL ORGANIC FUNCTIONALITY.** Yanfeng Liu, University of New Mexico and Sandia National
Since the discovery of surfactant-templated silica mesophases by Mobil researchers in 1992, a considerable effort has been devoted to the development of organic modification schemes to impart functionality to the pore surfaces or to selectively alter their physical or chemical properties. We report herein a class of bridged polysiloxane mesostructured thin films and particles with integral organic functionality by spin-coating, dip-coating, or screen printing. Our synthesis procedure begins with a homogeneous solution of ethanol, water, HCl, bridged silsesquioxanes precursors (RO)\textsubscript{3}Si-R-Si(OR)\textsubscript{3}, where R = -(CH\textsubscript{2})\textsubscript{n}, phenyl, -(CH\textsubscript{2})\textsubscript{n}O(CH\textsubscript{2})\textsubscript{n}CH\textsubscript{2} and surfactant, in which the initial surfactant concentration is tailored to the concentration of the organic template. Preferential ethano solvent evaporation accompanying the film or particle formation processes concentrates the sol in water, surfactant and silsesquioxane species, driving self-assembly of polysiloxane-surfactant micelles and their further organization into liquid crystalline mesophases. This new mesostructured organization allows molecular engineering of mechanical properties, hydrophilicity, dielectric constant and thermal stability, which are important for current applications of silica mesophases like low dielectric constant coatings for the next generation of microelectronics, environmental sensors, and high temperature membranes.

9:30 AM CC3.4
SYNTHESIS OF METALLIC NANOPIRLE/DENDRIMER COMPOSITES SOLUBLE IN ENVIRONMENTAL FRIENDLY SOLVENTS. Lee K. Yeung and Richard M. Crooks, Texas A&M University, Dept. of Chemistry, College Station, TX.

Fluorinated solvents are considered to be chemically inert and non-toxic when compared to their hydrocarbon counterparts. Considerable efforts have been made at exploring the possibilities of using these solvents for synthetic purposes. We would like to report the use of these solvents in the synthesis of novel inorganic/organic nanocomposites. These composite materials are envisioned to make contributions to a variety of fields from fuel-cell technology to catalysis. In this study, polypropyleneimine (DAH-D4) dendrimers were rendered soluble in fluorocarbons and used as monomers in the formation of organic-inorganic nanoparticles. The DAH-D4 dendrimers have perflourinated poly ether chains grafted onto the exterior and are shown by UV-Visible absorption spectroscopy to effectively extract metal ions from aqueous solutions. Upon chemical reduction, this is a change in the spectra corresponding to the formation of inorganic nanoparticles. High-resolution electron microscopy (HREM) confirms the presence of monodispersed nanoparticles and suggests that the metal particles reside in the interior of the dendrimers. These composite materials are highly stable at ambient conditions for months in fluorocarbon solvents and are also quite soluble and stable in supercritical CO2. More importantly, the materials can be subjected to elevated temperatures in solution without any detectable aggregation, oxidation, or dissociation of the metal nanoparticles.

9:45 AM CC3.5
HYDRO SILICA/POLYMER NAPRITICLES THROUGH EMULSION AND DISPERSON POLYMERIZATION. Elodie Bourgeret-Lami, Jose-Louis Xavier Luna, Alain Gayot, Laboratoire de Chir et Procedes de Polymerisation, CNRS, Villeurbanne, FRANCE.

In recent years, it has been a growing interest in the synthesis of hybrid materials containing both organic and inorganic compounds dispersed on a nanometric scale. One approach, used in our laboratory, is the conversion of incipient microemulsion inorganic precursors to organo-silica materials by radical polymerisation in dispersed media. Following this line, encapsulation of small silica particles has been successfully achieved by either dispersion or emulsion polymerisation. Two very different approaches have been developed. In the first one, the silica nanoparticles are first made hydrophobic by grafting on their surface the coupling agent 2-trimethoxysilylpropy methacrylate which did copolymerise with the monomer. In a second approach, we use the 2-(2,3-aminopropyl) methacrylate. This polymerises to give the two polymer nanoparticles which morphology highly depends on the encapsulation process and on the experimental conditions, namely the size and concentration of the silica, the nature and concentration of the stabiliser as well as that of the monomer.

10:30 AM CC3.6
DENDRITIC AND MULTIPODAL LIQUID-CRYSTALLINE MATERIALS BASED ON SLS/SILSESQUIOXANE AND SILAZANE CORES. G.H. Mehl, R. Ekeness, K.J. Shepperson, A.J. Thornton, J.W. Goodby, Department of Chemistry, University of Hull, Hull, GREAT BRITAIN.

In recent years great advances have been made in the synthesis of organo-inorganic hybrid materials, whether they are oligomeric, multipodal, polymeric or dendrimeric in structure. Of particular interest are liquid-crystalline systems representing a new class of the supramolecular behaviour of these systems allowing for the addressing of the macroscopic properties of these materials. This presentation will focus on investigations of silsesquioxane and silahelicates decorated with suitable organic groups leading to liquid-crystalline phase behaviour. The structural and chemical features which govern the phase behaviour will be discussed. Important features are the size, geometry, structure and microheterogeneity of the inorganic core, the flexibility, branching and length of the spacer linking inorganic cores and the organic groups, which promote liquid-crystalline phase behaviour. The effects of a variety of mesogenic structures on the liquid-crystalline phase behaviour and stability range will be discussed.

11:00 AM CC3.7
HYBRID NONPOROUS MATERIALS WITH SPATIALLY ORGANIZED MOLECULAR MONOLAYERS AND COATINGS. Yongsoo Shin, Jun Liu, Glen E. Fryxell, Li-Qing Wang, William D. Samuels and Gregory J. Faraclas, Pacific Northwest National Laboratory, Richland, WA.

Hybrid nonporous materials with functional monolayers have demonstrated great potential for a wide range of applications. This paper will discuss the formation of molecular monolayers and coatings of both organic and inorganic materials in the ordered nonporous structure. First the properties of long chain molecules and short chain molecules will be discussed, and these properties will be related to the molecular chain length and the pore size. In addition, strategies to spatially organize the molecules and functional groups in one- and two-dimensional patterns will be presented. The formation of these patterns within the microporosity may lead to materials that mimic the highly sophisticated functionality in biology. Finally, the formation of ordered inorganic coatings and its potential application will be discussed.

11:15 AM CC3.8
SILICA-BLOCK COPOLYMER COMPOSITES WITH MACROSCOPIC ORDERING DOMAINS. Nick Michalski, Brad Cline, Chengu, University of Santa Barbara, Dept of Chemical Engineering, Santa Barbara, CA; Patrick Davidson, Universite Paris-Sud, Laboratoire de Physique des Solides, Orsay, FRANCE.

A number of structural morphologies have been demonstrated using block copolymers as structure directing agents for a polymerizing inorganic species. Films, fibers, powders and monoliths with mesoscopic order have been synthesized through the combination of block copolymer and sol-gel processing techniques. While highly structurally organized, the nature of the domains and orientations within these materials have remained largely unknown. We will discuss recent results on the synthesis and characterization of transparent silica/block copolymer monoliths with large (∼1 cm) oriented single hexagonal and cubic mesostructured domains. Two-dimensional X-ray diffraction (XRD) analyses of transparent mesostructured silica/block copolymer composite monoliths reveal single-crystal-like patterns that correspond to well-ordered hexagonal domains that are greater than 1 cm x 1 mm x 1 mm in size. XRD and TEM results also show that the composite monoliths have large wellordered cubic mesophase domains in the mesoporous regions of the samples. Boundaries between the hexagonal and cubic domains in the monoliths reflect gradual transitions between the two epitaxially related structures. Such mesoscale block-copolymer and cubic mesostructures were furthermore preserved following removal of the organic species by calcination to produce mesoporous silica monoliths.

11:30 AM CC3.9
PERIODIC MESOPOROUS ORGANOSILICAS (PMOS)'S WITH FUNCTIONAL ORGANIC GROUPS INSIDE THE CHANNEL. Wallis, T., Tomasini, A., Neil Koumb, University of Toronto, Department of Chemistry, Toronto, Ontario, CANADA; Omer Dog, Bilkent University, Department of Chemistry, Ankara, TURKEY; Chikio Yoshin-Ishii, Mark MacLachlan, Geoffrey Osz, University of Toronto, Department of Chemistry, Toronto, Ontario, CANADA.

Inorganic-organic hybrid materials often display properties unique compared to the individual constituents. Surface-templated mesoporous silica represents an important new class of materials that on removal of the template can host polymeric organic, inorganic, and organometallic guests. Mesoporous materials
made from oxides, sulfides, phosphates, and metals inspire interest in their utility for catalysis, adsorption, sensing, and nondestructive electron microscopy. Xerogels are amorphous silicates that have attracted attention for their potential application in catalysis but, because of their random network of polydisperse pore sizes, they lack the shape and size selectivity desired for catalytic applications. Although xerogels have incorporated large organic ligands since 1972, there are few reports of periodic mesoporous hybrid materials containing a terminal bonded and none before our work for a bridge-bonded organic moiety as part of the inorganic framework. Here we report the first examples of periodic mesoporous organosilica (PMO) materials, in the form of powders and oriented film, with bridge bonded methylene, ethane, ethene, benzene, thiophene and ferrocene groups integrated into the framework. Support can be solvent-extracted or ion-exchanged to create a high surface area periodic mesoporous organosilica with the framework and the organic group intact. The organic groups are accessible for reaction to give a new type of chemistry of the channels. This work enables a fusion of organic synthesis and solid state chemistry.

SESSION CC4: CHEMICAL ROUTES TO NANO/MESOSTRUCTURED HYBRIDS MATERIALS
Chairs: Ulrich Schubert, Ferdi Schuth and Guido Krickelberk
Tuesday Afternoon, April 25, 2000
Metropolitan III (Argent)

13:00 PM *CC4.1
TAILORING OF ORGANICALLY-MODIFIED SILICA MCM-41 TYPE MATERIALS WITH OPTICALLY ACTIVE MOLECULE.
Béatrice Lebœuf, Laboratoire de Matériaux Minéraux, CNRS, Mulhouse, FRANCE; Christelle E. Fowler, Stephen Mann, School of Chemistry, University of Bristol, Bristol, UNITED KINGDOM.

One-pot synthesis, involving the co-condensation of tetraethoxysilane (TESO) and 3,3′,4,4′-dihydroxydiphenylmethane (DHDM) in the presence of the surfactant hexadecyltrimethylammonium bromide (CTAB) was used to covalently attach an organic silicate into silica materials with MCM-41 architecture. Under alkaline conditions, hexagonally well-ordered mesoporous di-functionalized silica materials were prepared with various dye contents (up to 40 wt%). These materials were synthesized in the form of powders, excluding their use in thin film applications, such as required for membrane and optical devices. Therefore, an acidic synthesis procedure was used to prepare transparent mesosstructured dye-functionalized silica thin films and monoliths. Analogous materials, consisting of dye-functionalized MCM-41 with increased channel size, were fabricated by addition of the micelle swelling agent 1,3,5-trimethoxybenzene (TMB) to the reaction mixture or by replacing CTAB surfactant by an amphiphilic triblock copolymer (polyethylene oxide)-block-propylene oxide)-block-poly(ethylene oxide), PEG-PPO-PPO). This synthetic route, based on an aggregation-induced self assembly process was also used to produce multiscale mesosstructured dye-modified silica materials by using both hexa siles and C12-t-CTAB micelles as organic structure-directing agents. Small-angle X-ray diffraction patterns transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) indicated hexagonally mesosopic order in all materials and a significant increase in the pore size associated with swelling of the C12-t-CTAB surfactant micelles or templating with PEG-PPO-PPO block copolymer, which are present in the dye was confirmed by Fourier transform infrared (FTIR) spectroscopy. In addition, 13C CP MAS NMR experiments confirmed that the dihydroxydiphenylmethane chromophore was covalently linked into the mesosstructured materials as an intact unmodified moiety. Optical properties of the ordered dye-functionalized silica materials were investigated by UV-vis and fluorescence spectroscopies. The data indicated that the optical activity of the dye moiety is retained when covalently linked to the silica network of the mesosstructures.

2000 PM CC4.2
STRUCTURAL EVOLUTION OF SILICEOUS-OXIDE-BASED ORGANIC/INORGANIC NANO COMPOSITES NETWORKS.
Christopher L. Sides, Eric K. Lin, Wen-ji Wu, National Institute of Standards and Technology, Gaithersburg, MD; Chunlin Zhang, Richard M. Linke, Dept of Materials Science and Engineering, Univ. of Michigan, Ann Arbor, MI.

The Si-O tetrahedron of silica can easily be assembled into eight cornered cubes (cubic silsesquioxanes - RSiO1.5n). In some respects, these cubes represent the smallest unit of ceramic silica. The corners of the nanocube-structured cubes can be functionalized with organic groups such as an oxirane ring (epoxy). Hence, they can be polymerized into organic/inorganic hybrid materials. In this work, we seek to understand the role of flexibility, rigidity and length of the organic segment in determining the structure and physical properties of these nanostructured composites. Several experimental techniques are used to characterize the structure and corresponding physical properties of these cubic silsesquioxanes. X-ray diffraction measurements show that the inter-cube distance can change in a non-intuitive manner with organic segment length. Networks cured with the shortest organic segments result in larger inter-cube distances than those with longer segments, thus could be due to increased steric restrictions during network formation. The corresponding physical properties are also being explored.

2:15 PM CC4.3
PREDICTING PHASE DIAGRAMS FOR POLYMERIC CLAY NANOCOMPOSITES.
Valery V. Ginzburg, Dept of Chemical and Petroleum Engineering, Cherukuri V. Singh, Dept of Physics and Astronomy, Anna C. Bhatia, Dept of Chemical Engineering, University of Pittsburgh, Pittsburgh, PA.

We combine a density functional theory (DFT) with a self-consistent field (SCF) to calculate the phase behavior of clay-organic hybrid materials. Surfactant coated with surfactants and dispersed in a polymer melt. We investigate the effect of the surfactant's characteristics (grafting density $\gamma$, length $N_p$, and the surfactant-surfactant interaction energy $\epsilon$) on the phase behavior of the clay particles. The model is validated using previous experimental results. The results predict a phase diagram that is in excellent agreement with the experimental data. The model can be used to predict the phase behavior of clay-organic hybrid materials.

2:30 PM CC4.4
POLYPROPYLENE CLAY NANOCOMPOSITES.
D.D. Keener, S.D. Hasler, Y. Li, J. Morn, H. Zhang, W. Wong, Case Western, Cleveland, OH.

Polypropylene (PP) nanocomposites with improved modulus and strength and whose ductility exceeds conventional composites have been produced. In addition, we find significant improvements in resistance to environmental stress cracking. The clay is first treated with a few percent of an organosilane coupling agent. The same functionalized particles are then reacted with melt-PP through aminaliation to produce grafted chains. Reactions were confirmed by NMR and DRIFT spectroscopy, and by X-ray diffraction (XRD) analysis, which showed intercalation of both coupling agent and polymer. These particles were compounded with pure PP using a mini twin screw extruder. The particles were finely dispersed as evidenced by both XRD and TEM analyses, indicating some exfoliation and also the existence of high aspect ratio aggregates, 2 to 5 layers in thickness. Mechnical properties showed a twofold increase in tensile modulus and a modest increase in yield strength at 5% clay content while retaining some ductility. At 10% filler level, the modulus increase was 40% and the ultimate elongation was in excess of 1000%. For control samples missing either the coupling agent or the clay grafts, these properties suffered significantly. Environmental stress cracking (ESC) resistance tests were performed on rectangular double notched specimens as constant load, while immersed in liquid water. The solution of nonionic surfactant in distilled water. The crack dimensions were measured as a function of time, the time to failure was recorded and the fracture surface texture was examined using scanning electron microscopy (SEM). At 10% filler loading, the time to failure was increased by a factor of three.

2:45 PM CC4.5
USE OF POLYMETHYLENEOXIDE-B-POLYSTYRENE AS A MODIFIER IN MONTMORILLONITE. Rick Beyer, Nora Beck Tui, U.S. Army Research Laboratory, Aberdeen, MD; Amr Shams, Mary Galvin, University of Delaware, Newark, DE.

