

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

Chairs: 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 POLYSILSESQUIOXANES. A MOLECULAR BASED APPROACH FOR 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 sol-gel polymerization of monomers that contain a variable organic component and at least two trifunctional silyl groups. The resulting xerogels and aerogels 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 sol-gel polymerization of monomers that incorporate functionality in the variable organic bridging group. The functional groups, which include carbonates, mercaptans, disulfides, and amines, can provide handles for modifying bulk morphology and/or provide function to the xerogels. The applications of these materials include ion exchangers, stationary phases for chromatography, protoresists and high capacity chemical absorbents.

9:00 AM *CC1.2

FUNCTIONAL ORGANOTIN ALKYNIDES AS PRECURSORS OF TIN-BASED HYBRID MATERIALS. Pascale Jaumier, Bernard Jousseau, Thierry Toupance, Univ Bordeaux I, Laboratoire de Chimie Organique et Organométallique, Talence, FRANCE; Mohamed Lahcini, Univ Cadi Ayyad, Dépt 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 trialkoxides are known and their preparations are more limited. Difficulties have been experienced in trying to introduce functional or polymerisable 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 alkoxy groups on the metal. That is why new functional organotin trialkynides have been prepared to solve this problem and thus allow an easy and general access to functional organotin trialkoxides and oxides. In this study, organotin trialkynides were obtained either by classical alkylation of the corresponding trichlorides, when they are available, or by a novel alkylation reaction of tetraalkynyltins with Grignard reagents(1), when the trichlorides are not stable. In contrast to the use of lithium reagents, this transmetallation reaction is very selective and leads to monoorganotin trialkynides in high yield. Then, organotin trialkynides were hydrolyzed to the corresponding oxides leading to the same clusters as organotin trialkoxides. They could also be alkoxylated with alcohols(2) giving the corresponding trialkoxides and transformed with organic acids into oxoorganotin carboxylates(3). Functional oxides and oxoorganotin carboxylates were co-polymerised in the presence of suitable monomers to give tin-based organic-inorganic hybrids.

(1) P. Jaumier, B. Jousseau, M. Lahcini, *Angew. Chem., Int. Ed. Engl.*, 1999, 32, 402.

(2) P. Jaumier, B. Jousseau, M. Lahcini, F. Ribot, C. Sanchez, *J. Chem. Soc., Chem. Commun.*, 1998, 369.

(3) P. Jaumier, B. Jousseau, *J. Main Group Met. Chem.*, 1998, 21, 325.

9:30 AM CC1.3

SOL-GEL CHEMISTRY OF TRIALKOXY-SILANES. Duane A. Schneider, Douglas A. Loy, Kamyar Rahimian, Catalysts and Chemical Technologies Department, Sandia National Laboratories, Albuquerque, NM.

Hydrolysis and condensation of trialkoxysilanes, $\text{HSi}(\text{OME})_3$ and $\text{HSi}(\text{OEt})_3$, has been used to prepare polyhydrosilsesquioxanes for dielectric applications. In this study we examined the ability of trimethoxysilane (1) and triethoxysilane (2) to undergo sol-gel polymerization to afford gels. Sol-gel 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 in the hundreds of square meters per gram. Solid state 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 polysilsesquioxanes with very little loss of

hydride functionalities. In gels prepared under basic conditions the hydride groups were completely gone leaving silica gels. Gels prepared with neutral water lost approximately two thirds of the hydride groups.

9:45 AM *CC1.4

ORGANOPHOSPHORUS-BASED ORGANIC/INORGANIC HYBRIDS. A. Vioux, P.H. Mutin, J. Le Bideau, D. Leclercq, Univ Montpellier 2, FRANCE.

The aim of this talk is to highlight the interest of organophosphorus precursors, especially phosphonate and phosphinate 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 organic-soluble 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 sol-gel 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 Tamaki, Yoshiki Chujo, Kyoto Univ, Dept of Polymer Chemistry, Kyoto, JAPAN.

This paper describes new methods for the preparation of organic-inorganic polymer hybrids. (1) In-situ polymerization method: The radical polymerization of N,N-dimethylacrylamide or styrene was carried out simultaneously together with the sol-gel reaction (hydrolysis and condensation of alkoxy-silanes) to produce homogeneous and transparent polymer hybrids. IPN (Interpenetrating polymer network) hybrids were prepared by this method using bifunctional vinyl monomers (methylenebisacrylamide or divinylbenzene). The IPN polymer hybrids obtained showed excellent solvent-resistant properties. (2) In-situ hydrolysis method: The sol-gel reaction of tetraethoxysilane 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 sol-gel reaction of tetraethoxysilane was carried out in the presence of poly(vinyl acetate). During the formation of silica matrix, the acid-catalyzed hydrolysis of poly(vinyl acetate) took place. As a result, the homogeneous polymer hybrids 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 sol-gel 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(diallyl phthalate) were also prepared starting from phenyltrimethoxysilane.

11:15 AM *CC1.6

HYBRID SILICA BASED MATERIALS AS NEW SOLID PHASE EXTRACTANTS. Jean-Charles Broudic, Olivier Conocar, Joël J-E Moreau, Daniel Meyer, Michel Wong Chi Man, Laboratoire de Chimie Organométallique, CNRS UMR 5076, Ecole Nationale Supérieure 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 silsesquioxane gels, which are prepared by sol-gel hydrolysis condensation of organic molecules containing two or more trialkoxysilyl substituents. These hybrids consist of a mixed three-dimensional network, where the organic fragment, cross-linking siloxane chains, is part of the framework. Owing to the presence of a strong Si-C 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 heterogenised 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 functionalised by SiOR_3 groups. New hybrid silica based materials containing malonamide ligands have been prepared by sol-gel hydrolysis of functionalised precursors and have been used as solid phase extractants for the complexation of actinides. This approach is quite different from the classical immobilisation procedure of complexing agents. The sol-gel 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. Raef Shaltout, Douglas Loy, Mark McClain, Sandia National Laboratories, Albuquerque, NM; Sheshasayana Prabhakar, University of New Mexico, Albuquerque, NM; John Greaves, Kenneth Shea, University of California, Irvine, CA.

Novel bridged polysilsesquioxanes, 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 modification of the material's architecture. The monomers used to prepare these materials were derived through the Diels-Alder reaction of (trans)-1,2-bis(triethoxysilyl)ethylenylene or (trans)-1,2-bis(trichlorosilyl)ethylenylene and cyclopentadiene or furan. The resulting monomers were polymerized through hydrolysis and condensation under standard sol-gel conditions and dried as xerogels. The dry gels were thermally treated to induce the retro Diels-Alder (Retro-DA) process. The retro-DA reaction of the cyclopentadienyl Diels-Alder adduct occurred at temperatures above 250°C. At this temperature the norbornenyl bridging group underwent some carbonization. Retro-DA of the oxonorbornenyl adducts, however, occurred at lower temperature allowing for conversion of the bridging group without degradation of the polymer. The materials were characterized before and after the retro-DA reaction by solid state ¹³C and ²⁹Si NMR, nitrogen sorption porosimetry and scanning electron microscopy.

SESSION CC2: WELL-DEFINED NANOBUILDING BLOCKS PRECURSORS FOR HYBRIDS

Chairs: Joseph D. Lichtenhan, Douglas A. Loy and Joel J.E. Moreau
Monday Afternoon, April 24, 2000
Metropolitan III (Argent)

1:30 PM ***CC2.1**

MAJOR ADVANCES IN THE SYNTHESIS OF POSS MONOMERS. Frank J. Feher, Raquel Terroba, Ren-Zhi Jin, Sabine Luecke, Frank Nguyen, Richard Brutchey, Kevin D. Wyndham, Department of Chemistry, University of California, Irvine, CA.

Polyhedral oligosilsesquioxanes (POSS) are an interesting class of three-dimensional Si/O clusters derived from the hydrolytic condensation of trifunctional organosilicon monomers (i.e., RSiX₃). Since their discovery in 1946, many stoichiometrically well-defined POSS frameworks have been reported, but it was only recently that POSS frameworks suitable for use as mono- or di-functional monomers have emerged. Over the past four years we have been exploring the fundamental reaction chemistry of fully condensed [RSiO_{3/2}]_n (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 THE ASSEMBLING OF ORGANOTIN OXO-CARBOXYLATES CLUSTERS. Francois O. Ribot, 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 BuSnO(4 NH₂C₆H₄CO₂)₆ has been prepared and characterized. As several other organotin oxo-carboxylate clusters, it has a hexagonal prismatic oxocore with the carboxylate groups on the six lateral square faces, which offer a ionic-covalent organic-inorganic interface. The assembling step was performed in two ways: directly, via the reaction of diisocyanates with the amino functions, or step wise via the functionalization with isocyanato-3-propyltriethoxysilane (ICPTES), which yields the new cluster BuSnO(O₂CC₆H₄NHCONH(CH₂)₃Si(OEt)₃)₆, followed by hydrolysis condensation (sol-gel route). Other BuSnO(O₂CR)₆ clusters were also studied to investigate different strategies of assembling. Solution and solid state

(MAS) ¹¹⁹Sn NMR has been used to probe the clusters integrity along the assembling procedures.

2:15 PM ***CC2.3**

INORGANIC-ORGANIC HYBRID POLYMERS FROM SURFACE-MODIFIED OXOMETALLATE CLUSTERS. Ulrich Schubert, Gregor Trimmel, Bogdan Moraru, Ivan Mijatovic, Guido Kickelbick, Institut für Anorganische Chemie, Technische Universität Wien, AUSTRIA; Peter Fratzl, Metal Physics Institute, University of Leoben, AUSTRIA.

Reaction of Ti(OR)₄ or Zr(OR)₄ with an excess of carboxylic acids results in the formation of crystalline carboxylate-substituted oxotitanium and oxozirconium clusters in which the surface of the clusters is covered by the organic groups. The water needed for slow hydrolysis is generated by esterification reactions. The cluster size and structure can be influenced by the reaction conditions. The methacrylate-substituted clusters Zr₆(OH)₄O₄(OMc)₁₂, Zr₄O₂(OMc)₁₂ and Ti₆O₄(OEt)₈(OMc)₈ (OMc = methacrylate) were copolymerized with methylmethacrylate or other olefins to give inorganic-organic hybrid polymers with the clusters as the inorganic component. They act as structurally well-defined nanoparticles with a diameter of about 1 nm, and reinforce and crosslink the organic polymers. SAXS measurements show that the cluster are retained in the polymer, but have a tendency towards micro-phase separation. The swelling behavior in organic solvents and the thermal decomposition of the polymers is distinctly changed by incorporation of the functionalized clusters.

2:45 PM **CC2.4**

TITANIUM ALKOXIDES MODIFIED BY PHOSPHONATES AND PHOSPHINATES: BUILDING-BLOCKS FOR THE SOL-GEL PROCESSING OF NOVEL ORGANIC-INORGANIC HYBRID MATERIALS? M. Mehring, G. Guerrero, P.H. Mutin, A. Vioux, Univ. Montpellier 2, FRANCE.