Polyethylene-oxide-polystyrene block copolymers have been used to modify montmorillonite, a 2:1 layered silicate known for its cation exchange properties. For use as filler in polymeric nanocomposite materials, montmorillonite is typically functionalized with small, quaternary-amine terminated surfactants. However, PEO is known to melt intercalate montmorillonite freely upon annealing a mixture of clay and polymer, a result of the strong affinity of polar PEO for the silicate layer surface. Interactions of PEO is indicated by significantly enhanced ordering of the silicate layers and an increase in the layer gallery height. Melt processing of PEO-b-PS and montmorillonite also produces a change in the layer periodicity, indicating intercalation of the block copolymer in the galleries. However, block copolymer volume fraction and total molecular weight on intercalation have also been examined. Layered silicates modified with block copolymers may provide an alternate to materials modified by traditional cation exchange reactions for use as filler materials in nanocomposites.
3:15 PM *CC4.6
NEW INSIGHT INTO THE STRUCTURE-PROPERTY

The demand for multi-purpose, high-performance polymer systems has resulted in a need for advancing polymer properties beyond what traditional systems can offer. Only through control/alternation at the molecular level can one maximize property enhancements to meet current military and commercial needs. Over the last seven years the Air Force Research Laboratory has developed and incorporated discrete SiO framework (POSS = Polyhedral Oligomeric Silsesquioxanes) into traditional organic polymer systems. This research has resulted in new hybrid inorganic-organic polymer systems with remarkable enhancements in mechanical and physical properties including dramatic increases in both glass transition and decomposition temperatures, reduced flammability, increased moduli and oxidation resistance. We have shown that these enhancements result from the chemical composition (SiO core) and size (~15 A in diameter) of the POSS framework, and can be copolymerized, grafted, or even blended using traditional processing methods.

Recently, we have focused our efforts on understanding and controlling the molecular structure-property correlations between POSS framework within the polymer matrix. The development of new POSS monomers has allowed us to study how functionality, size, and geometry enhances the bulk properties of these hybrid materials. For example, increasing the solubility of side groups on the POSS framework results in greater POSS-polymer matrix interactions and increased Tg and storage moduli. Recent studies with POSS blends have resulted in increases in hardness, and reductions in dielectric constants and coefficients of thermal expansion. New results in polymer synthesis, characterization and applications will be discussed with a strong emphasis on the versatility of this new nanotechnology to many polymer systems.

3:45 PM CC4.7
PAMAM DENDRIMERS AND OCTASILSESQUIOXANES IN NANOCOMPOSITES. Chuan Xin Zhang, Lijie Bilih, Donald A. Tomalin, Center for Biologic NanoTechnology, University of Michigan, Ann Arbor, MI; Richard M. Laine, Department of Material Science and Engineering, University of Michigan, Ann Arbor, MI; Gary L. Hagnauer, AFSRL-WMMA, US Army Research Laboratory, APG, MD.

Nano-composites can have improved macroscopic properties, such as strength, toughness and hardness, as a result of the enormous interfacial area formed between their nanoscopic [1-100 nm] building blocks. Dendrimers and hyperbranched polymers are novel nanocapsules entities that have received considerable attention because of their potential utility in catalysis, biomedical applications, electronics and materials science. It has been demonstrated that these dendritic polymers can serve as efficient tougheners for epoxy-based composites. In this work, poly(amidoamine) PAMAM dendrimers have been studied in the context of improving epoxy resins. PAMAM generations 2 to 7 were used to prepare commercial-grade curing agents [Anacryl, Ar Products]. These microchemicals, as such, are very strong, fracture toughness and impact resistance of the resultant nanocomposites will be reported. Simultaneously, PAMAM/Anacryl combinations were also used to cure epoxy-functionalized octa- silsesquioxanes to make inorganic/organic hybrid nanocomposites. The processing and properties of these nanocomposites will also be discussed.

4:00 PM CC4.8

Multifunctional nanocomposite coatings and bulk materials have been developed on the basis of a combination of purely organic compounds as well as hybrid organic-inorganic polymer systems and nanoscopic synthetic and natural clays. These clays have been chemically modified in such a way that they become compatible to the different systems. Clay particles may be separated by modification with an organic molecule that contains two or more charged functional groups. One functional group is exchanged with orions or anions located between the clay sheets, which results in clay particles coated with charges carrying a molecule dispersed in between themselves. Depending on the nature of the organic molecule coloured or colourless coatings and polymeric bulk materials, containing homogeneous dispersed separated clay platelets, have been obtained. While retaining the basic functional properties of the materials new and/or improved properties have been introduced. This regards in particular improved barrier properties, such as a decreased permeability for oxygen and water, improved corrosion resistance and increased thermal stability. The composition of the wet coating systems is such that they can be properly applied and thermally or photo-chemically cured on various substrates such as steel, aluminum and plastics. The bulk materials can be processed into final product shape by conventional polymer processing techniques.

SESSION CC5: MESO- OR NONSTRUCTURED POROUS MATERIALS

Chair: Yoshiaki Chuo, Andrew Vioxax and Frank J. Fether
Tuesday Afternoon, April 25, 2000
Metropolitan III (Argent)

4:15 PM CC5.1
MOLECULAR ENGINEERING OF POROSITY WITH BRIDGED POLYSILSESQUIOXANES. Douglas A. Loy, Catalysis and Chemical Technologies Department, Sandia National Laboratories, Albuquerque, NM; Kenneth J. Shen, Department of Chemistry, University of California, Irvine, CA.

Bridged polysil sesquioxanes are a class of hybrid organic-inorganic materials that permit molecular engineering of bulk properties including porosity. Prepared by sol-gel polymerization of monomers with two or more trialkoxysilyl groups, the materials are highly cross-linked amorphous polymers that are readily obtainable in gels. The bridging configuration of the hydrocarbon group insures that network polymers are readily formed and that the organic functionality is homogeneously distributed throughout the polymeric scaffold at the molecular level. This permits the bulk properties, including surface area, pore size, and dielectric constant to be engineered through the selection of the bridging organic group. Numerous bridging groups have been incorporated. This presentation will focus on the effects that the length, flexibility, and substitution geometry of the hydrocarbon bridging groups have on the properties of the resulting bridged polysil sesquioxanes. Details of the preparation, characterization, and some structure property relationships of these bridged polysil sesquioxanes will be given.

4:45 PM CC5.2
PREPARATION OF MESOPOROUS ZrO2–Ni ANODES FOR SOLID OXIDE FUEL CELLS. Fanglin Chen, Meolin Liu, Georgia Inst. of Tech., Molecular Design Inst., School of Mater Sci & Engr, Atlanta, GA.

Mesoporous electrodes can dramatically improve the performance of solid state ionic devices because of their large surface area for gas transport and electrochemical reactions. In this study, two approaches have been applied to prepare mesoporous ZrO2–Ni anode for solid oxide fuel cells. The first approach is to obtain the mesoporous ZrO2–NiO through the self-assembly of organic surfactant and inorganic precursors. The second approach is to obtain mesoporous ZrO2–NiO through dispersing of NiO nanoparticles in a zirconia sol. The structures of ZrO2–NiO composites are tailored by adjusting solution conditions, such as surfactant concentration, counterion polarizability and charge, pH, temperature, and the addition of co-surfactants or additives. The pore size can be tailored by varying the chain lengths of the surfactant and addition of auxiliary oxides (or swelling agents), thus altering the rate of molecular gas transport through the pores. Various analytical techniques such as FTIR, small angle XRD, TEM, DTA–DSC, and BET have been used to characterize the molecular structure of the surfactants and the resulting mesoporous ZrO2–NiO composites. Further, the electrochemical properties of mesoporous ZrO2–NiO anodes, which are obtained by isostatic reduction of ZrO2–NiO composites, are studied to establish the correlation among synthesis, structure, and electrode performance.

SESSION CC6: POSTER SESSION

Tuesday Evening, April 25, 2000
8:00 PM
Metropolitan Ballroom (Argent)

CC6.1
PREPARATION OF ORGANICALLY MODIFIED ZIRCONIUM CLUSTERS AND ZIRCONIUM CLUSTERS FROM THE ALKOXIDES AND THEIR INCORPORATION IN ORGANIC POLYMERS. Bogdan Morari, Gregor Tmimmel, Silviu Gross, Ulrich Schubert, Inst fur Anorganische Chemie, Tech Univ Wien, AUSTRIA.
Well defined octametallate clusters bearing polymerizable groups on the surface were synthesized from titanium and zirconium alkoxides with an excess of acrylic acid, methacrylic acid or methacrylic acid anhydride. Some aspects of the formation mechanism and the influence of the preparation parameters are discussed. Radical polymerization of divinyl ether containing these clusters with methacrylic acid or styrene leads to the formation of inorganic-organic hybrid polymers. This process also offers the possibility to prepare optically transparent films. Terpolymer films were obtained when TiO\(_2\) (0.15) \(+\) (0.65) (OME) or ZrO\(_2\) (0.15) \(+\) (0.65) (OME) \(+\) (0.20) (H\(_2\)O) were polymerized with methacrylamide, whereas glassy, transparent polymers were synthesized from methylenethacrylate. The choice of the solvent also plays an important role regarding the polymerization.

By varying the solvent mixture, the solubility of the polymers, and thus their structure (powder, glassy) can be controlled. Polymers doped with 2 mol\% functionalized clusters do not thermally depolymerize as the undoped polymers. The swelling rate of the copolymers decreases linear with the portion of the octametallate clusters. The BET surface of the polymers prepared from methacrylic acid increases with the portion of the inorganic component. In case of the titanum cluster, the ethoxy groups are still present after drying of the polymers.

**CCG.5**

**HYBRID NANOSTRUCTURED MATERIALS OBTAINED FROM TITANIUM-OXO NANOBUILDING BLOCKS.** Elmentsanchez, G.J. de A.A. Soler-Illia, L. Rezea, Chami de la Matei Condeza, Univ. Pierre et Marie Curie, Paris, FRANCE. A. M. Carmine, C. O. Gris, J.P. Mayol, Laboratoire de Chimie de Coordination, CNRS, Toulouse, FRANCE.

Considerable effort is being currently directed to the obtention of nanostructures in hybrid materials. Developed as an extension of the structure directing concepts origined by zeolite chemistry, this synthesis approach relies in the appropriate use of ordered lyotropic phases as templating agents. The obtention of these new oxide phases can be driven through the appropriate obtention of a precursor hybrid phase, consisting in a mesoscopically ordered metal-surfactant gel. The polymerization of the metallic species in the aqueous phase leads to the obtention of a hybrid precursor with periodical organic arrangement. The calcination or extraction of these precursors may give rise to a highly controlled porous solid. So far, a large amount of work has been devoted to silica based materials which have been shaped as mesosporous powders, films or fibers. The chemistry of the silica-surfactant systems starts to be well understood. On the contrary, the organic-inorganic interfaces built from non-silicate precursors are more difficult to control, because the tuning of the hydrolysis and assembly processes is sometimes difficult to achieve. Consequently, for many transition metals, their higher reactivity towards hydrolysis precludes the easy obtention of long-range ordered phases. In this work, we use Ti[IV] nanobuidling blocks to create mesoscopically ordered phases, in films or powders. Clusters of TiO\(_2\) (0.1) \(+\) (0.9) (H\(_2\)O) or TiO\(_2\) (0.1) \(+\) (0.9) (OME) \(+\) (0.1) (H\(_2\)O) (formed by arrangements of micelles, such as block copolymers) or attached to ordering agents, such as dendrimers, molecules. The obtention of a given phase (identified by XRD and TEM) depends on the specific interactions between the surfactant and the preformed bricks. The composition of the Ti[IV] surface by the nucleophilic constituents of the organic components (determined by IR, multinuclear NMR) gives rise to a well-defined interface.

**CCG.6**

**HIGH-SURFACE AREA ZIRCONIA PREPARED BY THE SOL-GEL METHOD IN THE PRESENCE INORGANIC AND ORGANIC ADDITIVES.** Olga Metelkina, Nicola Iusuei, Ulrich Schubert, Institut fuer Anorganische Chemie, Technische Universität Wien, AUSTRIA.

Zirconia attracts more and more attention as a promising component for heterogeneous catalysis due to it mechanical strength, high thermal stability and well developed surface. We present a new approach towards the preparation of zirconia-based catalysts using co-hydrolysis and condensation of zirconium and aluminum alkoxides in the presence of acetic acid or acetylacetone to modify the reactivity of the metal alkoxides. Particularly high-surface area were obtained when ethanolic solutions of zirconium polymers (triethyl or diblock copolymers, polyethylene glycol) were added. The urea-terminated hybrid inorganic-organic material were dried supercritically, hydrothermally or under ambient conditions to obtain zirconia with low alumina content (1-10%) in a form of the powder in the shape of the cubes, leads to high surface area materials (about 200 m\(^2\)/g) with a low extent of crystallinity. The solids were found active for the reduction of NO by propane.

**CCG.7**

**HYBRID COMPOSITE MATERIALS CONTAINING MAGNETIC NANO-PARTICLES.** C. Chandez, E. Tonne, J.P. Julier, Chami de la Matei Condeza, University Pierre et Marie Curie, Paris, FRANCE.

The control of the organic oxide-particle interactions allows the dispersion of the particles in water or non-aqueous solvents and the synthesis of composite materials by organic or inorganic polymerization inside the dispersion. Calibrated \(\gamma\)-Fe\(_3\)O\(_4\) nanoparticles were prepared by co-precipitation of feric and ferrous ions in aqueous alkaline medium and further calcination in air medium. Such non-aggregated particles was obtained by dispersion in acidic water (pH=2).

The polymerization of silicic precursors (triethoxysilane or silicic acid) in the aqueous solution leads to the gellation of the dispersion forming xerogel. In such composites, the particles keep their hydration layers and no Si-O-Fe bonds are observed. Only hydrogen bond interactions between hydration layers of particles and remaining silhol groups are observed.

The dispersion of iron oxide particles in organic matrices needs the adsorption of coupling agents such as phosphonic or carboxylic acids in order to develop some interactions with an organic solvent. It is then possible to obtain organosiloxanes in which the polymerization of epoxy precursors, for instance, allows the synthesis of organic composites.

The observations of both types of composites by electron microscopy showed a homogeneous dispersion without noticeable aggregation of particles. The interactions at the iron oxide matrix interface were studied by thermal analysis, IR, NMR, and Mössbauer spectroscopies.

**CCG.8**

**STRUCTURAL, THERMAL, AND THERMOECHANICAL BEHAVIORS OF PHENOLIC-INORGANIC HYBRID COMPOSITES.** Samuel Amann, Vivek M. Mulloth, Dept. of Physics, Southern Illinois University, Carbondale, IL.

The potential applications of organic-inorganic hybrid materials are numerous since hybrid technology provides a vehicle by which mechanical properties of composites can be tailored for particular application. One area where hybrid materials can play an important role is frictional composites. Though wear mechanisms of the automotive brake composites are not completely understood, it is generally agreed that various additives in phenolic polymer are simply mechanically held. Therefore, under braking conditions the additive particles fall off contributing to the wear of the frictional composite. We have initiated systematic studies in which we are exploring strategies of developing cross-linking between the polymer and inorganic additives. We fabricated composites from phenolic polymer in which various inorganic phases were incorporated, i.e., A1203, SiO\(_2\), montmorillonite clay, or fly ash. How the incorporation of these additives affected the curing behavior of the phenolic polymer was examined with the help of diffuse reflectance FTIR and differential scanning calorimetry (DSC) measurements at 300 K < T < 700 K. Various surface treatments of the inorganic phase were undertaken to promote cross-linking between the inorganic and organic phases of the composite. The thermomechanical and mechanical properties, measured with the help of dynamic mechanical analyzer (DMA) and three-point bending test, respectively, suggested that the silicophenic composite has the largest flexural strength and highest modulus. However, extensive post-curing of the composite at 453 K resulted in the lowering of the flexural strength of the materials.
C6G.8 SYNTHESIS OF POTASSIUM NIOBATE/ORGANIC HYBRID
FROM METAL-ORGANIC. Toshikazu Yogo, Kouichi Banno, Wataru Sakamoto, Shinichi Hirano, Nagoya Univ, Dept of Applied Chemistry, Nagoya, JAPAN.

Nanocrystalline particle/polymer hybrids attract growing attentions as new inorganic/organic materials. This paper describes the processing of potassium niobate/organic hybrid from metal-organic precursor. Potassium niobate (KN) precursor was prepared from potassium niobate ethoxide through hydrolysis and condensation. The structure of the KN precursor was analyzed by IR and NMR spectroscopy. The precursor was found to be a double metal-organics in solution. The precursor was hydrolyzed and polymerized under the controlled reaction conditions. The formation conditions of nano-sized KN particles below 100 centigrade were investigated. The nanocrystalline particles in the organic matrix were analyzed by SAX and DEX. The particle size was found to depend upon the polymerization and hydrolysis conditions. The hybrid was inserted into film, being heated under pressure. The dielectric properties of the hybrid film were evaluated. The electro-thermoelectrical properties of the hybrid were also investigated.