We are currently exploring the homogeneous incorporation of phosphonate and phosphinate 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 (phosphinic) acid, the second step corresponds to the hydrolysis / condensation of the remaining alkoxy groups. In this work, we report the isolation of several molecular intermediates in this process, namely [Ti₄(O⁺Pr)₂(^tBuPO₃)₄] (1), [Ti₄(μ₃-O)(O⁺Pr)₅((μ-OiPr)₃(PhPO₃)₃]DMSO (2), [Ti₄((μ₃-O)(OiPr)₅(m-OiPr)₃(MePO₃)₃]DMSO (3), and [Ti(O)(O⁺Pr)(O₂PPh₂)₄] (4) which were characterized by single crystal X-ray structure analysis. These compounds are structural models for the hybrid materials based on TiO₂ and phosphonate (phosphinate) groups, giving information on the bonding of the phosphonato (phosphinato) ligands and the titanium atoms. In all cases the non-hydrolytic P-OH / Ti-O⁺Pr condensation is complete, and the phosphoryl oxygen is coordinated to a titanium atom, leading to RP(OTi)₃ and R₂P(OTi)₂ structural units. In addition, these clusters are soluble in common organic solvents and contain hydrolyzable alkoxy groups, which makes them potential building blocks in the sol gel process. Accordingly, the hydrolysis-condensation of clusters 1 and 2 was studied using multinuclear solution NMR (¹H, ³¹P). Partial hydrolysis of the titanium phosphonate 1 in the presence of titanium isopropoxide led to the oxotitanium phosphonate [Ti₄(μ₃-O)(O⁺Pr)₅(μ-O⁺Pr)₃(^tBuPO₃)₃]PrOH with the same structure as 2 and 3. The use of 2 as a single source precursors in the 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 SUPRAMOLECULAR SPECIES TO MATERIALS. Achim Müller, Fakultät für Chemie, Universität Bielefeld, Bielefeld, GERMANY.

In Nature, complex molecular systems like proteins have evolved (natura naturans) which are perfectly suited to their functions. These are produced in a sequence of steps under dissipative conditions that is, far from equilibrium. The challenge for the chemist is to synthesize correspondingly complex multi-functional molecules also under non-equilibrium (dissipative) conditions using multi-component one-pot reactions without having to separate and purify each single intermediate product. Relevant model reactions have been discovered in solutions of simple *oxoanions of the transition metals*: Novel types of molecular growth processes with feedback (including a type of induced cascade) are described leading to different *ring-shaped*, *electron-rich*, *mixed-valence*, *giant polyoxomolybdates with nanosized cavities*. These can due to the generation of defects be covalently linked together to form *chains* as well as *layered mesoporous compounds* with properties relevant for materials science. They can also start growing again. The largest polyoxometalate

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 clusters forming new types of supramolecular compounds*. The lecture will be highlighted with a report on the planned synthesis and structure of different *nanosized spherical clusters with icosahedral symmetry* which have similar structures as spherical viruses and *which can be linked in different ways even to layers*. For the first time, discrete molecular species with structures related to some of the Archimedean solids will also be reported.

A. Müller, F. Peters, M.T. Pope, D. Gatteschi, "Polyoxometalates: Very Large Clusters - Nanoscale Magnets", Chem. Rev. **98**, 239 (1998).

A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtman, F. Peters, "Organizational Forms of Matter: An Inorganic Super Fullerene and Keplerate Based on Molybdenum Oxide", Angew. Chem. Int. Ed. Engl. **37**, 3360 (1998).

A. Müller, Syed Q.N. Shah, H. Bögge, M. Schmidtman, "Molecular growth from a Mo_{176} to a Mo_{248} cluster", Nature **397**, **48** (1999).

4:00 PM **CC2.6**

HYBRID INORGANIC/ORGANIC DIBLOCK COPOLYMERS: NANOSTRUCTURE IN POLYHEDRAL OLIGOMERIC SILSESQUOXANE POLYNORBORNENES. Timothy S. Haddad, ERC, Air Force Research Lab, Edwards AFB, CA; Patrick T. Mather, Seung B. Chun, Institute of Materials Science, University of Connecticut, CT; Hong G. Jeon, Sysran Corp., Air Force Research Lab, Wright Patterson AFB, OH; Shawn Phillips, Air Force Research Lab, Edwards Air Force Base, CA.

Our main approach to the synthesis and study of hybrid organic/inorganic materials involves incorporating nano-size inorganic polyhedral oligomeric silsesquioxane (POSS) clusters into various polymeric resins. A typical POSS cluster is a discrete silicon and oxygen framework solubilized with organic groups and contains a single reactive site. This lone site of reactivity is used to covalently attach the inorganic macromers pendent to a polymer backbone without causing any crosslinking. This strategy permits the synthesis of melt processable, linear hybrid polymers containing pendent inorganic clusters, and allows us to study the effect these clusters have on chain motion, polymer properties and morphology. The synthesis of norbornenyl-based (POSS) macromers, their ring opening metathesis copolymerizations with varying amounts of norbornene, and analysis of the effect of the pendent POSS group is presented. Ring opening metathesis polymerization permits the easy synthesis of both random and diblock 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 diblock copolymers, as well as between polymers that differ only in the solubilizing cycloalkyl groups on the POSS cluster.

4:15 PM **CC2.7**

ORGANIC-INORGANIC HYBRID PARTICLES BY DENDRIMER NANOTEMPLATING. Franziska Groehn, 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 route for a variety of composites. Our motivation comes from a desire to understand the mechanisms of polymer nanotemplating 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(amidoamine) (PAMAM) dendrimers in aqueous solution via opposite charge or complexation to their amine end groups. Chemical reactions can be performed on 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 nanocomposites. 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 nanoscale synthesis (G6 to G10). For these higher generation dendrimers, inorganic colloids are formed inside single dendrimer molecules and the size of the nanocrystal 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 ***CC2.8**

CUBEOCTAMERIC SILICATE-DIMETHYLSILOXANE HYBRIDS. Isao Hasegawa, Gifu Univ, Fac of Engineering, Dept of Chemistry, Gifu, JAPAN.

We have so far studied organic-inorganic hybrids with such network that the dimethylsilyl group links the cubeoctameric silicate ($Si_8O_{20}^{8-}$) building block. The hybrids were synthesized by the reaction of $Si_8O_{20}^{8-}$ formed selectively in a methanolic solution of tetramethylammonium silicate and dimethyldichlorosilane. The content of the dimethylsilyl group in the hybrids could be increased with increasing amount of dimethyldichlorosilane. With 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 dimethylsilyl group content. In this study, we have attempted another reaction to produce the hybrids in which a larger amount of the dimethylsilyl unit is introduced. The reaction has been carried out under alkaline conditions using (2-hydroxyethyl)trimethylammonium silicate as a source of $Si_8O_{20}^{8-}$ and dimethoxydimethylsilane. The content of carbon present as the methyl group in the hybrids has been increased to ca. 30 wt% by the reaction. This talk focuses on the reaction and the dimethylsilyl group-rich hybrids.

SESSION CC3: CHEMICAL ROUTES TO NANO/MESOSTRUCTURED HYBRID MATERIALS

Chairs: Bradley F. Chmelka and Francois O. Ribot
Tuesday Morning, April 25, 2000
Metropolitan III (Argent)

8:30 AM ***CC3.1**

THE INFLUENCE OF NEW BLOCK COPOLYMERS IN THE FORMATION OF MESOSTRUCTURED MATERIALS. Guido Kickelbick, Nicola Hüsing, Josef Bauer, Dietmar Sturmayer and Beatrice Launay, Institut für Anorganische Chemie, Technische Universität Wien, AUSTRIA.

Hybrid materials, especially organic-ceramic nanocomposites and their porous analogues, have recently attracted much interest because they offer promise for novel properties and therefore new applications. The template-based approach towards these materials allows for a deliberate design of the network and pore structure. However, so far it was mainly limited to commercially available organic templates such as amphiphilic 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 pore sizes, shapes and phases. Controlled polymerization techniques were used to keep the polydispersities 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 **CC3.2**

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

Octasilsesquioxanes [$RSiO_{1.58}$, cubes] offer potential as rigid nanoplatforms to which various functional groups (R=epoxy, methacryloyl, etc) can be attached. Octafunctional macromonomers can be synthesized and 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 macroscopic properties. We describe here the synthesis, processing and properties characterization of cube nanocomposites. Selected nanocomposites exhibit nanoporosity; good-to-excellent mechanical, CTE and thin film properties, and much improved thermal stability (vs wholly organic composites).

9:15 AM **CC3.3**

EVAPORATION-INDUCED SELF-ASSEMBLY OF HYBRID BRIDGED SILSESQUOXANE FILM AND PARTICULATE MESOPHASES WITH INTEGRAL ORGANIC FUNCTIONALITY. Yunfeng Lu, University of New Mexico and Sandia National

Laboratories, Albuquerque, NM; Nilesh Doke, Hongyou Fan, University of New Mexico, Albuquerque, NM; Douglas A. Loy, Roger A. Assink, Sandia National Laboratories; C. Jeffrey Brinker, University of New Mexico and Sandia National Laboratories, Albuquerque, NM.

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. Here, we report the formation of a new class of bridged polysilsesquioxane mesostructured thin films and particles with integral organic functionality by spin-coating, dip-coating, or aerosol processing. Our synthesis procedure begins with a homogeneous solution of ethanol, water, HCl, bridged silsesquioxanes precursors $(RO)_3Si-R'-Si(OR)_3$ [where $R' = -(CH_2)_2-$, phenyl, $-CH_2-CH=CH-CH_2-$] and surfactant, in which the initial surfactant concentration is far below the critical micelle concentration. Preferential ethanol evaporation accompanying the film or particle formation processes concentrates the sol in water, surfactant and polysilsesquioxane species, driving self-assembly of polysilsesquioxane-surfactant micelles and their further organization into liquid crystalline mesophases. This new mesostructural organization allows molecular engineering of mechanical properties, hydrophobicity, 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 NANOPARTICLE/DENDRIMER COMPOSITES SOLUBLE IN ENVIRONMENTALLY 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 aimed 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, polypropylenimine (DAB-64) dendrimers were rendered soluble in fluorosolvents and used as nanotemplates for the in situ formation of inorganic nanoparticles. The DAB-64 dendrimers have perfluorinated 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, there 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 fluorosolvents 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

HYBRID SILICA/POLYMER NANOPARTICLES THROUGH EMULSION AND DISPERSION POLYMERIZATION.

Elodie Bourgeat-Lami, Jose-Luiz Xavier Luna, Alain Guyot, Laboratoire de Chimie et Procédés de Polymérisation, 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, consists in polymer encapsulation of inorganic materials by radical polymerization in dispersed media. Following this line, encapsulation of small silica particles has been successfully achieved by either dispersion or emulsion polymerization. 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 3-trimethoxysilylpropylmethacrylate which did copolymerize with the monomer. In a second approach, we use the 2,2'-Azobis 2-amidinopropanedihydrochloride cationic initiator to promote the interactions between the positively charged latexes and the negatively charged surface of the inorganic particles. We demonstrate using microscopic techniques, that the silica beads are successfully encapsulated by the two techniques giving silica/polymer nanoparticles which morphology highly depends on the encapsulation process and on the experimental conditions, namely the size and concentration of the silica beads, the nature and concentration of the stabilizer as well as that of the monomer.

10:30 AM *CC3.6

DENDRITIC AND MULTIPODAL LIQUID-CRYSTALLINE MATERIALS BASED ON SILSESQUIOXANE AND SILAZANE CORES. G.H. Mehl, R. Elsaesser, 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 organic-inorganic hybrid materials, whether they are oligomeric, multipodal, polymeric or dendritic in structure. Of particular interest are liquid-crystalline systems, as the control of the soft self-assembly behaviour of these systems allows for the addressing of the macroscopic properties of these materials. This presentation will focus on investigations of silsesquioxane and silazane cores 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 flexibility 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 NANOPOROUS MATERIALS WITH SPATIALLY ORGANIZED MOLECULAR MONOLAYERS AND COATINGS. Yongsoo Shin, Jun Liu, Glen E. Fryxell, Li-Qiong Wang, William D. Samuels and Gregory J. Exarhos, Pacific Northwest National Laboratory, Richland, WA.

Hybrid nanoporous 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 nanoporous structures. 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 nanoporosity 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 Melosh, Brad Chmelka, University of Santa Barbara, Dept of Chemical Engineering, Santa Barbara, CA; Patrick Davidson, Université Paris-Sud, Labatoire 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 domain sizes 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 mesoscopically ordered silica/block copolymer composite monoliths reveal single-crystal-like patterns that correspond to well-ordered hexagonal domains that are greater than 1 cm × 1 mm × 1 mm in size. XRD and TEM results also show that the composite monoliths have large well-ordered cubic mesophase domains in the meniscus regions of the samples. Boundaries between the hexagonal and cubic domains in the monoliths reflect gradual transitions between the two epitaxially related structures. Such large single-domain hexagonal 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 (PMO'S) WITH FUNCTIONAL ORGANIC GROUPS INSIDE THE CHANNEL WALLS. Tewodros Asefa, Neil Coombs, University of Toronto, Department of Chemistry, Toronto, Ontario, CANADA; Omer Dag, Bilkent University, Department of Chemistry, Ankara, TURKEY; Chiaki Yoshina-Ishii, Mark MacLachlan, Geoffrey Ozin, University of Toronto, Department of Chemistry, Toronto, Ontario, CANADA.

Inorganic-organic hybrid materials often display properties unique compared to the individual constituents. Surfactant-templated mesoporous silica represents an important new class of hybrid 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 nanoelectronics. 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 organic groups since their conception, there are few reports of periodic mesoporous hybrid materials containing a terminally 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 powder and oriented film, with bridge bonded methylene, ethane, ethene, benzene, thiophene and ferrocene groups integrated inside the silica framework. Surfactant 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 Kickelbick

Tuesday Afternoon, April 25, 2000

Metropolitan III (Argent)

1:30 PM *CC4.1

TAILORING OF ORGANICALLY-MODIFIED SILICA MCM-41

TYPE MATERIALS WITH OPTICALLY ACTIVE MOLECULE.

Bénédicte Lebeau, Laboratoire de Matériaux Minéraux, CNRS, Mulhouse, FRANCE; Christabel E. Fowler, Stephen Mann, School of Chemistry, University of Bristol, Bristol, UNITED KINGDOM.

One-pot synthesis, involving the co-condensation of tetraethoxysilane (TEOS) and 3-(2,4-dinitrophenylamino)-propyltriethoxysilane (DNPTES) in the presence of the surfactant hexadecyltrimethylammonium bromide (C_{16} TMABr) was used to covalently attach an organic chromophore into silica materials with MCM-41 architecture. Under alkaline conditions, hexagonally well-ordered mesoporous dye-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 mesostructured 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-trimethylbenzene (TMB) to the reaction mixture or by replacing C_{16} TMABr surfactant by an amphiphilic triblock copolymer (poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide): PEO-PPO-PEO). This synthetic route based on an evaporation-induced self assembly process was also used to produce multiscale mesostructured dye-modified silica materials by using both latex spheres and C_{16} TMAB micelles as organic structure-directing agents. Small angle X-ray diffraction patterns transmission electron microscopy (TEM) indicated hexagonal mesoscopic order in all materials and a significant increase in the pore size associated with swelling of the C_{16} TMAB surfactant micelles or templating with PEO-PPO-PEO block copolymer. The presence of the dye was confirmed by Fourier transform infrared (FTIR) spectroscopy. In addition, ^{13}C CP MAS NMR experiments confirmed that the dinitrophenylaminopropyl chromophore was covalently linked into the mesostructured 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 mesostructures.

2:00 PM CC4.2

STRUCTURAL EVOLUTION OF SILSESQUIOXANE-BASED ORGANIC/INORGANIC NANOCOMPOSITE NETWORKS.

Christopher L. Soles, Eric K. Lin, Wen-li Wu, National Institute of Standards and Technology, Gaithersburg, MD; Chunxin Zhang, Richard M. Laine, 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 - $(RSiO_{1.5})_8$). In some respects, these cubes represent the smallest unit of ceramic silica. The corners of the nanometer-sized 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 cube-based epoxy resins. 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 linkages. This effect 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 POLYMER/CLAY

NANOCOMPOSITES. Valeriy V. Ginzburg, Dept of Chemical and Petroleum Engineering; Chandralekha Singh, Dept of Physics and Astronomy; Anna C. Balazs, Dept of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA.

We combine a density functional theory (DFT) with a self-consistent field model (SCF) to calculate the phase behavior of oblate clay particles coated with surfactants and dispersed in a polymer melt. We investigate the effect of the surfactants' characteristics (grafting density ρ_{gr} and length N_{gr} and the polymer-surfactant interaction energy on the polymer-clay phase diagram. Depending on the values of these critical parameters and the clay volume fraction, ϕ , the system can exhibit an isotropic or nematic phase (which corresponds to an exfoliated composite). The system can also form a smectic, crystal, columnar, plastic solid (house-of-cards) phase, as well as a two-phase (immiscible) mixture. We find that increasing the product $\rho_{gr}N_{gr}$ leads to the stabilization of the homogeneous, exfoliated phases (the isotropic and nematic regions) and to the narrowing of the immiscible two-phase regions, in agreement with earlier qualitative arguments.

2:30 PM CC4.4

POLYPROPYLENE CLAY NANOCOMPOSITES. B.D. Keener,

S.D. Hudson, Y. Li, I. Moran, 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 aminosilane coupling agent. The amine functionalized particles are then reacted with maleated PP through amidization 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. Mechanical properties showed a two-fold increase in tensile modulus and a modest increase in yield strength at 25% clay content while retaining some ductility. At 10% filler level, the modulus increase was 40% and the ultimate elongation was in excess of 300%. For control samples missing either the coupling agent or the chain grafts, these properties suffered significantly. Environmental stress cracking (ESC) resistance tests were performed on rectangular double notched specimens at constant load, while immersed in a 20% 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 POLYETHYLENEOXIDE-B-POLYSTYRENE AS A

MODIFIER IN MONTMORILLONITE. Rick Beyer, Nora Beck Tan, U.S. Army Research Laboratory, Aberdeen, MD; Arnab Dasgupta, Mary Galvin, University of Delaware, Newark, DE.

Polyethyleneoxide-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. Intercalation 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 of the silicate. The effects of 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 RELATIONSHIP OF HYBRID (INORGANIC/ORGANIC) POSS THERMOPLASTICS. Shawn H. Phillips, Rusty L. Blanski, Air Force Research Laboratory, Edwards AFB, CA; Timothy S. Haddad, ERC Inc., Edwards AFB, CA; Andre Lee, Michigan State University, Dept. of Mat. Sci. & Mechanics, Lansing, MI; Joseph D. Lichtenhan, Hybrid Plastics, Fountain Valley, CA; Frank J. Feher, UCI, Chem Dept, Irvine, CA; Patrick Mather, Univ of Connecticut, Inst. Mat. Sci. & Chem. Eng., Storrs, CT; Benjamin H. Hsiao, State U. of NY at Stony Brook, Stony Brook, NY.

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/alteration 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 Si-O frameworks (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 (Si-O core) and size (~15 Å in diameter) of the POSS frameworks, and can be copolymerized, grafted, or even blended using traditional processing methods. Recently, we have focused our efforts on understanding and controlling the molecular level interactions between POSS frameworks and 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 T_g 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. Chunxin Zhang, Lajos Balogh, Donald A. Tomalia, Center for Biologic Nanotechnology, University of Michigan, Ann Arbor, MI; Richard M. Laine, Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI; Gary L. Hagnauer, AMSRL-WM-MA, US Army Research Laboratory, APG, MD.

Nanocomposites can have improved macroscopic properties, such as strength, toughness and hardness, as a result of the enormous interfaces formed between their nanoscopic (1-100 nm) building blocks. Dendrimers and hyperbranched polymers are novel nanoscale entities that have received considerable attention because of their potential utility in catalysis, biomedical applications, electronics and materials science. It has been demonstrated that hyperbranched 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 5 were reacted with commercial polyamide curing agents (Ancamides, Air Products), and used to cure epoxy resins. Key mechanical properties, such as tensile strength, fracture toughness and impact resistance of the resultant nanocomposites will be reported. Simultaneously, PAMAM/Ancamide combinations were also used to cure epoxy functionalized octasilsesquioxanes 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. L.F. Batenburg, R.A. van Dam, H.R. Fischer, L.H. Gielgens, M.P. Hogerheide, H.A. Meinema, C.H.A. Rentrop, TNO-TPD, Eindhoven, THE NETHERLANDS.

Multifunctional nanocomposite coatings and bulk materials have been developed on the basis of a combination of purely organic, as well as hybrid organic-inorganic polymeric systems and anisotropic synthetic and natural clays. These clays have been chemically modified in such a way that they became compatible to the different systems. Clay platelets may be separated by modification with an organic molecule that contains two or more charged functional groups. One functional group is exchanged with the cations or anions located between the clay sheets, which results in clay platelets coated with charges causing a molecular dispersion of themselves. Depending on the nature of the organic molecule coloured or colourless coatings and polymeric bulk

materials, containing homogeneously 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, aluminium and plastics. The bulk materials can be processed into final product shape by conventional polymer processing techniques.

SESSION CC5: MESO- OR NANOSTRUCTURED POROUS MATERIALS

Chairs: Yoshiki Chujo, Andrea Vioux and Frank J. Feher
Tuesday Afternoon, April 25, 2000
Metropolitan III (Argent)

4:15 PM *CC5.1

MOLECULAR ENGINEERING OF POROSITY WITH BRIDGED POLYSILSESQUIOXANES. Douglas A. Loy, Catalysts and Chemical Technologies Department, Sandia National Laboratories, Albuquerque, NM; Kenneth J. Shea, Department of Chemistry, University of California, Irvine, CA.