C6G.9 IN VITRO, IN VIVO STUDIES OF 5a-AMP HYDROXYAPATITE
COMPOSITE. Shunro Yamauchi, Osaka Univ, The Institute of Scientific and Industrial Research. Tatsuki Matsuura, Hiroki Nakao, Masayuki Tsuji, Junzo Takahashi, Osaka Univ, Faculty of Dentistry; Masayuki Okono, Hiroshima Univ, Kiyoaki Sakamoto, Osaka Sangyo Univ, Masato Tani, Atsushi Nakahara, Kyoto Institute of Technology, JAPAN.

Many researchers have been studying of inorganic/organic composite materials for hard tissue biomaterials use. One of the demands for hard tissue is porous structure available forvascularization or cellular infiltration. In this study, we synthesized adenosine 5-monophosphate (5a-AMP)-HAP composite and examined its physical-chemical properties and biocompatibility. 5a-AMP is a component of RNA and can be synthesized in the laboratory. Raman diffraction patterns and NMR results showed the obtained products are compounds of 5a-AMP and HAP. TEM photographs showed the products possessed layered and porous structure. Both results suggested that 5a-AMP is binding to hydroxyapatite crystal through phosphate ions. In order to examine its insolubility properties and biocompatibility with hard tissue, 5a-AMP-HAP composite pellets were implanted surgically beneath the peristeme crani of 8-week-old SD rats under pentobarbital anesthesia. It was observed that the implanted composites contact well with the surrounding bone by scanning electron micrographs.

C6G.10 HYDROGELS OF POROUS SILICA PREPARED STARTING FROM A HYBRID CONTAINING CHITOSAN. Pedro Zaballa, Carolina Lafuente, Univ de Chile, Fac of Physical and Math Sci, Dept of Chemistry and Chemical Engineering, Santiago, CHILE.

The combination of silicone sol, prepared by the sol-gel method under conditions of linear polymerization, with solutions of the biopolymer chitosan has allowed us to obtain hybrid materials in the form of films or particles. In these composites the organic and inorganic phases are associate through hydrogen bonds. In this work we present the preparation of hybrid xerogels of spherical morphology and their transformation in hollow spherical particles of silica with high specific area (higher than 270m²/g). The xerogel particles were obtained by precipitation and then the chitosan was partially extracted with acetic acid. Finally the product was calcined at 550°C for 2h. The TEM micrographs shows the resulting silica obtained as hollow spheres with size in the range between 10 and 100 micrometers, showing larger magnification, it was found that the surface of these hollow spheres is constituted by much smaller and regular spheres, of about 0.05 micrometer. The porosity analysis show the presence of micropores as well as mesopores. The observed morphology is discussed on the basis of a precipitation process conditioned by an association of both organic and inorganic phases in the precursor hybrid sol. The results obtained from porosity measurements and SEM micrographs of silica particles, prepared in a similar way, but without the extraction step previous to calcination, will be also presented.

Acknowledgments: Projects RTD 1025 and Fondecyt 197-0730.

C6G.11 CHARACTERIZATION OF INORGANIC COMPONENTS
DERIVED FROM METAL ALKOXIDES IN PDMS-BASED HYBRIDS. Shingo Kawanaka, Keiko Kawakami and Noriko Yamada, Nippon Steel Corporation, Advanced Technology Research Labs, Funabashi, JAPAN.

Inorganic/organic hybrids prepared from trimethoxysilane (TEOS) and polydimethylsiloxane (PDMS) have unique mechanical properties such as flexible and rubbery properties. However, they have only an inorganic component of the silicone network derived from TEOS. We have successfully incorporated various inorganic components into PDMS based hybrids using modified metal alkoxides as a precursor of the inorganic components. The chemical modification of metal alkoxides formed no precipitate in the synthesis process, resulting in homogeneous and transparent hybrids that contain various inorganic components derived from Al, Ti, Zr, Si alkoxides. The inorganic components have been found to affect the mechanical properties. In this work, the inorganic components derived from metal alkoxides were characterized by XRF, EXAFS and TEM. The XPS study revealed the inorganic species were slightly different from the simple oxide. The X-ray diffraction of EXAFS spectra showed that the peak of second neighbor atoms increased with the inorganic content, meaning that the state of the inorganic component became similar to that of the oxide. The TEM study showed that the hybrids had no inorganic particles with several nm size. Therefore, the inorganic components derived from metal alkoxides were less than several nm sizes, being considered as molecular-level species.

Research supported by NEDO, under the Synergy Ceramics Project of the ISTP program promoted by AIST, MITI, Japan.

C6G.12 HIGH REFRACTIVE INDEX ORGANIC/INORGANIC HYBRID
MATERIALS PREPARED BY POLYMERIZABLE METAL ALKOXIDES. Wei-Fang Su, Hsin-Kuan Yen, Institute of Materials Science and Engineering, Chih-Yuan Fang, Advanced Instrumentation Center, National Taiwan University, Taipei, TAIWAN.

Two high refractive index organic/inorganic hybrid materials have been prepared via sol-gel processing using polymerizable metal alkoxides. One material consists of TiO₂ (15.26 wt.%) and poly(2-hydroxy ethyl methacrylate) which has a refractive index of 1.614 (at 632.8nm). The other material consists of a mixed TiO₂ (1.01 wt.%), Bi₂O₃ (10.18 wt.%) and poly(2-hydroxy ethyl methacrylate) which has a refractive index of 1.684 (at 632.8nm). The Bi₂O₃ containing material has a higher refractive index than the TiO₂ containing material due to the higher density of Bi₂O₃. This is in agreement with the Lorentz-Lorenz Law. High density materials exhibit high refractive index. Two polymerizable metal alkoxides: titanium methacrylate ethoxide and titanium bis(methacryl) methyl ether ethoxide were synthesized through alcohol exchange of conventional metal alkoxide with 2-hydroxy ethyl methacrylate. For the preparation of hybrid material, the hydrolysis step was carried out first to obtain inorganic metal oxide dispersed in acrylate monomer, then the monomer mixture was subsequently polymerized either by heat or UV radiation. A transparent monolith (5-5.5mm thick) or film (micron thick) material was obtained. A > 95% transmission in the visible region was observed for a film about 5 micron thick. The transmission electron microscopy study of the material indicated that the TiO₂ and Bi₂O₃ particles were about 10nm in diameter and well dispersed in the polymer matrix. The hybrid materials have shown improved optical dispersion and thermal stability over near acrylate polymer. These new materials with good optical and thermal properties will find potential applications in optics, opto-electronic devices, optical devices, and optical communication.

C6G.13 DIELECTRIC SPECTRA OF BATHO-POLYMER COMPOSITES. C.K. Chiang, R. Popielcz, R. Noszki and J. Olezak, Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD.

High dielectric constant materials are needed for supporting next generation of electronic devices used in wireless communication and related applications. This stimulates the revisited dielectric properties of polymeric and inorganic materials with high dielectric constant. We report the dielectric spectra of BATHO-polymer composites. The wide-range dielectric spectrum covering the frequency from 10⁵ to 10¹² Hz was used to examine the dielectric behavior of the composite constituents and the interaction between them. The results are interpreted in terms of known mixing rules. The role of polymer matrix and the interaction between the components are discussed.

C6G.14 UV-CURABLE ORGANIC-INORGANIC HYBRID MATERIALS. Guang-Wen Jiang, Ren-Jye Wu, Yung-Ching Sheen, Yi-Hui Lin, Union Chemical Laboratories, Electronic Chemical Technology Division, Hsinchu, TAIWAN ROC.

This work successfully prepared an UV curable organic-inorganic hybrid material consisting of organic modified colloidal silica. Applications of UV curable organic-inorganic hybrid materials include ultraviolet-curable coatings, photo-curable resin-based thin films and
waguedges. Colloidal silica containing reactive functional groups were also prepared by reacting organic silane and tetraethyl orthosilicate (TEOS) solutions. In addition, using organic moieties onto silica nanoparticles was investigated by applying TGA and FTIR techniques. A strong interdependence between surface modification efficiency and solution pH was observed. Acrylate-Silica hybrid formation could result in a shifting of thermal degradation temperature of organic component from about 200°C to near 400 degree C. This work also discusses the stability of organic modified colloidal silica in UV curable formula and the physical properties of resulting coatings. Furthermore, SEM and TEM were used to investigate the morphology of modified colloidal silica.

**CG.15**

**NANOPARTICLES IN POROUS METAL OXIDE NETWORKS VIA A POLYMER GEL COATING TECHNIQUE.** Jan H. Scholze, Rachel A. Caruso and Markus Antonietti, Max Planck Institute of Colloids and Interfaces, Potsdam, GERMANY.

Metal oxides are used in a wide range of applications, such as catalysis and photocatalysis. By means of incorporating metal or metal sulfide nanoparticles into those metal oxides the properties of these materials can be improved, and new applications can be accessed. In this study the technique of polymer gel coating, which has been used to produce porous metal oxides, has been extended to homogeneously incorporate nanoparticles into these networks. Initially nanoparticles were produced in the polymer gel. Afterwards a metal oxide precursor, e.g. titanium isopropoxide, was incorporated in the gel and hydrolysed by addition of water. The resulting polymer/o metal oxide-hybrid was calcined to remove the organic material giving a highly porous metal oxide network. The surface areas of these materials range from 10 to 100 m²g⁻¹, depending on the initial polymer gel used in the coating process. Electron microscopy and X-ray diffraction was used to determine the morphology of the material, regarding network structure and pore size as well as size and distribution of the nanoparticles. Information on the crystal structure of the metal oxide was gained from X-ray measurements.


**CG.16**

**THE EFFECT OF SYNTHESIS CONDITIONS ON PYRIDINE TEMPLATED OPEN FRAMEWORK GALLOPHOSPHATES.** David S. Wrigg, Iver Bull, Gary B. Hix and Russell E. Morris, Department of Chemistry, University of St. Andrews, St. Andrews, Fife, UNITED KINGDOM.

The rational design of zeolite related open framework materials is an established goal of materials science. Specifically designed frameworks could prove invaluable in catalysis allowing very precise shape selective product targeting. Most open framework materials are prepared by sol-gel or hydrothermal techniques, the mechanisms of which are still poorly understood. In many such systems the initial synthesis conditions have a strong influence over the final product, with pH, temperature, heating time and solvent content being of great importance to the structure and mechanism of formation. This is due to a simple gulliam phosphate (GaPO₄) system in which gulliam acts as both solvent and template has been found to lead to a variety of different phases depending on the conditions of synthesis. The gulliam-GaPO₄ system with fluoride ions as mineralising agent is ideal for this type of study as the products are commonly reasonably large single crystals suitable for X-ray structure determination. Synchrontron microcrystal XRD techniques have also been used in cases where the crystals obtained were too small for structure determination using a conventional laboratory X-ray source. It is hoped that the work will lead to a better understanding of how the synthesis conditions applied lead to different structural types and that this in turn will improve our understanding of the mechanism of formation and the interactions between template, framework and solvent.

**CG.17**


The increasing interest in porous materials in various fields of application has motivated the search for new high-technology thin films with pore size, structure and organization controlled by the presence of organoclayates. Silica thin films with different mesostructures have been deposited on glass and silicon substrates by dip-coating. The templating agents were either a cationic low molecular weight surfactant (CTAB) or triblock copolymers (PEG-PPO-PEG). They have been removed by different techniques, either calcination or solvent extraction, and the efficiency of the procedure has been controlled by Rutherford Back Scattering experiments. The structure of the films was investigated by X-ray diffraction in transmission as well as reflection modes, and transmission electron microscopy performed on film sections. Under our experimental conditions, highly ordered hexagonal structure through the complete film thickness was obtained with CTAB, while in the films prepared with the block copolymer, ordered regions are mainly observed at the film surface. Furthermore the pore size, thickness and porosity were deduced from ellipsometry measurements for a large variety of synthetic parameters.

**CG.18**

**FUNCTIONALIZED INORGANIC/Organic HYBRID BLOCK COPOLYMERS.** Josef Bauer, Guido Kieckhöfl, Nicola Hüsinger, Institut für Anorganische Chemie, Technische Universität Wien, WIEN, AUSTRIA.

Novel types of block copolymers offer new possibilities in the formation of hybrid mesostructured materials. By changing their properties like polarity or block-length they have a direct influence on the pore size, shape and wall-thickness of the resulting materials. In this work we present our results on new hybrid inorganic-organic amphiphilic block copolymers which are composed of a hydrophobic polydimethylsiloxane (PDMS) block and a second polysiloxane block with varying functionality. The synthesis of these block copolymers is carried out by living anionic ring opening polymerisation of cyclooctylmethyldimethoxysilane (CODS3 and 1,3,5,7-tetramethylycyclohexasiloxane D4V3) which is epoxidized in a second step. Following the epoxidation, a variety of ring-opening reactions of the oxiranes are applied to introduce a wide selection of different functional groups (diols, dienes, diacids). The functional groups introduced in the second step provide the possibility to stabilize not only the oil-water interface (the classical problem of amphiphiles), but any interface between different materials with different cohesion energies or surface tensions. By the choice of the repeat units of each block, the length and the functionality of both polymer parts we are able to adjust our molecules very specific to the demands and doublets in a much wider range compared to previously used low molecular weight surfactants. These novel amphiphilic block copolymers are tested as templating molecules in the synthesis of mesostructured materials.

**CG.19**

**ON THE PROPERTIES OF AN IONIC CONDUCTOR SYSTEM INCORPORATED INTO HYBRID FILMS.** Guillermo Gonzalez, Pedro J. Retortu, Sandra Puentes.

By blending the biopolymer chitosan (CHI) with a sol containing poly(malicpropylsiloxane) oligomers (PAPS), transparent and flexible hybrid films can be obtained. A self-assembled layered morphology has been determined for some of these blends. On the other hand, composites of polyethylene oxide (POE) with alkaline salts are well known ion conductors systems, where the crystallinity tends to diminish in the composite. In this work we have incorporated both POE and lithium perchlorate (LiClO⁴) in the hybrid films. A good compatibility among all the constituents was established for a determined range of compositions. It was found that the Molecular Weight (Mw) of the used POE is of paramount importance because the length of the micromolecular chains influence the crystalline characteristics of the composite film. Several compositions were tested in order to obtain homogeneous films. Chitosan of high molecular weight and POE with Mw= 4*10⁶, both from Akrich, were used. The ionic conductivity of selected samples was evaluated by complex impedance spectroscopy. A ionic conductivity of 1.7*10⁻⁵ Ohm·cm⁻¹ is a typical result obtained by measurement of a film with the molar composition POE:CHI:PAPS:LiClO₄ = 1:0.2:2:0.1. This value is similar to that of good ionic conductive systems. The influence of the variation of the relative amount of each of the components of the film on morphological and electrical properties is discussed.

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**CG.20**

**CURING BEHAVIOR, THERMAL AND SURFACE PROPERTIES OF SOME EPOXY-POLYHONOMONONORPOLYDIALYL-DI-SESQUIOXANES.** Yukih Lin, K.P. Pramoda, Weiyu Chen, T.S. Chung, Institute of Materials Research and Engineering, SINGAPORE.

In our research toward the modification of epoxy resins with silicones for electronic applications, several types of epoxy-containing ladder-like polydisiokosanines have been synthesized. They are poly(ethoxy-phenyl-bisiloxanes) (PEPs), polydisiokosanine (QOS), polydisiokosanine (PSAs), and polydisiokosanine (PEPs). Using behaviour of these ladder-like polydisiokosanine...
silsequioxanes have been studied both in the absence and presence of curing agents. Differential scanning calorimeter was employed to examine the curing kinetics of these polymers. The results show that the apparent activation energy for the curing follows this order: PEAS > PEAPS > PEPS. Thermal stability of the cured polymers was studied by the TGA. It was found that PEPS has the highest thermal stability, while PEAS the lowest. Also, polyorganosiloxanes cured with a diamine has higher thermal stability than that cured in the absence of a curing agent. Surface properties of these cured polymers have been characterized by both contact angle measurement for surface energy and XPS for surface atomic percentage. Good correlation was found between the surface energy and atomic percentage.