Bridged polysilsesquioxanes 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 obtained as 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 scaffolding 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 polysilsesquioxanes. Details of the preparation, characterization, and some structure property relationships of these bridged polysilsesquioxanes will be given.

4:45 PM CC5.2

PREPARATION OF MESOPOROUS ZrO₂-Ni ANODES FOR SOLID OXIDE FUEL CELLS. Fanglin Chen, Meilin 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 anodes 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 nano-particles 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 organics (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-Ni anodes, which are obtained by in-situ 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 OXOTITANIUM AND ZIRCONIUM CLUSTERS FROM THE ALKOXIDES AND THEIR INCORPORATION IN ORGANIC POLYMERS. Bogdan Moraru, Gregor Trimmel, Silvia Gross, Ulrich Schubert, Inst fuer Anorganische Chemie, Tech Univ Wien, AUSTRIA.

Well defined oxometallate 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 these clusters with methylmethacrylate, methacrylic acid or styrene leads to the formation of inorganic-organic hybrid polymers. This process also offers the possibility to prepare optically transparent films. White powders were obtained when $Ti_6O_4(OEt)_8$ (OMc)₈ or $Zr_6O_4(OH)_4(OMc)_{12}$ (OMc= methacrylate) were polymerized with methacrylic acid, while glassy, transparent polymers were synthesized from methylmethacrylate. The choice of the solvent also plays an important role regarding the structure of the polymer. 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 linearly with the portion of the oxometallate clusters. The BET surface of the polymers prepared from methacrylic acid increases with the portion of the inorganic component. In case of the titanium cluster, the ethoxy groups are still present after drying of the polymers.

CC6.2

HYBRID NANOSTRUCTURED MATERIALS OBTAINED FROM TITANIUM-OXO NANOBUILDING BLOCKS. Clément Sanchez, G.J. de A.A. Soler-Illia, L. Rozès, Chimie de la Matière Condensée, Univ. Pierre et Marie Curie, Paris, FRANCE; A.-M. Caminade, C.O. Turrin, J.-P. Majoral, Laboratoire de Chimie de Coordination, CNRS, Toulouse, FRANCE.

Considerable effort is being currently directed to the obtention of nanostructured oxides. Developed as an extension of the structure directing concepts originated by zeolite chemistry, this synthesis approach relies in the appropriate use of ordered lyotropic phases as templating agents. The obtention of these new oxidic 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 arrangements. 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 mesoscopic 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) nanobuilding blocks to create mesoscopically ordered phases, as films or powders. Clusters of $Ti_{16}O_{32}(OEt)_{32}$ and anatase nanoparticles are placed in a lyotropic medium (formed by arrangements of micelles, such as block copolymers) or attached to ordering agents, such as dendrimeric molecules. The obtention of a given nanophase (identified by XRD and TEM) depends on the specific interactions between the surfactant and the preformed bricks. The complexation 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.

CC6.3

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

Zirconia attracts more and more attention as a promising component for heterogeneous catalysts due to its 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 areas were obtained when ethanolic solutions of nonionic polymers (triblock or diblock copolymers, polyethyleneglycol) were added. The as-synthesized hybrid inorganic-organic materials were dried supercritically, hydrothermally or under ambient conditions to obtain zirconia with low alumina contents (1-10%). Calcination of the samples leads to high surface area materials (about 200 m²/g) with a low extent of crystallinity. The solids were found active for the reduction of NO by propane.

CC6.4

HYBRID COMPOSITE MATERIALS CONTAINING MAGNETIC

IRON OXIDE NANOPARTICLES. C. Chanéac, E. Tronc, J.P. Jolivet, Chimie de la Matière Condensée, University Pierre et Marie Curie, Paris, FRANCE.

The control of the iron oxide particle-solution 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 γ -Fe₂O₃ nanoparticles were prepared by co-precipitation of ferric and ferrous ions in aqueous alkaline medium and further oxidation in acidic medium. A sol of non-aggregated particles was obtained by dispersion in acidic water (pH=2).

The polymerization of silicic precursors (triethoxysilane or silicic acid) in the aqueous sol leads to the gelation of the dispersion-forming xerogels. 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 silanol 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 organosols 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, NIR, and Mössbauer spectroscopies.

CC6.5

STRUCTURAL, THERMAL, AND THERMOMECHANICAL BEHAVIORS OF PHENOLIC-INORGANIC HYBRID COMPOSITES. Samuel Amanuel, Vivak M. Malhotra, 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., Al₂O₃, SiO₂, 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, suggest that the silica-phenolic 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.

CC6.6

GRAFTING OF ALUMINA BY PHOSPHONATE AND PHOSPHINATE COUPLING AGENTS. G. Guerrero, G. Chaplais, P.H. Mutin, J. Le Bideau, D. Leclercq, A. Vioux, Univ Montpellier 2, Montpellier, FRANCE.

As metal-carbon bonds are generally not hydrolytically stable, anchoring of an organic group to a metal oxide support requires the use of coupling agents. Usual coupling agents are organosilanes (M-O-Si-C linkage), carboxylates and β -diketonates (M-O-C linkage). However the modification of metal oxide surfaces with phosphonic acids RPO(OH)₂ (M-O-P-C linkage) is currently attracting growing interest. The present study deals with the grafting of alumina either with phosphonate or phosphinate groups, under various conditions. Phenylphosphonic and diphenylphosphinic acids were compared with their parent ethyl and (trimethyl)silyl esters as coupling agents. The balance between surface complexation (namely grafting) and surface phase transformation (namely deposition of aluminum phosphonate or phosphinate phases) was investigated by means of ³¹P solid-state MAS NMR and powder XRD, using model crystalline phases synthesized in a parallel work.

CC6.7

Abstract Withdrawn.

CC6.8

SYNTHESIS OF POTASSIUM NIOBATE/ORGANIC HYBRID FROM METAL-ORGANIC. Toshinobu Yogo, Kouichi Banno, Wataru Sakamoto, Shin-ichi 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 ethoxide, niobium ethoxide and methacrylate derivative. 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 nano-crystalline particles in the organic matrix were analyzed by SAD and EDX. The particle size was found to depend upon the polymerization and hydrolysis conditions. The hybrid was shaped into films by heating under pressure. The dielectric properties of the hybrid film were evaluated. The electro-rheological properties of the hybrid were also investigated.

CC6.9

IN VITRO-, IN VIVO-STUDIES OF 5 π -AMP-HYDROXYAPATITE COMPOSITE. Shunro Yamaguchi, Osaka Univ, The Institute of Scientific and Industrial Research; Takuya Matsumoto, Hiroyuki Nakao, Masayuki Taira, Junzo Takahashi, Osaka Univ, Faculty of Dentistry; Masayuki Okazaki, Hiroshima Univ; Kiyoko Sakamoto, Osaka Sangyo Univ; Masato Tamai, Atsushi Nakahira, Kyoto Institute of Technology, JAPAN.

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

CC6.10

HOLLOW MICROSPHERES OF POROUS SILICA PREPARED STARTING FROM A HYBRID CONTAINING CHITOSAN. Pedro J. Retuert, Raul Quijada, Catalina Lafourcade, Univ de Chile, Fac of Physical and Math Sci, Dept of Chemistry and Chemical Engineering, Santiago, CHILE.

The combination of siloxane sols, prepared by the sol-gel method under conditions of lineal 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 SEM micrographs shows that the resulting silica was obtained as hollow spheres with size in the range between 10 and 100 micrometers. By using 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 form but without the extraction step previous to calcination, will be also presented.

Acknowledgments: Projects Fondef 1025 and Fondecyt 197-0730.

CC6.11

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

Inorganic/organic hybrids prepared from tetraethoxysilane (TEOS) and polydimethylsiloxane (PDMS) have unique mechanical properties such as flexible and rubbery properties. However, they have only an inorganic component of the siloxane network derived from TEOS. We have successfully incorporated various inorganic components into PDMS-based hybrids using chemically 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 and Ta 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 XPS, EXAFS and TEM. The XPS study revealed the inorganic species were slightly different from the simple oxide. The Fourier transforms of EXAFS spectra shows 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 ISTF program promoted by AIST, MITI, Japan.

CC6.12

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

Two high refractive index organic/inorganic hybrid materials have been prepared via sol-gel process 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 1.694 (at 632.8nm). The Bi₂O₃ containing material has a higher refractive index than the TiO₂ containing material due to the higher density of Bi₂O₃. The result is in agreement with the Lorentz-Lorenz Law: high density materials exhibit high refractive index. Two polymerizable metal alkoxides: titanium methacryl ethoxide and titanium bismuth methacryl 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 phase dispersed in acrylate monomer, then the monomer mixture was subsequently polymerized either by heat or UV radiation. A transparent monolith (3-5 mm 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 were well dispersed in the polymer matrix. The hybrid materials have shown improved optical dispersion and thermal stability over neat 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.

CC6.13

DIELECTRIC SPECTRA OF BATIO₃-POLYMER COMPOSITES. C.K. Chiang, R. Popielarz, R. Nozaki and J. Obrzut, 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 revisit of dielectric properties of the polymers and inorganic materials with high dielectric constant. We report the dielectric spectra of BATIO₃-polymer composites. The wide-range dielectric spectrum covering the frequency from 10⁻³ to 10⁹ 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.

CC6.14

UV CURABLE ORGANIC-INORGANIC HYBRID MATERIALS. Guang-Way Jang, Ren-Jye Wu, Yuung-Ching Sheen, Ya-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 abrasion resistant coatings, photo-patternable thin films and

waveguides. Colloidal silica containing reactive functional groups were also prepared by reacting organic silane and tetraethyl orthosilicate (TEOS) using sol-gel process. In addition, the efficiency of grafting organic moiety 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 TEM study was performed to investigate the morphology of organic modified colloidal silica.

CC6.15

NANOPARTICLES IN POROUS METAL OXIDE NETWORKS VIA A POLYMER GEL COATING TECHNIQUE. Jan H. Schattka, 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 photovoltaics. 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.¹ In this study the technique of polymer gel coating, which has been used to produce porous metal oxides,² 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/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 (SEM and TEM) 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 phase of the metal oxide was gained from WAXS measurements.

1. P.V. Kamat, Chem. Rev. 1993, 93, 267-300.
2. R.A. Caruso, M. Giersig, F. Willig, M. Antonietti, Langmuir, 1998, 14(22), 6333-6336.

CC6.16

THE EFFECT OF SYNTHESIS CONDITIONS ON PYRIDINE TEMPLATED OPEN FRAMEWORK GALLOPHOSPHATES.

David S. Wragg, Ivor 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 solvothermal 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 product and its crystallinity. In this study a simple gallium phosphate (GaPO) system in which pyridine acts as both solvent and template has been found to lead to a variety of different phases depending on the conditions of synthesis. The pyridine-GaPO 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. Synchrotron 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 solvothermal synthesis and the interactions between template, framework and solvent.

CC6.17

STRUCTURAL CHARACTERIZATION OF SURFACTANT-TEMPLATED MESOPOROUS SILICA THIN FILMS PREPARED BY SOL-GEL DIP-COATING. David Grosso, Florence Babonneau, Chimie de la Matière Condensée, UMPC/CNRS, Paris, FRANCE; Pierre-Antoine Albouy, Lab de Physique des Solides, Univ Paris-Sud, Orsay, FRANCE; A.R. Balkenende, Philips Research Labs, Eindhoven, NETHERLANDS.