CCG.21 INVESTIGATION OF ANION EXCHANGE IN INTERCALATED LAYERED DOUBLE HYDROXIDES Alexey V. Lukashin, Elena V. Lukashina, Moscow State University, Higher School of Materials Science, Moscow, RUSSIA; Gennady A. Babushkov, Moscow State University, Radiophysics Div., Chemistry Dept., Moscow, RUSSIA; Alexey A. Vertegel, Moscow State University, Inorganic Chemistry Div., Chemistry Dept., Moscow, RUSSIA.

Development of depot drugs is very actual problem now. One of the ways to achieve the gradual release of the drug is the use of layered double hydroxides (LDH) intercalated with biologically active compounds. It is based on a unique property of these materials to exchange cations in aqueous solution. LDHs have a general formula \( M'^{2+}_{x}M''^{2+}(OH)_{x}(\text{intercalate})_{y} \), where \( M' \) and \( M'' \) are metals in the oxidation state +2 and +3, respectively, and the intercalate is virtually any inorganic or organic anion (including biologically active anions), which does not form a stable complex with \( M' \) or \( M'' \). The structure of LDH consists of positively charged hydroxide layers \( [\text{layer}^{2+}]_{x} \) bonded with negatively charged anions, which occupy the interlayer space. In the present work, we investigated the exchange process between large organic anions in Mg-Al LDHs and some inorganic anions in aqueous solution. Tritium labeled anions of amino acids, carboxylic acid, acetic acid, etc. were intercalated into LDH interlayer space by reaction of Mg-Al layered double oxides. The obtained materials were treated with aqueous solutions containing CO\(_3\)^{2-}, NO\(_3\)^{-}, and Cl\(^{-}\) with different concentrations. Dependencies of the suspension radioactivity versus time of anion exchange were studied and analyzed. The effect of the size and structure of organic and inorganic anions on their mobility is discussed.

CCG.22 PREPARATION AND CHARACTERIZATION GRAPHITE-LIKE/EThYLENE-VINYLACETATE COPOLYMER NANOCOMPOSITE. Peng Xiao, Kecheng Gong, Polymer Structure & Modification Res. Lab., South China University of Technology, Guangzhou, PR CHINA.

Organic polymer intercalated layered inorganic solids nanocomposites have attracted wide attention recently. These nanocomposites exhibit unexpected hybrid properties synergistically derived from organic and inorganic components. Here we report a new nanocomposite derived from ethylene-vinylacetate copolymer (EVA) intercalated graphite-like layered intercalation compound (PVA intercalated graphite oxide) (GO) nanocomposite prepared by polymerizing vinylacetate monomer in the interlayer of GO modified GO. Then a graphite-like/PVAc nanocomposite with high electrical conductivity was obtained by chemically reducing the PVAc/GO nanocomposite with aqueous hydrazine hydrate (50% w/v) solution. Finally the graphite-like/PVAc composite was mixed with EVA at 80°C. XRD analysis shows that in the resulting composite the graphite-like layer and polymer layer are alternatively interstratified at molecular level. Also FTIR, DSC, TG and DMS were conducted to characterize the nanocomposite.

CCG.23 SELF-ASSEMBLED LITHIUM-AMINE AGGREGATES IN THE INTERCALATION OF DIETHYLAMINE IN MOLYBDENUM DISULFIDE. E. Benitez, Universidad Tecnologica Metropolitana, Department of Chemistry, Santiago de Chile; V. Sanchez, M.A. Santa Ana, G. Gonzalez, Universidad de Chile, Faculty of Sciences, Santiago de Chile; A. C. Blaise, J.P. Donoso, C.J. Magón, J. Schneider, Universidad de Sao Paulo, Instituto de Física, Sao Carlos, SP, BRAZIL.

The organization of the organic phase in the interlayer spaces of nanocomposites obtained from the intercalation of diethylamine in molybdenum disulfide in the form of molecular lithium aggregates is reported. The reaction of diethylamine with exfoliated MoS\(_2\) leads to the formation of the compound Li_2MoS\(_2\)J\(_{10}\)R\(_{0.2}\). The product is a layered organic-inorganic nanocomposite with an electrical conductivity of the order of 10\(^{-3}\) S cm\(^{-1}\) at room temperature.

Conventional intercalation models like those proposed for similar intercalates are considered, both, the intercalation distance detected by X-ray diffraction and the amount of intercalated amine determined elementally and thermal analyses, appear to be anomalous. Indeed, according to molecular dimensions calculated by building models using both, von der Waals atomic radii and an optimized amine configuration, the diethylamine would be highly contracted in the intercalated state, being there more dense than in the liquid state. However FTIR and, specifically, solid state NMR analyses of the product permit to explain such paradoxical results by the interaction of aggregated EDA ions with the intercalated species in a weakly coordinated amine and the presence of alkylammonium ions may be moreover disregarded. Although the relatively low lithium concentration of the nanocomposite, \(^{7}Li\)NMR spectrum at low temperature has a second moment (5.2 Gauss) at 173 K \(\approx\) assignable to \(\text{Li}^+\) 60% and \(\text{Li}^+\) 40% magnetic dipolar contributions. NMR data including variation of the linewidth and spin-lattice relaxation time with the temperature agree with the presence of aggregates formed by three Li atoms and six amine. Low volume molecular models, permitting not only to explain observed structural and analytical data but also to describe the product as a pillared structure, are discussed.

Acknowledgments

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CCG.24 SIZE CONTROL OF BLOCK POLYMER TEMPLATED MESOPOROUS SILICATE MATERIALS. Taka Yamada, Keisuke Arakawa, Kenkichi Ishigame, The Univ. of Tokyo, Dep. of Quantum Engineering and Systems Science, Tokyo, JAPAN; Akira Endo, National Institute of Materials and Chemical Research, Tsukuba, JAPAN; Hao-Shen Zhou, Ichiro Homma, Electrotechnical Laboratory, Tsukuba, JAPAN.

Mesoporous materials have attracted considerable interest because of applications in molecular sieve, catalyst, and adsorbent. Efforts to create sensor, electronic and photonic device, based on ordered molecules, have been inspired by these self-assembled mesoporous materials. If functional molecules incorporate into pore of mesoporous materials, new novel functional device might be appeared. For such a new functional devices, it is necessary to synthesis mesoporous materials with large pore size and to control them. But ordinary mesoporous materials like MCM-41 have too small pore size to incorporate some functional molecules. Sticky group reported new mesoporous materials with large pore size using commercially available poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) triblock copolymer as template. And we succeed controlling pore size of mesoporous materials using block copolymer by synthesis conditions. The mesoporous material was prepared as follow: Block copolymer was dissolved in water and HCl solution with stirring at some temperature. Then tetraethylsilane (TEOS) was added into that solution with stirring at some temperature. The mixture was aged without stirring, and then solid product was recovered in mixture solution and filtered, washed, and air-dried at room temperature. Finally, calcination was carried out these materials. The characterization of mesoporous materials is investigated by XRD measurement and nitrogen adsorption-desorption isotherm measurement. The XRD and the nitrogen adsorption-desorption isotherm results show that these materials exhibit ordered and oriented mesostructure. The desorption, phase state, pore size, and surface area could be controlled by synthesis condition and triblock copolymers.

CCG.25 ORGANIC/INORGANIC HYBRID MATERIALS ON MOLECULAR SCALE FROM A NOVEL TYPE OF PRECURSORS. Weikang Wang, Kecheng Gong, Polymer Structure & Modification Research Lab. South China University of Technology, Guangzhou, CHINA.

Organic/inorganic hybrid materials have recently attracted much attention. How to overcome the thermodynamic tendency to phase separation and controlling the structure at nanoscale is critical for the preparation of high performance materials. Here, we introduce a novel type of precursors whose structure and stability can be adjusted easily to produce organic/inorganic hybrid materials within a molecular scale. The hybrid materials can be produced by the simple, low-cost, low-temperature processes. The precursors are transparent liquid or solid and soluble in some organic solvent. The key is they are from cheap materials or agricultural disposal and synthesized at relatively low temperature.

CCG.26 IN SITU ONE-STEP FABRICATION OF POLYSTYRENE/COS HYBRID NANOCOMPONENTS. CONTROLLABLE SHAPE AND SIZES OF CdS NANO-CRYSTALLITES BY A SIMPLE SOLUTION ROUTE. Shu-Hong Yu
and Masahiro Yoshimura, Center for Materials Design, Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, JAPAN.

A novel one-step solution route was successfully developed for the in situ fabrication of polystyrene/CdS nanocomposites embedded with colloidal CdS nanocrystals. The polymerization of the styrene monomers in the presence of radical initiator AIBN (2,2'-azobisisobutyronitrile) and the formation of the CdS nanocrystals using thiourea as sulfur sources in ethylene oxide media confirms the maximum temperature range of 88-140°C. The effects of several factors, such as solvents, temperature, reaction time, the ratio of the monomer/CdS, and the polymerization, the formation of CdS, the particle size, and shape were investigated. Both temperatures and solvents were found to play a key role in the controllable synthesis of the nanocomposites. The CdS nanocrystals embedded in the polystyrene matrix are composed of homogeneously nanofibers with widths of 4-10 nm and lengths up to one to several micrometers. UV-Vis absorption spectra and photoluminescence (PL) spectra demonstrate that the materials display obvious quantum size effects. This work has been supported by the Japan Society for Promotion of Science (JSPS) as part of the Research for the Future Program No. 96R06901.

**C6.27**

**THE SYNTHESIS OF HYBRID MATERIALS BY THE BLENDING OF POLYHEDRAL OLGOSILSESQUIOXANES INTO ORGANIC POLYMERs.** Rody L. Blau, Shawn H. Phillips, Kevin Chaffee, Air Force Research Laboratory Edwards AFB, CA; Joseph Lichtenhan, Hybrid Plastics, Chico, CA; Andrew Lee, Hsing Peng Geng, Department of Materials Science and Engineering, Michigan State University, East Lansing, MI.

The study of organic/inorganic hybrid materials has become an increasingly widespread research focus. The advantage derived from such materials is the combination of two very different compounds which may result in materials that bridge the performance gap between the two systems. We have previously reported such hybrid systems prepared by incorporating polystyrene oligosilsesquioxanes [POSS] into traditional organic polymers by the copolymerization of POSS monomers and organic monomers. This presentation will discuss a more convenient method of incorporating POSS into a polymer: the blending of POSS into organic polymers. The research discussion will focus on the development of the POSS macromers used in our studies as well as the POSS polymer blends synthesized. The observed property enhancements of the POSS polymer blends will also be discussed.

**C6.28**

**PREPARATION OF EXFOLIATED POLYSTYRENE-MONTMORILLONITE HYBRIDS.** Jae Goo De, Jeong Ghi Koo, Cheil Industries Inc., R & D Center, Kyungkido, KOREA; Iwhan Cho, Kangnam Advanced Materials Engineering Dept., Advanced Materials Engineering, Seoul, KOREA.

Two types of polystyrene (PS)-organically modified montmorillonite (organ-MMT) hybrids, organically intercalated and exfoliated hybrids, were prepared by radical polymerization with proper comonomers in organo-morphic MMT phase. The impregnation of montmorillonite intercalant ammonium MMT was followed by the polymerization by radical intercalation and intercalated and exfoliated structures of polymerized PS/organ-MMT hybrids were identified by XRD and TEM. The homopolymerization of the polymer matrix in the interlayer of organo-MMT resulted in intercalated PS/organ-MMT hybrid. This intercalated hybrid exhibited microstructure very similar to the unintercalated organically modified layered silicate (org-MMT). Since the increased basal spacing associated with hybrid formation arises from the expansion of the interlayer to accommodate the intercalating polymer matrix, the regions of intercalated and unintercalated galleries can be distinguished from the difference in interlayer spacing. The exfoliated hybrids exhibited microstructures with increased layer disorder and layer spacing. In these exfoliated hybrids, the extensive layer separation associated with delamination of the original silicate structure in the polymer matrix resulted in the eventual disappearance of any coherent X-ray scattering from the layers. Copolymerizations of styrene and proper comonomer with larger size or polyc group in organ-MMT were very good candidates for formation of exfoliated PS-MMT hybrids. As a result of this, a transition from intercalated to exfoliated hybrids was observed by the joint use of DSC, IR, and XRD. Introduction of large molecule or polyc group in comonomer inserted between the interlayers before the onset of polymerization would be the major factor causing the delamination of the MMT interlayers by the extensive intercalation of PS-based copolymer between the interlayers.

**C6.20**

**NEW MESOPOROUS MATERIALS BY TAILORMADE BLOCK COPOLYMER SURFACTANTS.** Nikola Husein, Guido Kickelbick, Beatrix Lanyi, Institute of Inorganic Chemistry, Vienna University of Technology, Vienna, AUSTRIA.

Liquid crystal-like arrays have been widely used as templates in the formation of mesoporous inorganic materials. In this work we present how pore structures can be modified through the use of tailor-made block copolymer surfactants. Amphiphilic inorganic/organic hybrid di- and tri-block copolymers (poly(tetrahydrofuran)/poly(siloxane) and polymers that contain rigid chains have been used as structure directing agents for the synthesis of inorganic-organic hybrid materials. By varying the properties of the polymer blocks systematic studies of the influence on the structure of the final material could be performed. The polarity and therefore the hydrophilicity, the ratio of the length of the different blocks, and the overall size of the block copolymers have been investigated. Solvent evaporation induced self-assembly for the formation of this film as well as hydrothermal treatment was used to prepare solid materials which were characterized by solid state NMR, nitrogen sorption and X-ray diffraction etc. The polymer was removed by calcination or washing to yield inorganic mesoporous materials with tunable pore sizes and high surface areas.

**C6.30**

**FORMATION OF HIGHLY DISPERSE METALLIC PARTICLES IN POROUS POLYMERIC MATTRESSES.** Nina I. Nikonorova, Elena S. Trofimchuk, Elena V. Semenova, Alexander I. Volynskii, Nikolai F. Bikoev, Chemistry Dept., M.V. Lomonosov Moscow State Univ., Moscow, RUSSIA; Gennady B. Lomov, Dept. of Physics, M.V. Lomonosov Moscow State Univ., Moscow, RUSSIA.

A novel approach to the formation of hybrid organic/inorganic polymer composites with submicron metal particles is developed. This approach is based on the reduction of metals from their salts within the nanopores in a polymeric matrix (PM), the porous structures of which is produced by the mechanism of solvent crazing. Solvent crazing provides an universal means for the formation of new composite materials with high level of the dispersion of components. Metal is introduced into the pores of PM via the method of countercurrent diffusion of metal compound and reducing agent. The nanopores serve as a microreactor in which the formation of metallic particles occurs. The formation of the metallic phase in the PM was shown to proceed in a way different than that in the bulk solution. This approach allows the preparation of polymer composite materials (PCM) containing up to 20 Volume % and 200 Weight % of metal and with crystallites sizes up to 40 nm. The advantages of this method of preparing PCM refer to the possibilities of controlled changes in the qualitative and quantitative composition of composites and the character of distribution of metallic filler particles in the PCM.

Metallized particles can be distributed uniformly in the PM volume or can be concentrated as a layer with a thickness of 5-40 nm. The systems of magnetic metallic particles in PM under the influece of external magnetic field allowed to change the resulting PCM fine structure and morphology in a controllable way. The mechanical properties of the PCM prepared by this method are similar to those of pure polymer matrix. The prepared PCM allows unique properties of the interaction of electric and magnetic fields. This contribution reports results concerning the PCM films on the base of PET, PP, PE, PVC with Ni and Cu metal particles.

**C6.31**

**SOL-GEL CHEMISTRY OF 3-ISOCYANATOPROPYLTRIETHOXYSILANE.** Colleen Brauger, Douglas A. Loy, Catalysts and Chemical Technologies Department, Sandia National Laboratories, Albuquerque, NM.

3-Isoctanepropyltriethoxysilane is commonly used as a coupling agent. The reactive isocyanate group readily reacts with alcohols or amines to give strong urethane or urea linkages. Because of this reactivity 3-isocyanatopropyltriethoxysilane is often used as a reagent for forming new monomers for preparing hybrid organic-inorganic materials. In this study we examined the sol-gel chemistry of 3-isocyanatopropyltriethoxysilane by itself and its formation of polysiloxanes gels. The monomer was reacted in ethanol or neat with acidic (HCl), basic [NaOH or tetrabutylammonium hydroxide] or neutral water. Under neutral and acidic conditions no gels were obtained. Under basic conditions monolithic gels were obtained. Solid state NMR revealed complete conversion of the isocyanate groups into urea groups to provide an in-situ formed bridging group that appears to facilitate the formation of polysiloxane gels. Tetraethylammonium hydroxide was particularly useful for working phase separation during solgel processing and acquiring homogenous gels.

**C6.32**

**AMINE-FUNCTIONALIZED POLYSILSESQUIOXANES.** Arturo

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Sánchez, Douglas A. Loy, Catalysts and Chemical Technologies Department, Sandia National Laboratories, Albuquerque, NM.

Ammonium-functionalized trialkoxysilanes have been extensively used as coupling agents and, more recently, as co-monomers with tetraalkoxysilanes or other organoalkoxysilanes in hybrid organic-inorganic materials. In this study, we examined the sol-gel chemistry of (meth)acryloyltrimethoxysilane (1), (meth)acryloyltiethoxymethylsilane (2), N,N-dimethylaminoethyltrimethoxysilane (3), N-(2-trimethoxysilyl)ethylmethacrylate (4), 3-(trimethoxysilyl)methacrylamide (5) and α-cyanoacrylate (6). The monomers were reacted with dicyclopentadiene to yield monomer adducts that were isolated by column chromatography. GPC and 1H and 13C NMR spectroscopy were employed to characterize the monomers. These results are expected to be useful in developing novel organosilicon materials.

CCG.33
RAPID PROTOTYPING OF PATTERED ORGANIC-INORGANIC MULTIFUNCTIONAL NANOSTRUCTURES. Hongyou Fan, Yunfeng Lu, Randy Schank, Scott T. Reed, Tom Buer, Gabriel P. López and C. Jeffrey Brinker.

Whether it be the origin of life, crystal growth, or the natural formation of a complicated biological nanocomposite like a sea shell, the inherent properties of the extended structure on multiple length scales (micro-, meso-, macroscopic) such as shape, mechanical strength, color, and so forth vary widely as the molecules or atoms assemble and make the critical transition from a few units with nanoscopic dimensions to micro-, meso- and macroscopic arrays. The chemists’ approach to the mesoscopic world has been focused on simple, inexpensive self-assembly techniques. For example, Yang et al. used surfactant-templated mesoporous silica on hydrophobic patterns produced by micro-contact printing using ECP. Tien et al. formed oriented mesoporous silica templates, using a micro-molding technique, and Wang et al. combined MIMIC, polystyrene spheres templating, and surfactant-templating to create oxides with three levels of structural order. Overall, great progress has been made to date in controlling the structure and function across several nanometers to micrometer scales. However, materials prepared have been limited to oxides with no specific functionality. In addition, the patterning strategies employed thus far require hours or even days for completion. Such slow processes are inherently difficult to implement in commercial environments. We have combined evaporation-induced (silica/surfactant) self-assembly (EISA) with rapid prototyping techniques such as pen lithography, ink-jet printing, and dip-coating on micro-contact printed substrates to form hierarchically organized silica structures in seconds. In addition, by co-condensation of tetrafunctional silanes ([Si(OR)4] with tri-functional glass oxides such as trimethylolpropane triacrylate, (RO1)3 Si(OR)3), we have selectively derivatized the silica framework with functional R groups or molecules. The resulting materials exhibit form and function on multiple length scales (microscope, meso-, and macroscopic).

CCG.34
POLYMETHYL SİLSESQUIOXANES THROUGH BASE-CATALYZED REDISTRIBUTION OF OLMOMETHYL-HYDRIDOSILANES. Kannan Rahimian, Douglas A. Loy, Sandia National Laboratories, Albuquerque, NM.

Polymeric silsesquioxanes have attracted increased attention in recent years as precursors to high temperature materials, and have shown great potential for use in numerous applications. They are typically synthesized through acid- or base-catalyzed hydrolysis of trichlorosilanes and/or trialkoxysilanes. Here, we report on the synthesis of polydimethyldimethylsiloxane (MeSiO2)₆, and its copolymer with diphenylsiloxane (MeOSiO2)₆, and poly(methylhydrosiloxane) (MeHSiO₃). These materials can easily be synthesized through the redistribution reaction of dimethylsiloxane and/or dimethylsilane, using tetrabutyllammonium hydroxide as catalyst. Conversion of the SiH group, in the starting oligosiloxanes, to MeOH can be easily controlled by the amount of catalyst used, as well as pressure or addition of water. Further work will also report on the properties of the above materials and their potential applications.

CCG.35
ACID-CATALYZED RING-OPENING POLYMERIZATION OF DISILANOCYCLOPENTANES. Kannan Rahimian, Douglas A. Loy, Sandia National Laboratories, Albuquerque, NM.

We have recently shown that disiloxacyclopentanes provide an excellent alternative to traditional sol-gel precursors. They can easily be polymerized through ring-opening polymerization (ROP) to provide thermally stable materials. Even though these behave as sol-gel type materials, they are without the drawbacks that are normally associated with traditional sol-gel chemistry such as VOCs and shrinkage. Previous studies have indicated that ROP of disiloxacyclopentanes can in fact be polymerized using acids. Here, we report on the ring-opening polymerization of disiloxacyclopentanes using organic acids as well as photoacid generators (PAG). This methodology has opened the door for the use of these materials in film applications and conformal coatings, which will also be discussed.

CCG.36
AFM STUDIES ON BLOCK COPOLYMER TEMPLATED MESOPOROUS SILICA MATERIALS. Akira Endo, Shinichiro Mizuno, Masaru Naito, Takashi Nakane, National Institute of Information and Communications Technology, Tsukuba, JAPAN; Toyo Yamada, Hsu-Shen Zhou, Itaru Yokota, Electrochemical Laboratory, Tsukuba, JAPAN.

Highly ordered mesoporous silica materials, which were synthesized using the micellar structure of surfactants as templates have been attracted much attention in the field of nanoscale material processing. Usually, the low angle XRD and nitrogen gas adsorption are used for characterization of mesoporous and pore size distribution, and TEM is used for visual characterization of mesoporous and microstructure. In this study, AFM measurement in dynamic force mode was applied to the visual observation of highly ordered mesoporous silica materials. Mesoporous silica materials were synthesized by condensation of tetraethylorthosilicate(TEOS) in the presence of [poly(propylene oxide)-]₃-[poly(propylene oxide)] triblock copolymer and the removal of template by thermal treatment in the nitrogen atmosphere. The XRD and nitrogen gas adsorption results revealed that the obtained silica powder had hexagonal structure and pore diameter and wall thickness were 5.2 and 6.5nm, respectively. The periodic structure of about 1nm which corresponded to distance between pore centers in hexagonal planes was observed very clearly by AFM and this results showed good agreement with the structure characterized by low angle XRD and nitrogen gas adsorption measurements. AFM can be a strong and useful tool for the structure characterization of mesoporous materials because of its potential resolution and ease of sample preparation.

CCG.37
PREPARATION AND PROPERTIES OF PCT/P(VDF-TrFE) 0.3/0.7 NANOCOMPOSITE THIN FILMS. Qin Zhou, Qingyi Zhang, Department of Physics, Zhejiang University, Hangzhou, CHINA; H.L.W. Chan and C.L. Choy, Department of Applied Physics and Materials Research Centre, The Hong Kong Polytechnic University, Kowloon, Hong Kong, CHINA.

Poly(vinylidene fluoride-trifluoroethylene) copolymer (P(VDF-TrFE)) powder was synthesized from dicyclopentadiene consisting of the PCT and P(VDF-TrFE) nanocomposite thin film consisting of the PCT powder imbedded in a vinylidene fluoride-trifluoroethylene copolymer [P(VDF-TrFE)] matrix deposited on silicon substrate to form pyroelectric sensor. The pyroelectric and photoelectric properties of the composite film were investigated. The current and voltage responsivities of the sensor were determined. The results show that this kind of composite material has a good potential for pyroelectric sensor applications.

CCG.38
MECHANICAL QUALITY FACTOR OF LEAD ZIRCONATE TITANATE/EPOXY COMPOSITES. K.C. Cheng, H.L.W. Chan, S.W. Or and C.L. Choy, Dept. of Applied Physics and Materials Research Centre, The Hong Kong Polytechnic University, HungHom, Kowloon, Hong Kong, PR. CHINA.

The mechanical quality factor Qₜ of 1-3 piezoelectric lead zirconate titanate/epoxy composites with ceramic volume fractions α ranging from 0.18 to 0.82 have been measured. This range of α is wider than those previously investigated by other workers. The width-to-thickness ratio of the ceramic phase is sufficiently small that there are no significant mode couplings. The observed Qₜ agrees well with the prediction of the parallel model. It was found that Qₜ increases from 34 to 100 as changes from 0.18 to 0.82 and then increases slowly to reach a high value of 600 at α = 1. Therefore Qₜ can be tailored to give a wide range of values by varying α.

CCG.39
AN EFFICIENT REMOVAL OF THE ORGANIC PHASE TEMPLATE BY PHOTOCHEMICAL OXIDATION IN SUBSTRATE-SUPPORTED, ORIENTED ORGANOCAT/SILICATE MESSOSTRUCTURED FILMS. Theolna Clark, Jr., Atul N. Purik, Hongyou Fan, Jeffery C. Brinker and Bael T. Sessa.
The hierarchical co-assembly of self-organizing surfactant and inorganic solgel precursors templated at a solid surface can produce a wide range of inorganic mesoporous thin film materials with controllable morphologies and surface characteristics. These films hold considerable promise in a host of technologies including membranes based in separation, shape and size-selective catalysis, microelectronics, and biological and chemical sensing and detection, as well as in a host of fundamental studies involving locally confined surface chemical and biochemical reactions. But these applications require selective removal of the organic phase from the assembled organic-inorganic mesostructured thin film, currently accomplished using a high temperature thermal-chemical calcination process. The latter process owing to its aggressive thermal and high-temperature environment often damages the physical-chemical characteristics of the underlying substrate surfaces, thus limiting the usefulness of the approach in preparing mesoporous films over technologically relevant, but temperature sensitive, substrate materials and optical waveguide materials. Here, we report a simple, non-thermal room-temperature photochemical treatment for the rapid, reliable, and preferential removal of the organic template. The method offers additional significant advantages over the conventional thermal process for insitu and selective template removal in complex processes.

**CCG 42**

**ROLE OF SELF-ASSEMBLED MONOLAYERS ON THE MESOSTRUCTURE OF SURFACTANT TEMPLATED SILICA FILMS.** Nilesh S. Dake, University of New Mexico, Albuquerque, NM; Yunfeng Lu, Applied Materials, Santa Clara, CA; William C. Jackson, Goodrich Corp., Logan, Utah, Albuquerque, NM; C. Jeff Brinker, University of New Mexico and Sandia National Laboratories, Albuquerque, NM.

We used self-assembled monolayers (SAMs) of alkane thiol on gold (X(CH₃)₃SH; X = CH₃, OH) and alkyllithiums on silicon (CH₃(CH₂)₂SiCl₃) to vary surface hydrophilicity and alkyl chain length in order to study the effect of different surfaces on the mesostructure of surfactant templated silica films. These films, templated with tetrayltrimethylmonium bromide (CTAB), were deposited by aerosol assisted self-assembly. In this process the 1-dimensional hexagonal (1-dH) mesostructured particles coalesce to form a thin film on contacting a surface. Depending on the concentration of CTAB in the sol and the nature of the SAM surface, the 1-dH mesostructured particles congregate on the long chain (SAM= X=OH) to form a lamellar mesostructured film and on hydrophobic SAMs (X=CH₃) the particles retained the 1-dH mesostructure in the film. At low CTAB concentrations a 1-dH mesostructured film formed on both substrates. Thus, only at high CTAB concentrations, the hydrophilic substrate induces the transformation of 1-dH mesostructured particles to lamellar mesostructured particles. We also used alkyltrialkylsilanols SAMs with a long chain (n=17) and a short chain (n=1) to study the effect of mesostructure of film. With less than 5% CTAB in the sol, 1-dH mesostructured particles congregate on both substrates forming a 1-dH mesostructured film. On calcining those films, the 1-dH mesostructure of the film formed on the shorter chain SAM substrate transformed to an uncollapsed lamellar mesostructure while the film on the longer chain SAM retained its 1-dH mesostructure. This phase transformation on the shorter chain SAM takes place at about 190°C when the alkytrichlorosilane SAMs undergo loss of carbon. Using surfaces patterned with hydrophobic and hydrophilic SAMs prepared by micro-contact printing, we can use the above approach to pattern 1-dH and lamellar thin film mesophases.

**CCG 43**

**SOLVENTLESS SOL-GEL CHEMISTRY BY RING-OPENING POLYMERIZATION OF BRIDGED DISILAOXYCYCLO-PENTANES.** Kamyar Rahimian, Douglas A. Ley, Sandia National Laboratories, Albuquerque, NM.

Disilacyclopentanes have proven to be excellent precursors to solgel type materials. We have previously shown that phenylene bridged disilacyclopentanes can be ring opened polymerized, using catalytic tetrabutylammonium hydroxide, to produce thermally stable mesostructured materials without visible shrinkage. These materials are structurally similar to traditional solgels but are generated quite differently: no solvent, non-nucleophilic, no VOCs and little shrinkage is associated with them. We have extended this work to novel alkylene bridged disilacyclopentanes. Here, we report on the ring-opening polymerization (ROP) of these precursors using bases, as well as ROP using organic acids and photonic initiators (PAG).

**CCG 44**

Abstract Withdrawn.

**SESSION CCG 7**

**Meso- or Nanostructured Porous Materials**

Chair: Geoffrey A. Ozin, James E. Mack and Tom Bin

Wednesday Morning, April 26, 2000

**MCC 7.1**


Recent advances in the preparation of molecular sieve layers and thin films will be discussed, and their application in different types of chemical sensors will be described. The synthetic strategies include inorganic or a-need on substrates and growth on functional molecular layers. With the colloidal seed approach, nanocrystalline particles 40-100 nm in size were typically used. It is desirable to reduce the size of the zeolite crystals comprising the films in order to...
achieve fast transport and equilibration. Classical hydrothermal syntheses as well as micrometre processing enabled the controlled growth of dense layers of films of DEAC-MELA, LTA and AFI zeolite structures, in some cases with oriented molecular sieve channels. Selective chemical sensing was demonstrated using very different transduction mechanisms, including micromachined PZT, mass-sensing optical devices, and optical properties of zeolite-encapsulated solvatochromic dyes such as Nile red. In all these cases, the zeolite host imposes molecular size selectivity on the sensor response, thus greatly enhancing the intrinsic response of the respective transduction mechanism.

9:00 AM CC7.2
POROUS METAL OXIDES FABRICATED USING ORGANIC TEMPLATES. Rachel A. Caruso and Markus Antonietti, Max Planck Institute of Colloids and Interfaces, Potsdam, GERMANY.

The morphological properties of a material can be influenced by the use of templating procedures during its formation. Here the process of two templating techniques i) polymer gel coating and ii) self-assembly via layer-by-layer methods on latex particles, will be described. Both techniques have been used to produce inorganic materials after the removal of the initial organic template, which is usually achieved by heating to high temperatures. The resulting features of the material, including structure, shape, and pore size, are dependent on the initial template.

The polymer gel coating process has been used to produce metal oxide networks from the metal precursor. Examples of such networks include titania and zinc oxide. The initial gel, which is porous, is sintered in the metal oxide, then placed into a solvent containing water for hydrolysis and condensation reactions to proceed. After drying, the system is heated above 400 °C to decompose and remove the polymer. The final network is studied using electron microscopy to determine morphology and crystal phase.

The use of colloidal templates (e.g., latex particles) and the layer-by-layer deposition of nanoparticles, alternating with polyelectrolyte, has resulted in nanoparticle multilayer shells surrounding the colloidal core. Different nanoparticles have been used to build up the shell, including silica spheres and iron oxides. On removal of the template the hollow sphere containing the nanoparticles remains. Depending on the mode of template removal this process has produced inorganic as well as hybrid materials.

The main areas of interest for these materials are their application in photovoltaic and catalytic fields.