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 organic templates. 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 (PEO-PPO-PEO). They have been removed by different techniques, either calcination or Soxhlet 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 by 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-vapor interface. Refractive index, thickness and porosity were deduced from ellipsometry measurements for a large variety of synthetic parameters.

CC6.18

FUNCTIONALIZED INORGANIC/ORGANIC HYBRID BLOCK COPOLYMERS. Josef Bauer, Guido Kickelbick, Nicola Hüsing, Institut für Anorganische Chemie, Technische Universität 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 from 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 polymerization of cyclosiloxanes (hexamethylcyclotrisiloxane D3 and 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane D4Vi) 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 side groups (diamines, dicarboxylic acids). 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 doubtless 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.

CC6.19

ON THE PROPERTIES OF AN IONIC CONDUCTOR SYSTEM INCORPORATED INTO HYBRID FILMS. Guillermo Gonzalez, Pedro J. Retuert, Sandra Fuentes.

By blending the biopolymer chitosan (CHI) with a sol containing poly(aminopropyl siloxane) oligomers (pAPS), transparent and flexible hybrid films can be obtained. A self-assembled layered morphology has been determined for some organic/inorganic molar relations. On the other hand, composites of polyethylene oxide (POE) with alkaline salts are well known ion conductors systems, where the crystallinity tends to diminish the conductivity. 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 macromolecular 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 Σ 10⁶, both from Aldrich, were used. The ionic conductivity of selected samples was evaluated by complex impedance spectroscopy. A ionic conductivity of 1,7 Σ 10⁻⁵ Ohm-1cm-1 is a typical result obtained by measurement of a film with the molar composition POE:CHI:pAPS:Li+ = 1:0.5:0.6:0.2. 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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CC6.20

CURING BEHAVIOR, THERMAL AND SURFACE PROPERTIES OF SOME EPOXY-CONTAINING LADDER-LIKE POLYSILSESQUIOXANES. Yuhui 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 electronics applications, several types of epoxy-containing ladder-like polysilsesquioxanes have been synthesized. They are polyepoxy-phenylsilsesquioxane (PEPS), polyepoxy-alkylsilsesquioxane (PEAS), and polyepoxy-alkyl-phenylsilsesquioxane (PEAPS). Curing behaviour of these ladder-like polyepoxy-

silsesquioxanes 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, polyepoxysilsesquioxanes 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.

CC6.21
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. Badun, Moscow State University, Radiochemistry 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 anions in aqueous solution. LDHs have a general formula $M^{I}_{1-x}M^{II}_x(OH)_2[(anion)^{n-}]_x/n \cdot mH_2O$, where M^I and M^{II} are metals in the oxidation state +2 and +3, respectively, and anionⁿ⁻ is virtually any inorganic or organic anion (including biologically active anions), which does not form a stable complex with M^I or M^{II} . The structure of an LDH consists of positively charged hydroxide layers $[M^{I}_{1-x}M^{II}_x(OH)_2]^{n+}$ bonded with negatively charged anions, which occupy the interlayer space. In the present paper, 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, acetylsalicylic acid, ascorbic acid, etc. were intercalated into LDH interlayer space by reconstruction 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 are obtained and analyzed. The effect of the size and structure of organic and inorganic anions on their mobility is discussed.

CC6.22
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 because 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 a graphite-like layered inorganic solid. First a polyvinylacetate(PVAc) intercalated graphite oxide(GO) nanocomposite was prepared by polymerizing vinylacetate monomer in the interlayer of n-octanol 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 DMA were conducted to characterize the nanocomposite.

CC6.23
SELF-ASSEMBLED LITHIUM-AMINE AGGREGATES IN THE INTERCALATION OF DIETHYLAMINE IN MOLYBDENUM DISULFIDE. E. Benavente, Universidad Tecnológica 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. Bloise, J.P. Donoso, C.J. Magon, J. Schneider, Universidad de Sao Paulo, Instituto de Física, Sao Carlos, SP, BRAZIL.

The organization of the organic phase in the interlaminal spaces of nanocomposites obtained from intercalation of diethylamine in molybdenum disulfide in the form of an amine-lithium aggregates is reported. The reaction of diethylamine with exfoliated MoS_2 leads to the formation of the compound $Li_{0.1}MoS_2HNR_{2.0.22}$. The product is a layered organic-inorganic nanocomposite with an electrical conductivity of the order of $10^{-2} S cm^{-1}$ at room temperature. If

conventional intercalation models like those proposed for similar intercalates are considered, both, the interlaminal distance detected by powder X-ray diffraction analysis and the amount of intercalated amine determined by elemental and thermal analyses, appear to be anomalous. Indeed, according to molecular dimensions calculated by building models using both, van 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, specially, solid state NMR analyses of the product permit to explain such paradoxical results by the formation of aggregates. According to IR data, the intercalated species is a weakly coordinated amine and the presence of alkylammonium ions may be moreover disregarded. Although the relative low lithium concentration in the nanocomposite, 7Li -NMR spectrum at low temperature has a second moment (5.2 Gauss² at 173 K) assignable to 7Li -H 60% and 7Li -Li 40% magnetic dipolar contributions. NMR data including variation of the linewidths and spin-lattice relaxation time with the temperature agree with the presence of aggregates formed by three Li-atoms and six amines. Low volume molecular models, permitting not only to explain observed structural and analytical data but also to describe the product as a pillared species, are discussed.

Acknowledgments.
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CC6.24
SIZE CONTROL OF BLOCK POLYMER TEMPLATED MESOPOROUS SILICATE MATERIALS. Takeo Yamada, Keisuke Asai, Kenkichi Ishigure, The Univ of Tokyo, Dept of Quantum Engineering and Systems Science, Tokyo, JAPAN; Akira Endo, National Institute of Materials and Chemical Research, Tsukuba, JAPAN; Hao-Shen Zhou, Itaru Honma, 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. However, for new functional devices, it is necessary to synthesis new 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. Stucky 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 copolymers as template. And we succeed controlling pore size of mesoporous materials using block copolymer by synthesis conditions. The mesoporous materials was prepared as follow: Block copolymer was dissolved in water and HCl solution with stirring at some temperature. Then tetraethoxysilane (TEOS) was added into that solution with stirring at some temperature. The mixture was aged without stirring. The solid product was recovered in mixture solution and filtered, washed, and air-dried at room temperature. Finally, calcination was carried out these materials. The characteristic 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 exhibits ordered and oriented large periodic mesostructure. The d-spacing, phase state, pore size, and surface area could be controlled by synthesis condition and triblock copolymers.

CC6.25
ORGANIC/INORGANIC HYBRID MATERIALS ON MOLECULAR SCALE FROM A NOVEL TYPE OF PRECURSORS. Weixing 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 nano(or molecular) scale are 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 solution. The key is they are from cheap materials or agricultural disposal and synthesized at relatively low temperature.

CC6.26
IN SITU ONE-STEP FABRICATION OF POLYSTYRENE/CdS HYBRID NANOCOMPOSITES EMBEDDED WITH CONTROLLABLE SHAPE AND SIZES OF CdS NANOCRYSTALLITES BY A SOFT 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 soft solution route was successfully developed for in situ fabrication of polystyrene/CdS nanocomposites embedded with controllable shape and sizes of CdS nanocrystallites at lower temperature. The polymerization of the styrene monomers in the presence of radical initiator AIBN(2, 2'-azobisisobutyronitrile) and the formation of the CdS nanocrystallites using thiourea as sulfur sources in ethylenediamine media occur simultaneously in a temperature range of 80-140°C. The effects of several factors, such as solvents, temperature, reaction time, the ratios of the monomer/Cd²⁺ on the polymerization, the formation of CdS, the particle shape and sizes were investigated. Both temperatures and solvent were found to play a key role in the controllable synthesis of the nanocomposites. The CdS nanocrystallites embedded in the polystyrene matrix are composed of homogeneously nanofibers with widths of 4-10nm 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.

CC6.27

THE SYNTHESIS OF HYBRID MATERIALS BY THE BLENDING OF POLYHEDRAL OLIGOSILSESQUIOXANES INTO ORGANIC POLYMERS. Rusty L. Blanski, Shawn H. Phillips, Kevin Chaffee, Air Force Research Laboratory Edwards AFB, CA; Joseph Lichtenhan, Hybrid Plastics, Fountain Valley, CA; Andre Lee and Hei Ping 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 combining of two very different compounds which may result in something that bridges the performance gap between the two systems. We have previously reported such hybrid systems prepared by incorporating polyhedral 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.

CC6.28

PREPARATION OF EXFOLIATED POLYSTYRENE-MONTMORILLONITE HYBRIDS. Jae Goo Doh, Jeong Ghi Koo, Cheil Industries Inc, R & D Center, Kyungkido, KOREA; Iwhan Cho, Korea Advanced Institute of Science and Technology, Dept of Advanced Materials Engineering, Seoul, KOREA.

Two types of polystyrene (PS)-organically modified montmorillonite (org-MMT) hybrids, namely, intercalated and exfoliated hybrids, were prepared by radical polymerization with proper comonomers in organophilic MMT phase. The impregnation of monomer mixture into quaternary ammonium MMT was followed by the polymerization by radical initiator. The intercalated and exfoliated structures of polymerized PS/org-MMT hybrids were identified by XRD and TEM. The homopolymerization of the penetrated styrene between the interlayers of org-MMT resulted in intercalated PS/org-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, 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 polar group in org-MMT were very good candidates for formation of exfoliated PS-MMT hybrids. As the amount of these comonomers increases, a transition from intercalated to exfoliated hybrids was observed as judged by XRD. Introduction of large molecule in size or polar group in comonomer inserted between the interlayers before the onset of polymerization would be the main factor causing the delamination of the MMT interlayers by the extensive intercalation of PS-based copolymer between the interlayers.

CC6.29

NOVEL MESOPOROUS MATERIALS BY TAILOR-MADE BLOCK COPOLYMER SURFACTANTS. Nicola Huesing, Guido Kickelbick, Beatrice Launay, 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 (e.g. polysiloxane/ polyethyleneoxide/ polysiloxane) 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 thin films 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.

CC6.30

FORMATION OF HIGHLY DISPERSE METALLIC PARTICLES IN POROUS POLYMERIC MATRICES. Nina I. Nikonorova, Elena S. Trofimchuk, Elena V. Semenova, Alexander L. Volynskii, Nikolai F. Bakeev, Chemistry Dept, M.V. Lomonosov Moscow State Univ, Moscow, RUSSIA; Gennady B. Khomutov, Faculty 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. The approach is based on the reduction of metals from their salts within the nano-pores 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 nano-pore serves as a nano-reactor 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. Metallic particles can be distributed uniformly in the PM volume or can be concentrated as a layer with a thickness of 5 - 40 nm. The synthesis of magnetic metallic particles in PM under applied 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 as-prepared PCM show unique properties under the action 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.

CC6.31

SOL-GEL CHEMISTRY OF 3-ISOCYANATOPROPYL-TRIETHOXSILANE. Colleen Baugher, Douglas A. Loy, Catalysts and Chemical Technologies Department, Sandia National Laboratories, Albuquerque, NM.

3-Isocyanatopropyltriethoxysilane 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 polysilsesquioxane 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 gels. Tetrabutylammonium hydroxide was particularly useful for avoiding phase separation during sol-gel processing and acquiring homogeneous gels.

CC6.32

AMINE-FUNCTIONALIZED POLYSILSESQUIOXANES. Arturo

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

Amine-functionalized trialkoxysilanes have been extensively used as coupling agents and, more recently, as co-monomers with tetraalkoxysilanes or other organotrialkoxysilanes in hybrid organic-inorganic materials. In this study we examined the sol-gel chemistry of aminopropyltrimethoxy-silane (1), aminopropyltriethoxysilane (2), N,N-diethylaminopropyl-trimethoxysilane (3), N-(trimethoxy-silylpropyl)ethylenediamine (4), N-(trimethoxysilylpropyl)diethylenetriamine (5), and p-aminophenyltri-methoxysilane (6). The monomers were reacted with dionized water (1.5, 3.0 or 6.0 equivalents) at 1.0 M monomer concentration in methanol (1, 3-6) or ethanol (2) or without any added solvent. Polymeric products were analyzed by solution proton, C-13, and Si-29 NMR spectroscopy. These monomers generally react to afford soluble polymeric products. It is possible, however, to prepare gels through reaction of the amine functionalized polysilsesquioxanes with electrophilic reactants such as diisocyanates or dibromoxylene.

CC6.33
RAPID PROTOTYPING OF PATTERNED ORGANIC-INORGANIC MULTIFUNCTIONAL NANOSTRUCTURES. Hongyou Fan, Yunfeng Lu, Randy Schunk, Scott T. Reed, Tom Baer, Gabriel P. López and C. Jeffrey Brinker.

Whether it be the origin of life, crystallization, 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-, macroscale) such as shape, mechanical strength, color, conductivity, etc. are established very early as the molecules or atoms assemble and make the critical transition from a few units with nanoscale dimensions to micro-, meso-, and macroscopic arrays. The chemists' approach to the mesoscopic world has been focused on simple, inexpensive, molecule self-assembled methodology. For example, Yang et al. grew surfactant-templated mesoporous silica on hydrophobic patterns prepared by micro-contact printing μ CP. Trau et al. formed oriented mesoporous silica patterns, using a micro-molding in capillaries MIMIC technique, and Yang et al. combined MIMIC, polystyrene sphere templating, and surfactant-templating to create oxides with three levels of structural order. Overall, great progress has been made to date in controlling structure on scales ranging from several nanometers to several micrometers. 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 ($\text{Si}(\text{OR})_4$) with tri-functional organosilanes ($(\text{RO})_3\text{SiR}'$) or by inclusion of organic additives, we have selectively derivatized the silica framework with functional R' ligands or molecules. The resulting materials exhibit form and function on multiple length scales (microscale, mesoscale, and macroscale).

CC6.34
POLYMETHYLSILSESQUIOXANES THROUGH BASE-CATALYZED REDISTRIBUTION OF OLIGOMETHYL-HYDRIDOSILOXANES. Kamyar Rahimian, Douglas A. Loy, Sandia National Laboratories, Albuquerque, NM.

Polysilsesquioxanes have attracted increasing 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 polymethylsilsesquioxane, $(\text{MeSiO}_{1.5})_n$, and its copolymer with polydimethylsiloxane, $(\text{Me}_2\text{SiO})_n$, and polymethyl-hydridosiloxane, $(\text{MeHSiO})_n$. These materials can easily be synthesized through the redistribution reaction of oligomethylhydridosiloxane and/or its copolymer with dimethylsiloxane, using tetrabutylammonium hydroxide as catalyst. Conversion of the SiH group, in the starting oligosiloxanes, to MeSiH_3 can be easily controlled by the amount of catalyst used, as well as presence or absence of solvent. We will also report on the properties of the above materials and their potential applications.

CC6.35
ACID-CATALYZED RING-OPENING POLYMERIZATION OF DISILOXACYCLOPENTANES. Kamyar Rahimian, Douglas A. Loy, Sandia National Laboratories, Albuquerque, NM.

We have recently shown that disilaoxacyclopentanes 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 reports had stated that ROP of disilaoxacyclopentanes only occurs using base catalysts. We have recently discovered that disilaoxacyclopentanes can in fact be polymerized using acids. Here, we report on the ring-opening polymerization of disilaoxacyclopentanes using organic acids as well as photoacid generators (PAG). This methodology has opened the door for the use of these materials in thin film applications and conformal coatings, which will also be discussed.

CC6.36
AFM STUDIES ON BLOCK COPOLYMER TEMPLATED MESOPOROUS SILICA MATERIALS. Akira Endo, Shin'ichiro Matsumoto, Masaru Nakaiwa, Takashi Nakane, National Institute of Materials and Chemical Research, Tsukuba, JAPAN; Takeo Yamada, Hao-Shen Zhou, Itaru Honma, Electrotechnical 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 mesophase and pore size distribution, and TEM is used for visual characterization of mesophase 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-ethylene oxide)-(poly-propylene oxide)-(poly-ethylene oxide) triblock copolymers and the removal of template by thermal treatment in the air atmosphere. The XRD and nitrogen gas adsorption studies revealed that the obtained silica powder had hexagonal structure and pore diameter and wall thickness were 5.2 and 6.0nm, respectively. The periodic structure of about 11nm which corresponded to distance between pore centers in hexagonal phase was observed very clearly by AFM and that results showed good agreement with the structure characterized by low angle XRD and nitrogen absorption measurements. AFM can be a strong and useful tool for the structure characterization of mesoporous materials because of its potential resolution and easiness of sample preparation.

CC6.37
PREPARATION AND PROPERTIES OF PCT/P(VDF-TrFE) 0-3 NANOCOMPOSITE THIN FILMS. Qifa Zhou, Qingqi Zhang, Department of Physics, Zhongshan University, Guangzhou, 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.

Nanocrystalline calcium modified lead titanate $[(\text{Pb}_{0.72}\text{Ca}_{0.28})\text{TiO}_3$ or PCaT] powder was prepared by a sol-gel process. 0-3 PCaT/P (VDF-TrFE) nanocomposite thin film consisting of the PCaT powder imbedded in a vinylidene fluoride-trifluoroethylene copolymer [P(VDF-TrFE)] matrix was deposited on silicon substrate to form pyroelectric sensor. The dielectric and pyroelectric 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.

CC6.38
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 Q_m 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 Q_m agrees well with the prediction of the parallel model. It was found that Q_m increases from 34 to 100 as α changes from 0 to 0.82 and then increases sharply to reach a high value of 600 at $\alpha = 1$. Therefore Q_m can be tailored to give a wide range of values by varying α .

CC6.39
AN EFFICIENT REMOVAL OF THE ORGANIC PHASE TEMPLATE BY PHOTOCHEMICAL OZONOLYSIS IN SUBSTRATE-SUPPORTED, ORIENTED SURFACTANT/SILICATE MESOSTRUCTURED FILMS. Theotis Clark, Jr., Atul N. Parikh, Hongyou Fan, Jeffery C. Brinker and Basil I. Swanson.

The hierarchical co-assembly of self-organizing surfactants and inorganic sol-gel 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 membrane-based separation, shape and size-selective catalysis, microelectro-chemistry, and biological and chemical sensing and detection, as well as in a host of fundamental studies involving laterally 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 highly oxidative 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 substrates, e.g., thin metal films 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 in-situ and selective template removal in complex processes.

CC6.40

ZEOLITE DOUBLE FOUR-RINGS AS BUILDING BLOCKS FOR NEW INORGANIC-ORGANIC HYBRID MATERIALS.

Russell E. Morris, Bruce W. Manson and David S. Wragg, School of Chemistry, University of St. Andrews, St. Andrews, Fife, UNITED KINGDOM.

Inorganic microporous materials such as zeolites are an important class of solids, with applications in catalysis, ion exchange and adsorption technologies. Inorganic-organic hybrid materials offer the possibility of combining the architecture of inorganic crystalline solids with the flexibility of choice of functional group inherent in organic chemistry. In this presentation I will describe some of our attempts to prepare zeolite-related hybrid materials. The structures of zeolites and other microporous materials are often described in terms of secondary building units (SBU). One fairly common example of an SBU is the double four ring (D4R), which is present in materials like zeolite-A, and contains eight TO4 units arranged in a cube. Recently there have been many examples of molecules analogous to zeolite D4R units reported in the literature. In this presentation I will describe how we are using molecules such as polyhedral silsesquioxanes to prepare new inorganic-organic hybrid materials, and our attempts to derivatise them chemically to produce functional materials. I will also describe how a novel class of azamacrocycle containing inorganic-organic hybrid material can be prepared. This zeolite-related gallium phosphate material contains layers of D4R units with metal macrocycle complexes linking the layers into a three dimensional structure. I will describe the synthesis, characterisation and substitution patterns of this material.

CC6.41

ORGANIC-INORGANIC MULTIFUNCTIONAL MESO-STRUCTURED SILICA FILMS. Hongyou Fan, Yunfeng Lu, Scott T. Reed, Tom Baer, Randy Schunk, Gabriel P. Lopez and C. Jeffrey Brinker, The University of New Mexico/NSF Center for Micro-Engineered Materials, The Advanced Materials Laboratory, Sandia National Laboratories, Albuquerque, NM.

Organic/inorganic hybrid films and metal/inorganic and bioactive composite films exhibiting unimodal pore size distributions and ordered or disordered mesophases have been prepared by a simple dip-coating procedure. Beginning with a homogeneous solution of tetraethyl orthosilicate, organoalkoxysilane ($R/Si(OR)_3$, R / is a non-hydrolyzable functional ligand), surfactant (prepared with initial surfactant concentration $c <$ the critical micelle concentration cmc), and optionally other organic or bioactive additives, we rely on solvent evaporation to induce micellization and continuous self-assembly into hybrid silica-surfactant thin film mesophases. A low temperature heat treatment or washing procedure is used to remove the surfactant while preserving the organo-silicon bonds. Surface acoustic wave (SAW)-based nitrogen sorption measurements and high resolution transmission electron microscopy (HRTEM) indicate that the films have high surface areas and unimodal pore diameters in the range of 20-100 Å. Alternatively organic molecules (e.g. organic dyes) or bioactive molecules (e.g. proteins) are added to the starting sol. Film deposition results in optically active or bio-active mesostructured films. This approach offers a new pathway for the fabrication of functional porous thin films with both controlled pore structure and pore surface chemistry. In addition, patterned multifunctional nanostructures are produced combining rapid prototyping techniques such as pen lithography, ink-jet printing, and dip-coating on micro-contact printed substrates.