9:15 AM CC7.3

Mesoporous titanium phosphates were synthesised using three different approaches, involving reactions of titanium tetrakisopropoxide with long chain alkylphosphates and alkylphosphates, and thermal treatment of titanate gels at temperatures of 800 to 1150 °C for several days. The resulting powders were characterised using FT-IR, EXAFS, 31P-NMR, XRD, TEM and N2 sorption. The first approach involved the classical MCM methodology, with the modified titanate precursor being reacted with an alkylphosphate micellar solution. TEM showed that the as-synthesised solids possessed a highly organised, lamellar mesostructure. However, removal of the surfactant by either heating or leaching in strong bases or acids, solutions led to collapse of the lamellar mesostructure. TEM examination of samples heated at 400 °C confirmed that the collapsed structure consisted of a mixture of micro-porous, micro-porous-nanoporous and nanoparticulate (titanium-rich) phases. To promote a stronger interaction between the titanium (IV) and surfactant, and enhance the templating effect, a second strategy was devised; titanium alkoxide was pre-reacted with the long chain alkyl phosphate, then hydrolysed with a large excess of water prior to ageing. Although the structure of the as-prepared samples could be easily tamed by changing the processing parameters such as the alkyl phosphate chain length or phosphate/titanium ratio, surfactant removal by heating invariably led to the production of micro-porous samples, with low total pore volumes. To prevent the collapse of the structure upon heating, a third approach was devised. This involved the hydrolysis of titanium tetrakispophosphate, modified with acetic anhydride, with excess water. The alkyl phosphate was then introduced into the template and crystallisation under mild conditions destabilised the particles, leading to aggregation and subsequent gelation. As before, a diffusion peak was observed at low angles, suggesting the presence of a mesostructure. Upon heating, the peak dissipated, indicating a reduction in ordering. However, in contrast to the previous approaches, the pyrolysed solid contained a significant proportion of mesopores (34 nm) and a surface area greater than 300 m2 g⁻¹. Moreover, this strategy can also be extended to the synthesis of meso-porous titania with very high surface areas by the use of non de-chelating surfactants such as CTAB.

9:30 AM CC7.4
POROUS SILICA THIN LAYERS USING MESOPHASE TEMPLATING. Michael Kleitz, André Ayrat, Christian Guizard, Laboratoire des Matériaux et Préparations Membranaires, E.S.N.C. Montpellier, FRANCE.

Using conventional sol-gel routes, the synthesis constraints associated with thin film applications limit the ability to control the porosity of the resulting layers. The mesophasic templating technique which leads to ordered porous materials is an attractive method to increase the pore volume, to tailor the pore size, the pore size distribution and the porosity of the pore network in solgel derived thin films. However, specific conditions have to be found in order to prepare continuous defect-free layers exhibiting no expropriation. The example of the tempergels by hexagonal mesophasic silica will be used to show it is possible to succeed in the preparation of such layers. Simple considerations from data established in the case of the water-water surfactant binary diagrams are particularly useful to predict and optimize the synthesis conditions. On another hand the crystallinity of the ordered porous layers has to be taken into account. X-ray diffraction techniques and transmission electron microscopy are applied to evidence the size of the ordered domains, the morphology of the crystalline texture and the thermal evolution of the crystalline structure. The nanoparticle seeding enables us to modify the crystalline texture of the ordered porous layers. Results concerning this new approach will be finally presented and discussed.

10:30 AM CC7.5
SYNTHESIS AND CHARACTERIZATION OF NOVEL CATALYTICALLY ACTIVE ZrO2/Cu And ZrO2/CuS NANOCOMPOSITES. Michael Grün, Rachel A. Caruso and Markus Antonietti, Max Planck Inst. of Colloids and Interfaces, Potsdam, GERMANY.

The aim of this study was to synthesise hybrid materials composed of porous zirconia support and highly dispersed nanocrystalline Cu or CuS nanoparticles. These composite materials are promising catalysts in the car industry and method synthesis.

The mesoporous zirconia support was prepared by hydrolysis and condensation of tetramethylalkoxysilanes in the presence of hydrochloric acid as catalyst. Long-chain n-alkylphosphates and n-alkylamines were used as templates. The resulting materials exhibited pore diameters ranging from 2 to 4 nm and pore volumes between 0.2 and 0.5 cm³ g⁻¹. The CuS nanoparticles were independently prepared from aqueous sodium sulfide and copper nitrate solutions using polyvinylpyrrolidone as the protective polymer and then incorporated into the zirconia. The template was removed by calcination at 450 °C or by solvent extraction with isopropanol. Transmission and scanning electron microscopy were employed to characterise the pore structure and the nanoparticle distribution across the support material. Nitrogen sorption and X-ray diffraction measurements were used to determine the textural and crystallinity of the final product.

10:45 AM CC7.6
POROUS GELS OBTAINED BY PHASE SEPARATION IN ORMOGEL SYSTEMS. Kunishi Nishio, Norio Ishimasa, Satoshi Komen, Kazuyuki Hira, Dept. Material Chemistry, Graduate School of Engineering, Kyoto University, JAPAN.

Concurrent phase separation and sol-gel transition which result in well-defined mesoporous structures can be observed in a broad range of ORMOGEL compositions. The decreased functionality and increased hydrophobicity compared with the systems from tetrafunctional silanes provide the phase separation of ORMOGEL systems more poro-gel-like features. In bulk sol-gel formation, the sol-gel transition proceeds gradually along the sol-gel transition range, the transient structures developed by the phase separation process can be frozen-in in broader starting composition range than the case of pure silane systems. The addition of non-silica solvents results in drastically decreased drying shrinkage of the gel samples, which allows one to fabricate net-shape porous materials in an appropriate mold. By dip-coating the ORMOGEL compositions concurrently with the phase separation induced by the solvent evaporation, the well-defined porous structure can be frozen onto the substrate. In addition to the formation of phase domains by the spinodal decomposition, the concerning relation to the wetting on the substrate plays an important role in determining the final mesoporous morphology of the resultant films.

11:15 AM CC7.7
LASER ACTION FROM LASER DYE-LOADED POROUS MATERIALS. Ferdi Schuh, Guido Ihein, Ozlem Weiss, Frank
November 4, 2004

1:00 PM CCLS.1
HIERARCHICALLY ORDERED INORGANIC-ORGANIC COMPOSITES AND POROUS OXIDES. B.M. Chmelka, P. Yang, G. Wirsberger, H. Huang, N. Melosh, G.D. Stucky, Univ of California, Santa Barbara, Dept of Chemical Engineering and Chemistry, Santa Barbara, CA.

Mesostructured and mesoporous materials are being synthesized using the sol-gel method. These materials have micropores on the order of 1-2 nm, and mesopores on the order of 2-100 nm. The mesopores are usually isolated from each other, but in some cases they are connected. The pores are often filled with a liquid, such as water or an organic solvent.

These materials have many potential applications, including catalysts, adsorbents, and membranes. They are also being used in the development of new composites and ceramic materials. The synthesis of these materials involves the use of surfactants and other templates, which are removed after the synthesis is complete.

Since the discovery of the ordered mesoporous materials called M41s, researchers have been exploring their potential for use in a wide range of applications. These materials have high surface areas, which makes them ideal for use as adsorbents and catalysts. They also have high thermal and chemical stability, which makes them suitable for use in a variety of environments.

The use of these materials in the development of new composites and ceramic materials is also being explored. These composites have the potential to be used in a variety of applications, including electronics, energy storage, and structural materials.

We have been working on the synthesis, characterization, and application of these materials. In this talk, we will discuss our recent results, including the synthesis of new materials and the characterization of their properties. We will also discuss the potential applications of these materials and the challenges that must be overcome to realize their full potential.
investigations is to correlate the structures of the composites with the synthetic techniques used to prepare them, and with the mechanical properties. In this way the understanding of the relationship between the structure of the sol-gel materials and the properties of the final polymer can be achieved. The objective of this presentation is to discuss the relationship between the sol-gel structures of organically modified silicas and the mechanical properties of the final polymer. Co-hydroxylation of organosilanes and metal alkoxides can provide a means for the formation of co-condensation reactions between the different precursors. This will control the structural homogeneity of the final network. Solution state 29Si and 27O NMR may be used to provide information on the formation and stability of co-condensation species. In the final gel, solid state 29Si MAS NMR used in conjunction with cross-polarization (CP) and relaxed 29Si relaxation NMR correlation techniques, provides detailed information on dipole-dipole coupled 29Si and 1H species among different molecular moieties, and on their spatial proximity of these species. Similar information can be obtained by using 29Si homo-correlation NMR spectroscopy. Such experiments are now possible by combining high magnetic field with fast spinning rate (30 kHz). Finally, the use of 27O MAS-NMR with the newly developed MQMAS sequence that provides a direct detection of the various cross bridges that constitutes the hybrid network will be discussed.

4:00 PM CCB.6
MICROPHASES ALUMINOPHOSPHATE FORMATION IN SITU HYDROTHERMAL NMR, Corin Gerardin#, Mohamed Houas, Francis Taddele, Louis Pasteur University, Strasbourg, FRANCE, *CNRS-RHODIA Complex Fluids Laboratory, Cranbury, NJ, Thierry Loenza, Gerard Frey, University Versailles-Saint Quentin, Versailles, FRANCE.

Synthetic pathways describing the formation of microphases of materials under hydrothermal conditions are not yet elucidated. NMR is one of the most appropriate tools to investigate hydrothermal multiphase systems. The study is centered on the elucidation of the formation mechanisms of templated aluminophosphates. The objective was to get a more detailed and reliable description of the synthesis medium while microporous crystals grow. Tubes and methods were developed in order to perform in situ liquid-state NMR measurements up to 200°C under autogenous pressure. Quantification lead to the determination of distributions of atoms in the liquid and solid parts as a function of synthesis time. Information on mass transfers was crucial for discriminating between solution-mediated crystallization or solid to solid transformation. In situ solution speciation together with pH variation were obtained. Results were examined in relation with the question of the existence of solution in secondary building units and their role in phase formation. In situ NMR under reaction conditions (liquid/solid heterogeneous medium at high temperature) was necessary to reveal not only the primary units but also the prenucleation clusters responsible for the nucleation and growth steps. The evolution of those species during the three main stages (induction/dissolution-crystallization) was characterized.

4:15 PM CCB.7
ELECTROCHEMICAL INVESTIGATIONS INTO SILICA AND ZIRCONIA POLYMERIZING SOL-GEL SYSTEMS. A NEW APPROACH OF THE GELIFICATION KINETICS, Pierre Ausbauer, Samuel Mathieu, PPSM, ENS Cachan, Hélène Catty, LSEO, FRANCE, Univ Bourgogne, FRANCE and Clément Sanchez, Lab. Chimie Mat. Condensée, Univ P, FRANCE.

Through the information they can bring on the transport of electroactive species, electrochemical techniques, and especially chronocoulometry, are valuable tools to investigate the behaviour of polymer solutions and gels dynamics. Due to the fastness of the recording of the diffusion coefficients or related parameters, chronocoulometry is especially well suited to detailed investigations on gelling systems course and after. The dispersed electroactive probes into gelling systems and the subsequent gels, and we show how the variations of the diffusion coefficients of the electroactive species are typical of the structures of the sols and the gels. Electroactive probes can be either free, either linked through covalently bound spacers to the oxide skeleton, and also of various sizes, which allows a wide range of informations to be obtained by varying the probe kind into a single gel. After a short summary of previously obtained results concerning gels, particular emphasis will be put on the investigations on zirconia gels with the help of bounded ferrocenes, showing the very high mobility of the oxopolymers even in aged gels. As a conclusion, some recent results on modified electrodes that can be obtained from ferroelectric materials will be also briefly introduced.

4:30 PM CCC.8
HYBRID 170 NANOCOMPOSITES FROM ALKOXYSLIANES RELATIONSHIPS BETWEEN MORPHOLOGY AND MECHANICAL PROPERTIES, J-F. Gerardin1, H. Kiddani1, J-P. Passet1, P. Haji2, F. David2 and V. Giger2,3, UM CR CNRS, Laboratoire Matériaux Micronanométaboles, 79GEMPPM-UMR CR CNRS, Institut National des Sciences Appliquées, Villeurbanne, FRANCE.

Relationships between morphologies and mechanical properties of organic-inorganic nanocomposites synthesized from sol-gel chemistry of alkoxyalanes reported the literature are reviewed in the first part of this paper. In the second part, these relationships are illustrated for two series of I/O materials containing SiO2 contents synthesized from i) the hydrosisylation and condensation of alkoxyalanes-functionalized polyglycol and polyether oligomers synthesized from the reaction with -amine(oxycyanate) propylmethoxy-silane and -hydroxy terminated polydimethylsiloxane or polycrylate, respectively (about 4% wt. SiO2); ii) the simultaneous hydrosisylation/condensation of tetraethoxysilane and polyether functionalization of poly(dimethylmethoxysilane), HEMA (from 0 to 50% wt. SiO2). It can be demonstrated that the dynamic mechanical behavior, i.e. the complex modulus vs. temperature and frequency can be related to the nature of the morphology (dispersed silicon-rich phase or co-continuous organic-rich and inorganic-rich phases) and the purity and state of condensation of the phases. For example, from 10% wt. of SiO2 for the HEMA/TEOS, a fine co-continuous morphology, evidenced by SAXS, leads to a slight decrease of the storage shear modulus in the HEMA glass transition region. Its value in the rubbery state is strongly related to the condensation of silicon species studied by 29Si-NMR, i.e. the conditions of the solgel reactions of TEOS (polymerization temperature and the concentration of acid). From such studies, the mechanical properties of I/O materials can be defined from designing the morphology, i.e. the solgel reactions conditions.

SESSION CCB.9 PROCESSING AND PROPERTIES OF HYBRIDS (OPTICAL, ELECTRICAL, MECHANICAL...)
Chair: Giovanni Curtarolo, Martin Mennig and Florence Bobbourné
Thursday Morning, April 27, 2000
Metropolitan III (Aent)

8:30 AM CCC.9.1
NANOSTRUCTURED HYBRID POSS CHEMICAL FEEDSTOCKS: COMMERCIALIZATION, PROPERTIES, AND APPLICATIONS, Joseph D. Dziewczynski, Joseph J. Schwartz, Hybrid Plastics, Foothill Valley, CA.

Polymeric Oligomeric Silesquioxane (POSS) chemical is comprised of monosaccharide silicon-oxygen frameworks that externally contain a variety of reactive and nonreactive organic groups for solubilization and copolymerization. Hence, POSS chemical systems can be viewed as the smallest chemically discrete particle of silicon possible while the resins in which they are incorporated are structurally well defined molecular nanocomposites. Over the past decade, the US DoD and DoE have pursued development of this technology in an attempt to meet their demand for a new generation of polymeric materials. Consequently, the number of research reports and product development activities involving POSS chemical technology have increased explosively over the past 10 years. The demand for POSS is evidenced by the commercial availability of over 65 POSS reactants, monomers, and resins, and the emergence of five primary suppliers. A survey of markets, properties and applications for POSS technology will be presented along with a roadmap for research directions and the imminent emergence of the next generation of low-cost POSS compositions. Discussion of and refinements to the theoretical model for POSS-based nanocomposites will also be presented in light of recent experimental findings and property modeling studies.

9:00 AM CCC.9.2
PATTERNED PHOTONIC CRYSTALS WITHIN MICROCHANNEL NETWORKS. Abbas Rivi, Amer Choudhry, Pei Chong Yang, Department of Chemistry, University of California, Berkeley, CA.

Patterned macroporous materials are synthesized using close-packed microsphere templates self-assembled within microchannel networks. The microchannel network is formed between a patterned elastomer mold and a substrate. Different precursor solutions were infiltrated...
through and solidified within the microchannel after the microsphere self-assembly. Ordered framework with compositions from oxides, semiconductors, and metals were obtained using this methodology. In addition, different microchannel geometries (e.g. width, height) can be used to control the orientation (e.g. \(<100\) vs \(\{111\}\)) and interconnection of these ordered macroscopic materials. This synthetic process provides a simple process for patterning of photonic crystals on substrates with controllable ordering, dielectric contrast, orientation and interface.

9:15 AM CC9.3
HYBRID MICRO-OPTICAL SENSORS VIA SOL-GEL SOFT LITHOGRAPHY
Michael J. Loehr, Mark Chmer, Univ of New Hampshire, Dept of Chemical Engineering, Durham, NH.
Organically modified silica gels and dye-doped silica gels have been patterned into micrometer-scale structures on a substrate using micro molding in capillaries (MIC) or microimprinting molding. These approaches are from a class of elastomeric stamping and molding techniques collectively known as soft lithography. Soft lithography and solgel share attractive features in that they are relatively benign processes performed at ambient conditions, which makes both techniques compatible with a wide variety of organic molecules, molecular assemblies, and biomolecules. The combination of solgel and soft lithography, therefore, holds enormous promise as a tool for microfabrication of materials with optical, chemical, or biological functionality that are not readily patterned with conventional methods. This paper describes our investigations of micro-patterned organic/inorganic hybrid materials containing fluorescent dyes for active microfluidic devices and micro-optical sensors. Application of templated structures range from one to tens of micrometers in cross-section and are centimeters in length. Fundamental chemical processing issues associated with mold filling, gelation, aging, and shrinkage are addressed, as are the optical properties of the fabricated structures. Optical transduction of a chemical signal is demonstrated.

9:30 AM *CC9.4
ELECTRICAL AND OPTICAL INTERCONNECTION. TECHNOLOGY BASED ON ORMOCEM - INORGANIC-ORGANIC HYBRID MATERIALS.
Michael Poppi, Ralf Buestrich, Fachhochschule fur Siliciumforschung, Wuerzburg, GERMANY; Alexander Dinkel, Holger Stolle, Fachhochschule fur Siliciumforschung, Wuerzburg, GERMANY; Mats Robertsson, IMC- Microsystems, Ericsson Components AB, Kista, Stockholm, SWEDEN; Joachim Huglin, Simon Valumude, IMC- Microsystems, Linkoeping, SWEDEN; Lubomir Cengel, Motorola SPS, Geneva, SWITZERLAND; Daniel Lambert, BULL, VLSI Packaging, Les Clayes-sous-Bois, FRANCE; Maxime Schaub, W.C. Herrmann, Thickfilm, Hauzen, GERMANY.
Photopatternable hybrid inorganic-organic polymers with negative resist behavior have been developed and tested for evaluation in optical and electrical interconnection technology. They are composed of inorganic oxide structures cross-linked or substituted by organic groups, or chemical cross-linking/functionalization by sol-gel-processing in combination with organic cross-linking of polymericizable organic functions. As a result of these functionalities the properties of the ORMOCEMS are adjusted to the particular application requirements by changing the chemical composition. Furthermore, adaptation to micro system technology allows great flexibility in processing. The main features of these materials are: - Combined use as dielectric and passivation layers in electronic systems and devices as well as for coating baking of optical/RF components - High optical contrast with integrated waveguides are already achieved. Synthesis, optimization of the resists and their application to optical interconnections is the main focus of this contribution. The optimized materials will be discussed.

10:30 AM *CC9.5
CHEMICAL DESIGN OF NANOSTRUCTURED LUMINESCENT MATERIALS. Thierry Guaycin, Arnaud Haiqard, Jean-Pierre Baille, Laboratoire de Physique du Matiere Condensee, CNRS UMR, ENSCP, Polytechnique, Palaiseau, FRANCE.
Inorganic luminescent materials have practical applications in almost all device involving the artificial production of light. In the last few years, the development of flat electroluminescent, plasma or field emission displays with huge industrial applications increased the demand for materials with better characteristics in terms of stability, brightness, and industrial processing efficiency. The synthesis of new materials concerns less than the research of new chemical compositions or the optimization of the extrinsic properties of usual phosphors. Grain size, morphology, agglomeration, or surface passivation are indeed well known to have an impact on the phosphor efficiencies. The study of these parameters is clearly dependent on the development of new methods of elaboration. In this context, colloid chemistry offers versatile routes for the synthesis of nanocrystalline materials with passivation treatment and can be used in thin film techniques related to the sol-gel process. In this field, the example of chalcogenide materials is probably the most relevant to illustrate the efficiency of colloidal chemistry for the synthesis of nanomaterials with optimized optical properties. The obtaining of core-shell nanostructures or manganese doped particles lead to a decisive improvement of their luminescence quantum yields, opening the way to their applications as intrinsic optical phosphors. Moreover, the optimization of highly concentrated solutions, formed of highly stabilized particles, allows the extension of the sol-gel process to the non-aqueous synthesis of transparent chalcogenide materials. Now, we report the development of the principles used in the case of chalcogenide materials to other compounds, such as lanthanide-doped oxides.

11:00 AM CC9.6
ATTACHMENT OF FLUOROPOLYMERS TO GLASS SURFACES THROUGH PHOTOCATALYTIC SOL-GEL INTERFACES.
Elizabeth I. Movie, Eric Locher, A.E. Siegeman, Dept of Chemistry and The Materials Research and Technology Center, Florida State University, Tallahassee, FL.
We have successfully formed tightly bound polyvinylidene fluoride coatings to glass and metal surfaces. These coatings act as robust, low-surface-energy protective barriers and can be used to modify and protect a variety of surfaces. The fluoropolymer was attached using a sol-gel film composed of reactive metal-oxide sites bound into a silica gel matrix. The presence of the metal-oxide sites imparts unique photochemical reactivity to this organic-inorganic system, and allows for the use of strong acids to chemically etch the organic, monomer to be photopolymerized at the surface. Metalalka films of approximately 1 mm were made by spin-coating a sol containing the metal-oxide sites and dry tetramethyloxysilane onto glass microscope slides or stainless steel substrates. Dried films of this sol were placed in an evacuated chamber under a layer of condensed polyvinylidene fluoride and irradiated (>360 nm) to initiate polymerization. Characterization of the polyvinylidene fluoride coatings was carried out by XPS and microscopy (STM and AFM). These techniques revealed a uniform polymer coating approximately 900 Å thick bound through a polymer-silica nanocomposite interface to the substrate. Abrasion tests and treatment with organic solvents confirmed the durability of the coatings.

11:15 AM CC9.7
EVOLUTION OF LUMINESCENCE PROPERTIES RELATIVE TO SOL-GEL DERIVED HYBRID MATERIALS WITH Eu⁺³ ORGANIC CHLATE STRUCTURE. Anne-Christine Franville, Rochid Mahiou, Daniel Zanbon, Universite Blaise Pascal and ENSCCP, Laboratoire des Matériaux Inorganiques, Aubiere, FRANCE.
There is considerable interest in the optical properties of chalcogenide organic materials in sol-gel glasses for applications in laser materials, waveguides and more recently, very low loss transparent optical fibers. We have reported on sol-gel derived organic-inorganic hybrid materials usable as lumophores for lamps or screens. In a previous paper [1], we have shown that highly luminescent rare earth hybrids could be obtained by cosolvent gradient growth with organic chelates to a silicate based inorganic network. Suitable design of organics allows to shield Eu⁺³ ions from their environment, to prevent clustering and to improve absorption efficiencies of the derived compounds. Tailoring optical properties of these hybrid materials for practical useful applications can be performed by adjusting chemical composition of the inorganic network, by modifying organic ligand structure or by controlling guest-host interactions. These interactions were found to be determining for class I hybrid systems whereas solgel conditions and organic molecules have more separate influences on the Eu⁺³ emission properties when the two components are linked through covalent bonds. Silica/organic chelate molar ratios and synthesis conditions were previously used to modify the morphology and thermal stability and the transparency of the luminescent hybrids. In this paper, the luminescence properties of hybrid materials will be discussed in relation with the ligand structure and compared with that of the corresponding organic copolymers. The studied ligands are derived from dipicolinic acid with additional aromatic groups. The synthesized materials will be characterized by IR spectroscopy, by \(^{13}C\) and \(^{2}H\) NMR and by elemental analyses. Position of the organic ligands energy levels was derived from diffuse reflectance as well as from phosphorescence spectra relative to Ga⁺³ reference. As a result of ligand modifications, the absorption efficiency of the ligand is transfer the absorbed energy to Eu⁺³ and consequently the Eu⁺³ quantum yields are modified. In one particular case, hybrid materials exhibit different behavior compared to their coordination mode. Influence of silica on the Eu⁺³ local environment is therefore more or less sensitive depending on the chelate structure.
11:30 AM CC9.8
LOW Si-OH CONTROLLERS FOR DIELECTRICAL AND OPTICAL INTERCONNECTION TECHNOLOGY. Ralf Haaseitch, Frank Kahlenberg, Michael Pogall, Fraunhofer-Institut fuer Siliciumforschung, Wuerzburg, GERMANY; Joachim Hugland, Mats Robertscon, IMC-Microsystems, Linkoeping, SWEDEN.

Low Si-OH containing ORMOCERs (inorganic-organic hybrid polymers) were synthesized by a new sol-gel route. Optimization of the sol-gel process parameters (catalyst, temperature etc.) was performed to achieve reproducible results which are photo-patternable even in higher thickness layer up to 150 μm within one step without cracking or delamination. The materials combine low losses in the NIR region (0.2 dB/cm at 1310 nm and 0.5 dB/cm at 1550 nm without fluorination) with low dielectric constants (3.3 at 10 kHz). Beside the mentioned dielectric and optical properties the materials have a variety of additional advantages for interconnection technology (such as good wetting and adhesion on various substrates e.g. glass, silicon and several polymers), low processing temperatures (postbake below 160°C), high thermal stability (up to 250°C) and a tunable refractive index. Details of chemical synthesis encapsulated biological cells via immunolabeling or well as photo-lithographic processing of ORMOCER materials will be presented.

SESSION CC10: BIOMATERIALS AND BIOGELS

Chair: Shawn H. Phillips, Richard M. Laine and Albert E. Stiegen
Thursday Afternoon, April 27, 2000
Metropolitan III [Argent]

12:30 PM CC10.1
SiOx, ENTRAPMENT OF ANIMAL CELLS FOR BIO-Artificial ORGANS. Giovanni Curturati, Dept of Materials Engineering, Trento, ITALY; Renzo Dal Monte, TR B., Altmiliva, ITALY; Maurizio Marzec, Dept of Medical and Surgical Sciences, Padov, ITALY.

The Biscal method involves the sol-gel silicon oxide deposition directly on the surface of living cells by reaction of silicon alkoxides in glc phase with -OH groups and H2O of cellular membrane. This technique allows maintenance of cell viability and function and provides the advantage of (i) a definite encapsulation of the biomass with improvement of mass transfer from and to cells, (ii) a definite increase of the mechanical resistance and (iii) a valuable protection of encapsulated biological cells against immunological reactions. In the effort to design a bio-artificial liver, porcine or rat hepatocytes were cultivated in collagen gel to afford a monolayered structure close to in vivo liver morphology; deposition of 0.1 μm thick of sol-gel Me2SiH2O(2-)(aq)+O(2-)(aq) (x=0.3-0.5, y=0.1-0.2) resulted in the encapsulation of cells. Experimental results on protein diffusion across the silicon-oxide membrane substantiated a considerable molecular cutoff for proteins higher than 150,000 Da, which includes most immunoglobulins. The encapsulated cell mass incubation on the sol-gel hybrid silicon oxide were also calculated for proteins with different bulkiness. The specific functions of collagen-SiOx encapsulated hepatocytes were tested in the case of monoclonal anti bile salt production, albumin removal, and lipoprotein metabolism productions. The kinetics of these hepatocytes-assisted reactions indicated maintenance of functions which in some cases is exalted after encapsulation. The biocompatibility of the Biscal membrane was tested performing in vivo experiments which indicate the possible extension of this encapsulation process to xenogenic biomasses for permanent grafts. The definition of intrinsic mechanical properties was performed by flow experiments with different liquids at various speeds. Collected data concerning the forces demanded to bioartificial organs may be useful to design operative devices.

2:00 PM CC10.2
SOL-GEl ENTRAPMENT OF ENZYMES. Lucie Bergogne, Sound Fennouh, Cecile Roux, Jacques Livigne.

This test report on the encapsulation of two enzymes within a solgel silica matrix. The matrix have been synthesized from pure TMOS alkoxide by the two step solgel process without adding alcohol and with different amount of water. The first enzyme entrapped has been a lipase. Both enzymatic activities have been studied hydradysis and transeraseificion. In order to achieve reproducible results for a hydrolytic reaction, the kinetic parameters (M, Vmax) are not very affected by the lipase encapsulation within a wet gel. But the enzymes lose their catalytic activity after the drying. An opposite effect is observed when the amount of water is little. Then enzyme-substrate affinity is better in wet and dried gel than in solution. Moreover, over the dried gel, the entrapped lipase is less active than the native one for the hydrolysis reaction but can be almost 10 time more active for the transeraseificion. The second example corresponds to the encapsulation of B-galactosidase enzyme via bacteria. The enzymes have been induced in the bacteria before the encapsulation. Whole cell bacteria have been directly trapped, within sol-gel glasses by the enzymatic activity of B-galactosidase is measured using n-p-nitrophenyl-β-D-glactopyranoside as a substrate. In the wet gel transmission electron microscopy of entrapped cells show that bacteria are randomly dispersed within the sol-gel and retain their integrity. The Michaelis constant is KM=0.29 mM and better than those observed in solution (KM=0.45 mM). This might be due to the fact that bacteria are randomly dispersed in the gels where as they form aggregates in the aqueous suspensions. The studied system shows that the sol-gel process can be used to do an entrapped gel lose their integrity and then their catalytic activity.

2:15 PM CC10.3

Sol-gel methods have been used to encapsulate biopolymers in organic matrices. To preserve and enhance the biofunctionality, several new approaches have been taken. One is to use a process that does not contain any alcohol reactant or product. This precludes the use of the alcohol route. Instead, direct gelation of colloidal particles at room temperature and nearly neutral pH has proved to be effective for this purpose. Using different monocrystalline ceramic particles, we have also demonstrated an important size effect: the interceramic-particle pores should not be much larger than the biopolymers; otherwise the latter's structural stability cannot be preserved. Lastly, using inorganic solids of different surface properties, thin films with two or more biomolecules in a patterned structure can be prepared to enhance their biofunctionality in coupled reactions. Implications of enhanced biofunctionality of encapsulated biopolymers will be discussed.

2:30 PM CC10.4
POROUS INORGANIC SUBSTRATES FOR HIGH DENSITY DNA ARRAYS. Curt Frank, Marc Glick, Dept of Chemical Engineering, Stanford Univ, Stanford, CA; Jacqueline Bidman, Glenn McCull, Affymetrix, Santa Clara, CA.

Porous inorganic layers are proving to be promising candidates for future high density DNA arrays. DNA arrays are a combinatorial approach to DNA analysis in which probe-based hybridization is carried out in a layer of DNA that is immobilized on an inorganic substrate (usually flat glass). Short strands of DNA (probes) are grown and patterned on a surface using solution chemistry and photolithography. Unidentified strands of DNA (target) are then analyzed by hybridization to the arrays. In previous work (MRS, Spring 1998) we demonstrated the concept of using a porous inorganic support to increase the density of probes for a given “2D” area. A phase-separating sodium borosilicate glass was etched in a “subtractive” approach and stained with a fluorescent dye. Here we used more flexible “additive” approach in which porous layers are deposited, and present a full investigation of the hybridization behavior of the layers. Colloidal silica spheres deposited via spin coating form the majority of the porous matrix with TMOS (trimethoxymethyline) added to enhance stability. The advantage of the spin coating process is that layers of arbitrary thickness can be created by successive depositions, giving improvements in hybridization signal over an ordered sequence on test slides. Additionally the films have passed a variety of other tests. For thin films, feature edges do not show significant loss in resolution due to light scattering. Discrimination between matched and mismatched probes shows similar ratios to those obtained with flat glass. The films are stable against degradation in the high salt, elevated temperature buffer solutions used for typical DNA arrays. We will describe functional behavior in terms of the kinetics of hybridization and compare to existing models of adsorption such as fixed bed reactors. We will also present future directions for using sol-gel techniques to tailor the morphology for optimization of hybridization kinetics.

3:15 PM CC10.5
BIOMEDICAL SENSORS USING SOL-GEl ENCAPSULATION METHODS. Janna Cox, Esther Lan, Bruce Dunn, Dept. of Materials Science and Engineering; Jeffrey I. Zink, Dept. of Chemistry and Biochemistry, UCLA, Los Angeles, CA.

Sol-gel encapsulation has been demonstrated to be a successful approach for immobilizing biomolecules. Proteins and enzymes trapped in the pores of the sol-gel derived glass retain their spectroscopic properties and biological activity. Moreover, studies have shown that physical encapsulation of proteins in the inorganic matrix provides a durable and rugged environment that also stabilizes the biomolecule from thermal and chemical denaturation pathways. For these reasons, biomolecule-doped glasses synthesized via the sol-gel approach have been investigated as optical and electrochemical
sensing elements for a wide variety of analytes. The present paper reviews our recent work in extending the unique capabilities of biomimetically derived materials along with novel electrochemical device applications. One example is our research on neurotransmitter sensors. By encapsulating the enzyme glutamate dehydrogenase and the co-factor NAD+ in the sol-gel glass, it is possible to use a known assay method to detect glutamine or physiological levels. This is accomplished by monitoring the luminescence from the NADH produced from the enzymatic reaction. We are presently developing optical fibers for in-situ experiments in cultured cells. A second activity involves the sol-gel encapsulated biotin-streptavidin binding, a protein which is extremely useful in biochemical assays because of its high affinity for biotin. The prospect of enhancing the stability of biotin-streptavidin binding is quite attractive for bioanalysis applications because of the many biotinylation compounds presently available. Our experiments on biotin-streptavidin binding within a sol-gel film are reviewed.