CC6.42

ROLE OF SELF-ASSEMBLED MONOLAYERS ON THE MESOSTRUCTURE OF SURFACTANT TEMPLATED SILICA FILMS. Nilesch S. Doke, University of New Mexico, Albuquerque, NM; Yunfeng Lu, Applied Materials, Santa Clara, CA; William C. Jackson, Gabriel P. Lopez, University of New Mexico, Albuquerque, NM; C.J. Brinker, University of New Mexico and Sandia National Laboratories, Albuquerque, NM.

We used self-assembled monolayers (SAMs) of alkanethiols on gold ($X-(CH_2)_nSH$; $X = CH_3, OH$) and alkyltrichlorosilanes on silicon ($CH_3-(CH_2)_nSiCl_3$) 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 cetyltrimethylammonium 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 coalesce to form thin films with different mesostructures. We found that at CTAB concentrations greater than 4% in the sol, the 1-dH mesostructured particles coalescing on hydrophilic thiol SAMs ($X = OH$) formed a lamellar mesostructured film while on hydrophobic SAMs ($X = CH_3$) the coalescing 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 a lamellar mesostructured film. We also used alkyltrichlorosilane SAMs with a long chain ($n = 17$) and a short chain ($n = 1$) to study their effect on mesostructure of films. With less than 5% CTAB in the sol, 1-dH mesostructured particles coalescing on both substrates formed a 1-dH mesostructured film. On calcining these 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 alkyltrichlorosilane 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.

CC6.43

SOLVENTLESS SOL-GEL CHEMISTRY BY RING-OPENING POLYMERIZATION OF BRIDGED DISILOXACYCLOPENTANES. Kamyar Rahimian, Douglas A. Loy, Sandia National Laboratories, Albuquerque, NM.

Disilaoxacyclopentanes have proven to be excellent precursors to sol-gel type materials. We have previously shown that phenylene-bridged disilaoxacyclopentanes can be ring-open polymerized, using catalytic tetrabutylammonium hydroxide, to produce thermally stable materials without visible shrinkage. These materials are structurally similar to traditional sol-gels but are generated quite differently- no solvent, non-aqueous, no VOCs and little shrinkage is associated with them. We have extended this work to novel alkylene-bridged disilaoxacyclopentanes. Here, we report on the ring-opening polymerization (ROP) of these precursors using bases, as well as ROP using organic acids and photoacid generators (PAG).

CC6.44

Abstract Withdrawn.

SESSION CC7: MESO- OR NANOSTRUCTURED POROUS MATERIALS

Chairs: Geoffrey A. Ozin, James E. Mark and Clement Sanchez

Wednesday Morning, April 26, 2000
Metropolitan III (Argent)

8:30 AM *CC7.1

NANOSTRUCTURED POROUS FILMS: MOLECULAR SELECTIVITY FOR SENSOR DEVICES. Thomas Bein, Svetlana Mintova, Julia Meinershagen, Ken Yasuda, Department of Chemistry, University of Munich, Munich, GERMANY; Jaco Visser, Ford Motor Company, Dearborn, MI.

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 nanocrystal-seeded growth 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 microwave processing enable the controlled growth of dense, very thin films of BEA, MFI, LTA and AFI zeolite structures, in some cases with oriented molecular sieve channels. Selective chemical sensing was demonstrated using very different transduction mechanisms, including microcalorimetry on Si-chips, mass-sensing on piezoelectric devices, and optical responses 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.¹ Examples of such networks include titania and zirconia. The initial gel, which is porous, is soaked in the metal alkoxide solution, 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.² 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.

1. R.A. Caruso, M. Giersig, F. Willig, M. Antonietti, Langmuir 1998, 14, 6333.

2. F. Caruso, R.A. Caruso, H. Möhwald, Science 1998, 282, 1111.

9:15 AM CC7.3

SYNTHESIS OF MESOPOROUS TITANIUM PHOSPHATE.

C.J. Barbe, E. Drabarek, D.R.M. Mitchell, J. Hanna, V. Luca, K.S. Finnie, J.R. Bartlett and J.L. Woolfrey, ANSTO Materials Division, Menai, AUSTRALIA.

Mesoporous titanium phosphates were synthesised using three different approaches, involving reactions of titanium tetraisopropoxide with long chain alkylphosphates, and subsequent ageing at temperatures of 80 to 150 °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, where the modified titanium precursor was added to an alkylphosphate micellar solution. XRD and TEM revealed that the as-synthesised solids possess a highly organised, lamellar meso-structure. However, removal of the surfactant by either heating or leaching in strong basic, or acidic, solutions led to collapse of the lamellar meso-structure. TEM examination of samples heated at 400 °C confirmed that the collapsed structure consisted of a mixture of macro-porous, micro-porous and nano-particulate (titania-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-precipitated samples could be easily tailored 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 sample, with low total pore volumes. To prevent the collapse of the structure upon heating, a third approach was devised. This process involved the hydrolysis of titanium tetraisopropoxide, modified with acetyl acetone, with excess water. The alkyl phosphate was then introduced into the suspension. Subsequent ageing under acidic conditions destabilised, the particles, leading to aggregation and subsequent gelation. As before, a diffraction peak was observed at low angles, suggesting the presence of a meso-structure. Upon heating, the peak disappeared, indicating a reduction in ordering. However, in contrast to the previous approaches, the pyrolysed solid contained a significant proportion of mesopores (3-4 nm) and a surface area

greater than 300 m².g⁻¹. Moreover, this strategy can be easily extended to the synthesis of meso-porous titania with very high surface area by the use of non chelating surfactants such as CTAB.

9:30 AM *CC7.4

POROUS SILICA THIN LAYERS USING MESOPHASE TEMPLATING. Michaela Klotz, André Ayrat, Christian Guizard, Laboratoire des Matériaux et Procédés Membranaires, E.N.S.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 mesophase 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 tortuosity of the pore network in sol-gel derived thin films. However specific conditions have to be found in order to prepare continuous defect-free layers exhibiting no extraporesity. The example of the templating by hexagonal mesophases will be used to show how it is possible to succeed in the preparation of such layers. Simple considerations from data established in the case of the 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 anisotropy 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 synthesize hybrid materials composed of porous zirconia as support and highly dispersed nanosized Cu or CuS nanoparticles. These composite materials are promising catalysts in the car industry and methanol synthesis.

The mesoporous zirconia support was prepared by hydrolysis and condensation of tetra-n-alkoxyzirconates 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. 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 assess the pore structure and the nanoparticle distribution across the support material. Nitrogen sorption and X-ray diffraction measurements were used to determine the porosity and crystallinity of the final product.

10:45 AM *CC7.6

POROUS GELS OBTAINED BY PHASE SEPARATION IN ORMOSIL SYSTEMS. Kazuki Nakanishi, Norio Ishizuka, Souichi Kumon, Kazuyuki Hirao, Dept Material Chemistry, Graduate School of Engineering, Kyoto University, JAPAN.

Concurrent phase separation and sol-gel transition which result in well-defined macroporous structures can be observed in a broad range of ORMOSIL compositions. The decreased functionality and increased hydrophobicity compared with the systems from tetrafunctional silanes provide the phase separation of ORMOSIL systems more polymer-like features. In bulk samples, since the crosslinking reaction proceeds gradually around 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 silica systems. The addition of non-ionic surfactant 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 ORMOSIL 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 coarsening related to the wetting on the substrate plays an important role in determining the final macroporous morphology of the resultant films.

11:15 AM *CC7.7

LASER ACTION FROM LASER DYE LOADED POROUS MATERIALS. Ferdi Schuth, Guido Ihlein, Ozlem Weiss, Frank

Marlow, MPI fuer Kohlenforschung, Muelheim, GERMANY; Franco Laeri, Uwe Vietze, TU Darmstadt, GERMANY; J.U. Nockel, MPI fuer Physik Komplexer Systeme, GERMANY.

After unsuccessful attempts to create solid state lasers based on molecular sieves by doping them with various laser active transition metal or rare earth ions, such crystals loaded with organic laser dye molecules, on the contrary, did show laser action. So far the aluminum phosphate ALPO-5 with channels of about 0.75 nm diameter loaded with a laser dye with the trade name pyridinium 2 showed the best results. However, also other dyes can be incorporated, for instance different coumarins. We are also investigating alternative host crystals, such as those of the MFI structure type. The dye is preferably incorporated during the synthesis, as long as it does not decompose under the conditions of the molecular sieve synthesis. Alternative pathways, however, are also possible, such as loading via the gas phase. The composites show the typical properties expected for a lasing material, i.e. narrow emission spikes which appear at a distinctive threshold above the broad luminescence background and the intensity of which grows faster with increasing excitation energy than the background luminescence. All dye molecules are oriented by the host crystals channel system, so that emission from the composite is strongly polarized. The resonator is not a longitudinal one, but the hexagonal prism faces formed by the crystal planes of the host material produce a whispering gallery type resonator with the emission leaving the crystal predominantly at the edges.

11:45 AM CC7.8

ELECTROACTIVE METAL OXIDE MESOSTRUCTURES. Marc Mamak, Geoffrey A. Ozin, Materials Research Group, Department of Chemistry, University of Toronto, Ontario, CANADA.

Novel soft-chemistry, synthetic strategies have been devised that yield the first examples of binary and ternary, electroactive metal oxide mesostructures. It has been demonstrated that template removed materials are thermally robust and of high surface area. The structural integrity is maintained to around 800°C. Both the binary and ternary materials have pore diameters on the boundary of the mesoporous and microporous size regimes and have a framework that is comprised of nanocrystalline metal oxide. These observations bode well for the utilization of these materials in power generation applications.

SESSION CC8: CHARACTERIZATION METHODS

Chairs: C. Jeffrey Brinker and Georg H. Mehl
Wednesday Afternoon, April 26, 2000
Metropolitan III (Argent)

1:30 PM *CC8.1

HIERARCHICALLY ORDERED INORGANIC-ORGANIC COMPOSITES AND POROUS OXIDES. B.F. Chmelka, P. Yang, G. Wirmsberger, H. Huang, N. Melosh, G.D. Stucky, Univ of California, Santa Barbara, Depts of Chemical Engineering and Chemistry, Santa Barbara, CA.

Mesoscopic and/or macroscopic organization of network-forming metal oxides can be achieved by using sol-gel chemistry strategies, in conjunction with hydrophobic structure-directing agents. In these systems, hydrolysis and polymerization of the inorganic species tend to occur in hydrophilic regions of a sample, which are meso- or macroscopically phase-separated from the hydrophobic regions. Ordering length scales and periodicities are typically established by the dimensions and arrangements of the hydrophobic aggregates, according to liquid crystal or block-copolymer self-assembly physics, or on the packing of emulsion droplets or monodisperse latex spheres. Such composite systems can be produced in a variety of macroscopic forms, including powders, thin films, fibers, and macroscopic monoliths, often with substantial orientational ordering. Combined use of amphiphilic surfactant species, hydrophobic colloids, and/or micromold-patterning, permits the preparation of composite solids that are organized over multiple discrete and separately adjustable length scales from nanometers to centimeters. Recent results will be presented on NMR, XRD, and microscopy investigations of hierarchically ordered inorganic-organic composites and porous solids.