3:45 PM CC10.6
IN VITRO APATITE DEPOSITION AND BIOGRADERADATION OF POROUS GELATIN-SILICATE HYBRIDS. Lei Ren, Kunji Tsuru, Satoshi Hayakawa, Akioyshi Osaka, Okayama Univ., Dept of Bioscience and Biotech, Okayama, JAPAN.

Porous gelatin matrices have great potential in biomedical applications. They are biodegradable and biocompatible, but not bioactive enough to bond to living tissue. In the present study, highly porous and bioactive gelatin-silicate hybrids were prepared by solgel process and freeze-drying techniques. Under stirring, 3-(glycidoxypropyl)trimethoxysilane (GPMs) was added into a gelatin and calcium nitrate solution to attain several GPMs/gelatin and Ca(NO3)2/GPMs mass ratio. After gelation, the wet gels were soaked into an ammonium-formaldehyde solution and then lyophilized. They were soaked in a simulated body fluid (SBF) to evaluate the bioactivity by examining apatite deposition on their surface with FT-IR, XFRD, SEM and EDX. Bioactivity was evaluated by weight loss after the hybrids were soaked in a Tris(hydroxyethyl)aminomethane buffer solution. SEM observation demonstrated a network structure of heterogeneous pores with an average inner diameter 250 nm for hybrids having GPMs/gelatin ratio=1. XFRD patterns, FT-IR spectra and SEM photographs before and after soaking in SBF indicated that the calcium ion free hybrid failed to deposit an apatite layer even after 14 days. However, the calcium ion containing hybrids deposited apatite within 3 days of soaking. Moreover, the rate of apatite formation increased with the calcium ion content. The dynamics of weight loss indicated that the biodegradation rate decreased with the GPMs content. Nevertheless, the biodegradation rate decreased with the concentration of the ammonium-formaldehyde solution at the same mass ratio of GPMs/gelatin. These results were discussed in terms of gelatin-GPMs-gelatin bridging.

4:00 PM CC10.7
THE SYNTHESES AND CHARACTERIZATION OF DAM-1 TYPE MATERIALS. S. Kenneth J. Balfour, Jr., Lisa Washmon, Jessica Lucas, University of Texas at Dallas, Department of Chemistry, Richardson, TX.

Vitamin E TPGS is a sticky solid that makes storage and manipulation difficult. A free flowing powder form of this highly important antioxidant could lead to a significant improvement in transport and delivery. We have found that Vitamin E TPGS serves as a template for the synthesis of the hexagonal mesoporous siliceous phase referred to as DAM-1 (Dumbell Material). Details of the synthesis and characterization of this ordered composite powder will be presented. Additionally, the controlled release of Vitamin E TPGS under physiological conditions will be described.

4:15 PM CC10.8

In 1994, the U.S. Army initiated a research effort towards an effective material that acts both as a protective barrier and as an active destructive matrix against chemical warfare agents (CWA). We report results on our preparation and evaluation of Reactive Topical Skin Protectants (RTSPs). These creams are composite materials consisting of a base material (TSP) and a reactive moiety. Using an established base of perfluorinated-polyether and perfluoropolyethylene solids we incorporated over 60 reactive components. Classes tested included organic polymers, organosilicon hybrid materials, polyoxometalates (POM’s), enzymes, inorganic oxides, metal alloys and small molecules. We characterized these materials by light microscopy and FTIR. We determined the efficacy of these materials against both chemical warfare agents and prevalent nerve agents, using a penetration cell model coupled to a continuous air monitor and also by in vivo testing. Composite materials with optimal reactive compounds exhibit a 97% reduction of GD vapor breakthrough at 450 mg to 1.7 mg in a 3.6 fold increase (from 162 to 588 min) in the time 1000 ng of GD liquid penetrates through the material. Similar composite materials show a 99% reduction in HD vapor breakthrough after 20 hours (from 4040 min to 16 min), a 23 fold increase from 524 min to > 100 min in the time 1000 ng of HD vapor penetrates through the material, and an elimination of erythema versus control in an HD vapor challenge. These results indicate that an RTSP that protects against sulfur mustard and nerve agents is within reach.

SESSION CC11: PROCESSING AND PROPERTIES OF HYBRIDS (OPTICAL, ELECTRICAL, MECHANICAL, CATALYSIS...)

Chair: Michael Poppl, Bruce S. Dunn and Christine Gao

Friday, April 30, 2000

Metropolitan III (Argent)

8:30 AM CC11.1
PREPARATION OF ORGANIC-INORGANIC NANO COMPOSITES (NANOMERS) FOR OPTICAL APPLICATIONS. M. Menning, P.W. Oliveira, P. Ragon, A. Ger, H. Schmidt, Institute for New Materials, Starbruecken, GERMANY.

Synthesis and processing routes for organic-inorganic nanocomposites (Nanomers) are described for optical applications like dielectric multilayers, and holographic patterns. Nanoparticles with high TiO2 and low SiO2 refractive index are prepared by sol-gel synthesis and condensation of appropriate alkoxides in alcoholic solutions. The particles with sizes between 4 and 10 nm (determined by high resolution transmission microscopy) are coated with photo-polymerizable liquids (methacrylate monomers and organosilanes). These nanocomposite solutions with solid contents of about 3 wt% can be used for the deposition of dielectric optical coatings on different substrates by dip- or spin-coating and subsequent UV curing. On plastics, refractive index between 1.91 and 1.47 can be obtained. On glass, stacks of up to 7 single layers can be densified in one step, leading to refractive index between 2.3 and 1.46. The application of this system for the preparation of highly durable antireflective systems for automotive windshields and NIR reflective filters on glass and plastic is demonstrated using the angle dependent dip coating technique. Furthermore, holographic patterns and digital optical images can be prepared by embossing of wet TiO2 layers using flexible stamps and subsequent UV-curing. The patterns can be chelated with an SiO2 layer for protection. On glass or stainless steel substrates, the sandwich can be fired at 450°C, leading to closed holographic patterns with diffraction efficiencies of about 10%. These patterns withstand 1000 cycles of taber shaver test and can be used for product protection.

9:00 AM CC11.2
PATTERNING OF PHOTOACTIVE THIN FILM SILICA MESOPHASES. Dhawal A. Doshi1, Nicola Huesgen2, Hongyu Fan1, Alan J. Hunt3, C. Jeffrey Brinker1,2

1University of New Mexico, Albuquerque, NM, 2Vienna University of Technology, Vienna, AUSTRIA, 3Sandia National Laboratories, Albuquerque, NM.

Cooperative self-assembly processes of inorganic species and amphiphilic molecules have experienced major advances over the past eight years. Various pathways have been explored to access a wide spectrum of mesoscopic materials with tunable pore sizes and arrangements and good compositional control. A variety of micro- and macrostructures have been synthesized such as powders, fibers, membranes, thin films, hollow arrays, transparent hard spheres and mesoporous particles. Thin films are one of the most promising applications of so-called mesosstructures, and the ability to build hierarchial structures and functionality is the key to their successful implementation in future micro-systems. Recently, so-called micro-contact printing (µCP) and micro-molding in capillaries (MMIC) techniques have been used to create patterned thin film silica mesophases. Here we report a lithographic procedure that enables selective etching of silica mesophases (thereby serving as a latent negative resist process) and allows patterning of thin film mesostructure, refractive index, and wetting behavior. The process involves incorporation of a photonic generator in the coating solution. Dip/Spin coating results in the formation of a photonic mesostructured thin film. Selective UV exposure through a mask results in localized photocged generation. We exploit the pH sensitivity of supra-molecular self-assembly by affecting the silica condensation kinetics and also the mesostructured lumination to optically pattern structure and functionality in the film. Films made with both ionic and nonionic surfactants are characterized using X-ray diffraction, transmission and scanning electron microscopy, optical
microscopy, ellipsometry, MAS-NMR and atomic force microscopy. Our ability to spatially control structure and function on several length scales has opened up new research avenues for sensing new nano-reactors, photonic and fluidic devices, and low dielectric constant films.

9:15 AM CC11.3
Abstract Withdrawn.

9:30 AM CC11.4
CROSS-LINKED ORGANIC INORGANIC HYBRID THIN FILMS FOR CORROSION RESISTANCE: SPECTROSCOPIC AND SALT SPRAY CHARACTERIZATION. Tammy Metreko, Edward Knobbe, Oklahoma State University, Environmental Institute and the Department of Chemistry, Stillwater, OK.

Spray coated, epoxide-modified thin films are being investigated as corrosion resistant coatings for 204-T3 aluminum. Solid state 1H, 13CP/MAS-NMR results indicate that primary aliphatic amines and secondary amines act as effective crosslinkers for epoxide groups in epoxians. Accelerated salt spray and film tests have been conducted in order to study the corrosion resistance behavior of cominol thin films before and after crosslinking. The choice of curing agent was found to influence the film structure and corrosion resistance properties. Amincured thin films were hard and highly adherent to the aluminum alloy substrates, exhibiting good bare and film corrosion resistance, in addition to good compatibility with organic polymer paint systems. The adhesion of super acid cured thin films to aluminum alloy substrates was significantly less, producing films which readily delaminated from the substrate, providing poor corrosion resistance.

9:45 AM CC11.5

Feasibility of preparation and photo-polymerization of high dielectric constant BiTiO3/ acrylic resin composites has been investigated. A series of the photo-patterable resin formulations were prepared and photo-polymerized into thin films. Up to 45 vol% 82 wt% of BiTiO3 loading into the resin has been achieved. It was found that up to 100 μm thick wafers of highly cross-linked BiTiO3/polymer composites can be prepared by the photo-polymerization technique within the entire range of BiTiO3 loadings. Dielectric permittivity of the materials was investigated at frequencies from 100 Hz to 10 GHz and temperatures from -140°C to 40°C. The dielectric constant of the photo-patterable composites based on an acrylic resin exceeds 30 at highest BiTiO3 loadings. An empirical relationship between the BiTiO3 content and dielectric constant of the composite has been established.

10:00 AM CC11.6
CONTROLLED SYNTHESIS OF PERFLUOROARYL FUNCTIONALIZED HYBRID MATERIALS FOR OPTICAL APPLICATIONS BASED ON NMR SPECTROSCOPY AND MOLECULAR MODELING. Frank Kuhlenberg, Ralf Bauestrich, Michael Popall, Fraunhofer-Institut fuer Silicatsforschung, Wuensberg, GERMANY.

The synthesis of ORMOCERs (inorganic-organic polymers) for optical applications is studied in detail. Producing waveguide materials with the desired low optical loss at wavelengths of 1550 and 1300 nm requires a thorough control of the initial inorganic network formation, because absorption losses are particularly due to Si-OH bonds besides aliphatic C-H bonds. Therefore, the synthesis of UV- or thermally curable organopolysiloxane resins with minimized Si-OH content is crucial. The investigation of the sol-gel reaction of organosilyl-silanes by 29Si-NMR spectroscopy provides a detailed insight into the influence of reaction conditions on the species and networks formed. Reaction parameters were optimized towards the formation of ORMOCER resins suitable for waveguide applications. Finally, the material synthesis is completed by crosslinking organically polymerizable units present in the ORMOCER resin to establish the inorganic-organic hybrid network. The experimental work is accompanied by computational chemistry. Calculating electronic properties is of value in predicting silane reactivities as well as spectroscopic data of intermediates. Molecular modeling is a convenient tool for the visualization of structural details on the molecular level.

10:45 AM CC11.7

Self-assembly of molecular monolayers offers an effective and simple tool to get very thin films on different substrates. New application fields are opened up, using these new nano-reactors, photonic and fluidic devices, and low dielectric constant films.

11:00 AM CC11.8
STIFFNESS IMPROVEMENTS AND MOLECULAR MOBILITY IN EPOXY-CLAY NANOCOMPOSITES. Xavier Kornmann, Lars Bergkland, Lulea Univ, Div of Polymer Engineering, Lulea, SWEDEN; Henrik Lindberg, Lulea Univ, Div of Wood Material Science, Skelleftea, SWEDEN.

Interlaminated and delaminated nanocomposites based on a glassy epoxy matrix and an organopholic clay were synthesized as well as a conventional composite filled with untreated clay. The nanocomposite structures were characterised by x-ray diffraction and transmission electron microscopy. Due to the organophilic treatment, the dispersion of the clay on a microscale was finer for the nanocomposites as compared with that for the conventional composite according to scanning electron microscopy. Flexural moduli of the different polymer-clay composites were measured in three point bending at different clay contents and compared with the modulus of the pristine matrix. Stiffness improvements were not only dependent on the dispersion of the clay on a microscale but also to the degree of delamination of the clay on a molecular scale. Dynamic mechanical analysis of the three materials indicated a decrease in intensity in the glass transition peak but also in peaks corresponding to secondary transitions with the extent of delamination of the clay and the clay content. This suggests a restricted mobility of the polymer molecules in the vicinity of the clay layers. A shift in Tg of 20°C towards lower temperature was observed for the epoxy-clay nanocomposites cured at 100°C. It was possibly caused by thermal degradation of compatibilizing agents at high temperature.

11:15 AM CC11.9
SYNTHESIS AND CHARACTERIZATION OF PMMA-SILICA AND PMMA-TITANIA HYBRID OPTICAL THIN FILMS. Wen-Chang Chen and Shao-Lee Lee, Department of Chemical Engineering, National Taiwan University, Taipei, TAIWAN.

A series of PMMA-silica and PMMA-titania hybrid thin films was prepared by the in-situ sol-gel process combined with spin-coating and multi-step baking. The investigated acrylic monomers were MMA and 3-(trimethoxysilyl) propyl methacrylate (MSMA). The alkoxide monomers for the preparation of the inorganic segment were TEOS, methyl trimethoxycyanil, phenyl trimethoxycyanil, and Titan(IV) n-bis. The prepared hybrid materials show excellent thermal stability and without phase separation. The AFM study suggests that the prepared hybrid thin films have excellent photoreactivity for the PMMA-silica hybrid thin films. The refractive indices of the prepared hybrid thin films at 1,900,000 nm can be controlled by the silex group on the Si atom as well as by content of the inorganic moiety. For the PMMA-titania hybrid thin films, the variation of the titania content cannot not only tune the refractive index but also the position of absorption maximum. The refractive indices of the PMMA-titania hybrid thin films were in the range of 1,530 to 1,533, which linearly increase with the titania content. The shift of the absorption maximum of the prepared hybrid thin films from 310 nm to 310 nm can be correlated with the titania content. The hybrid polymer films have the silex numbers all above 30. The prepared hybrid thin films show very high optical transparency in the visible region. This result suggests that the prepared hybrid films have potential applications for optical devices.
The preparation of porous materials from polyhedral oligomeric silsesquioxane (POSS) building blocks is being investigated as a possible route to a range of new microporous catalysts. Functionalised POSS with the general formula [RSO2/2]8 are being developed with a view to linking these almost cubic molecules through their functional groups in a controlled manner. Due to the geometry of corner linked cubes, materials formed via this process have porous structures and properties determined by the type of building block used. Currently, attempts are being made to prepare POSS bearing carboxylic acid or pyridine groups which will allow these molecules to be linked together using a variety of molecular engineering strategies. Once methods have been developed to assemble microporous materials, attempts will be made to derive catalysts from these materials by incorporation of metal species into the POSS structure. Porous co-polymers can be prepared through the hydrolysis of suitably functionalised POSS and the conversion of these materials into metal bearing catalysts is also being investigated. Developments in both the molecular engineering and co-polymer areas of our studies will be presented along with the proposals for the next stages of our work.

11:45 AM CC11.11
REACTION OF SILANE COUPLING AGENTS WITH TITANIA GELS. Thomas Harris, Rachel McConnell, Timothy Swerzagen, University of Tulsa, Dept. of Chemistry and Biochemistry, Tulsa, OK.

It is possible to produce inorganic aerogels without supercritical drying if the surface of the inorganic material is first modified to a nonpolar and unsaturated state. With this objective in mind, the modification of titania gel through reaction with silane coupling agents is being investigated. Titania gel is produced from titanium (IV) butoxide, water and ethanol, with nitric acid as a catalyst. The water and ethanol in the gel may be exchanged with toluene by distillation. A silane coupling agent is then used to derivatize the titania. Trimethyldichlorosilane, which can be used to derivatize silica, would not react with the titania. Alkynylalkoxysilanes, such as dimethylmethoxysilane, do react, in either toluene or the original ethanol/water solvent system. The effect of this derivatization on the surface area and porosity of the resultant materials will be presented.

12:00 PM CONCLUDING REMARKS