2:00 PM CC8.2

CLUSTER SIZE DISTRIBUTIONS, PREFERENTIAL MASS STABILITIES, OPTICAL PROPERTIES AND SURFACE CHEMISTRY OF METAL NANOCLOUDS STUDIED BY LIQUID CHROMATOGRAPHY. J.P. Wilcoxon, J.E. Martin and P.P. Newcomer, Nanostructures and Advanced Materials Chemistry Dept., Sandia National Labs, Albuquerque, NM

We have been investigating the cluster size distributions, aging processes, and surface chemistry of nanosize clusters of Au, Ag, Pt, and Pd dispersed in organic solvents using high pressure liquid

chromatography (HPLC), dynamic light scattering (DLS), and transmission electron microscopy (TEM). The nanosize metals are formed by the inverse micelle synthetic process at room temperature in inert oils and range in diameter from 1-10 nm and are passivated by organic ligands. HPLC is used to monitor the changes in cluster size distribution and average cluster size as a function of sample age, surface passivating agent, and metal type. This technique is sensitive enough to discern changes in hydrodynamic volume corresponding to only 2 carbon atoms of the passivating agent or metal core size changes of $>4 \approx$ and we have determined how the total cluster volume (metal core + passivating organic shell) changes with the size of the passivating agent. At the same time we have measured the optical absorbance properties of these Au clusters and have demonstrated a significant blue shift and broadening of the plasmon absorbance as the Au cluster size is decreased. It is found that the cluster size distribution in these surfactant-stabilized dispersions narrows with age and this redistribution of cluster mass occurs even in the presence of strongly binding surfactants like thiols or amines. The rate of mass redistribution is most rapid for metals with the lowest bulk melting temperatures (e.g. Au, Ag), and slowest for those with the highest values (Pd, Pt). It occurs most rapidly with the weakest surface-active agents (polyethers). The narrowing of the cluster size distribution and the preference for certain discrete sizes argues that special structural stabilities overwhelm the expected kinetically-broadened Ostwald ripening process historically observed for larger colloids (i.e. >10 nm). We show how HPLC is particularly useful for studying the relative strength of binding of organic molecules to the nanocluster surface-a feature of paramount importance for catalytic applications.

Acknowledgment:

This work was supported by the U.S. Department of Energy under contract DE-AC04-AL8500. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the US Department of Energy.

2:15 PM CC8.3

STRUCTURAL INVESTIGATION OF SURFACTANT-TEMPLATED MESOPOROUS SILICA FILMS - CONTRIBUTION OF SMALL ANGLE X-RAY SCATTERING IN GRAZING INCIDENT. S. Besson, J.M. Berquier, C. Jacquiod, CNRS-SAINT-GOBAIN, Aubervilliers, FRANCE; T. Gacoin, J.P. Boilot, Ecole Polytechnique, Palaiseau, FRANCE; A. Naudon, D. Babonneau, Université de Poitiers, Futuroscope, FRANCE; C. Ricolleau, Université Paris 7, Paris, FRANCE.

Since the discovery of the ordered mesoporous materials called M41s, research on surfactant-templated materials and self-organized materials knows an always growing interest. If this attractive field has touched more particularly the domain of powdered materials, the interest for mesoporous films is now obvious and motivated by wide potential applications as membranes for filtration, selective sensors, high specific surface area materials as hosts to realize functional coatings or optical devices. In most of these applications, control of morphology and structure of the films is essential. Different methods have already been described to synthesize self-supported films grown at air-liquid or solid-liquid interfaces, or dip and spin-coated films, to result in various structures and crystallinity. Generally, structural investigations performed by X-Ray Diffraction are rather limited due to the low number of peaks accessible for phase identification, to texture effects and to an information restricted to only one dimension. On its side complementary approach by Transmission Electronic Microscopy is limited to extremely local view of the material. We describe here a microstructural study of mesostructured and porous sol-gel silica films by using, in parallel to traditional XRD and TEM observations, the technique of GISAXS (Grazing Incidence Small Angle X-Ray Scattering) that is shown to be particularly effective for such study. By this way it is shown that the extent of the channel hexagonal ordering and the texture can be optimized in MCM-41 type films by varying the composition of the deposited solution. Especially, critical values are clearly observed both for the size of silica units forming the walls in the mesophase and for the film thickness. All these results can be understood from the competition between structuration and gelation of the film during alcohol removal.

2:30 PM *CC8.4

SOME SCATTERING RESULTS ON ORGANIC-INORGANIC COMPOSITES. J.E. Mark, Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, OH.

A number of investigations are described to illustrate the use of small-angle x-ray and neutron scattering to characterize the structures of composites. The organic phase in these materials is typically a polymer such as poly(dimethylsiloxane), and the inorganic phase a condensed ceramic such as silica or titania obtained by in-situ hydrolysis and condensation of an organosilane or organotitanate in the usual sol-gel approach. Other inorganic phases of interest include porous material such as zeolites or Vycor glass. A major goal in such

investigations is to correlate the structures of the composites with the synthetic techniques used to prepare them, and with the mechanical properties obtained. Carrying out scattering measurements as a function of time can also be used to obtain kinetic results on the sol-gel reactions used to generate the dispersed phase.

3:30 PM *CC8.5

NMR TECHNIQUES FOR THE STRUCTURAL CHARACTERIZATION OF SOL-GEL DERIVED HYBRID MATERIALS.

Florence Babonneau, Chimie de la Matière Condensée, UPMC/CNRS, Paris, FRANCE.

The objective of this presentation is to discuss the appropriateness of various solution and solid state NMR techniques to describe structural aspects of sol-gel derived hybrid systems prepared by sol-gel process. Co-hydrolysis of organosilanes and metallic alkoxides can promote either self-condensation or co-condensation reactions between the different precursors, and this will control the structural homogeneity of the final network. Solution state ^{29}Si and ^{17}O NMR can give unique information on the formation and stability of co-condensing species. In the final gels, solid state ^{29}Si MAS used in conjunction with cross-polarization (CP) and related 2D ^{29}Si - ^1H heteronuclear NMR correlation techniques, provides detailed information on dipole-dipole coupled ^{29}Si and ^1H species among different molecular moieties, and thus on spatial proximity of these species. Similar information can be obtained using 2D ^1H homonuclear correlation NMR spectroscopy. Such experiments are now possible by combining high magnetic field with fast spinning rate (30 kHz). Finally, the use of ^{17}O MAS-NMR with the newly developed MQMAS sequence that provides a direct identification of the various oxo bridges which constitute the hybrid network will be discussed.

4:00 PM CC8.6

MICROPOROUS ALUMINOPHOSPHATE FORMATION BY IN SITU HYDROTHERMAL NMR.

Corine Gerardin*, Mohamed Haouas, Francis Taulelle, Louis Pasteur University, Strasbourg, FRANCE, *CNRS-RHODIA Complex Fluids Laboratory, Cranbury, NJ; Thierry Loiseau, Gerard Ferey, University Versailles-Saint Quentin, Versailles, FRANCE.

Synthetic pathways describing the formation of microporous 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 autogeneous 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 in solution of 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 CC8.7

ELECTROCHEMICAL INVESTIGATIONS INTO SILICA AND ZIRCONIA POLYMERIZING SOL-GEL SYSTEMS. A NEW APPROACH OF THE GELIFICATION KINETICS. Pierre Audebert, Samuel Matthieu, PPSM, ENS Cachan; Hélène Cattet, LSEO, FRANCE, Univ Bourgogne, FRANCE and Clément Sanchez, Lab. Chimie Mat. Condensée, Univ P6, FRANCE.

Through the informations they can bring on the transport of electroactive species, electrochemical techniques, and especially chronoamperometry 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, chronoamperometry is especially well suited to detailed investigations on gelling systems through the gelation course and after. We have 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. The 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 same gel. After a short summary of previously obtained results on silica 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 ferrocenes functionalized xerogels, obtained in a parallel way upon drying of the previously investigated wet gels will be also briefly introduced.

4:30 PM *CC8.8

HYBRID I/O NANOCOMPOSITES FROM ALKOXYSILANES RELATIONSHIPS BETWEEN MORPHOLOGY AND MECHANICAL PROPERTIES.

J.F. Gerard¹, H. Kaddami¹, J.P. Pascault¹, P. Hajji², L. David² and G. Vigier². ¹UMR CNRS, Laboratoire Matériaux Macromoléculaires, ²GEMPPM - UMR CNRS, Institut National des Sciences Appliquées, Villeurbanne, FRANCE.

Relationships between morphologies and mechanical properties of organic-inorganic nanocomposites synthesised from sol-gel chemistry of alkoxy silanes reported the literature are reviewed in the first part of this paper. In the second part, these relationships are illustrated for two types of I/O materials having SiO₂ contents: nanocomposites synthesized from i) the hydrolysis and condensation of alkoxy silane-terminated polyester and polyether oligomers synthesised from the refunctionalization with -amino(or isocyanato) propyltriethoxy- silane and -hydroxy terminated hydrogenated polybutadiene or polycaprolactone, respectively (about 4% wt. SiO₂); ii) the simultaneous hydrolysis/condensation of tetra-ethoxysilane and radical polymerization of hydroxyethylmethacrylate, 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 polyHEMA glass transition region. Its value in the rubbery state is strongly related to the condensation of silicon species studied by ^{29}Si -NMR, i.e. the conditions of the sol-gel 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 sol-gel reactions conditions.

SESSION CC9: PROCESSING AND PROPERTIES OF HYBRIDS (OPTICAL, ELECTRICAL, MECHANICAL...)

Chairs: Giovanni Carturan, Martin Mennig and Florence Babonneau
Thursday Morning, April 27, 2000
Metropolitan III (Argent)

8:30 AM *CC9.1

NANOSTRUCTURED HYBRID POSS CHEMICAL FEEDSTOCKS: COMMERCIALIZATION, PROPERTIES, AND APPLICATIONS.

Joseph D. Lichtenhan, Joseph J. Schwab, Hybrid Plastics, Fountain Valley, CA.

Polyhedral Oligomeric Silsesquioxane (POSS) chemicals are comprised of nanoscopic silicon-oxygen frameworks that externally contain a variety of reactive and/or nonreactive organic groups for solubilization and compatibilization. Hence, POSS chemical systems may be viewed as the smallest chemically discrete particles of silica possible while the resins in which they are incorporated are structurally well defined molecular nanocomposites. Over the past decade, the US DoD and DoC have pursued development of this technology in an attempt to meet its 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 reagents, 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 new 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 CC9.2

PATTERNED PHOTONIC CRYSTALS WITHIN MICROCHANNEL NETWORKS.

Abbas Rizvi, Amer Choudrey, Peidong 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 to metals were obtained using this methodology. In addition, different microchannel geometries (e. g. width, height) can be used to control the orientation (e.g. $\langle 100 \rangle$ vs $\langle 111 \rangle$) and interconnection of these ordered macroporous materials. This synthetic process provide a simple approach for patterning photonic crystals on substrates with controllable ordering length, dielectric contrast, orientation and interface.

9:15 AM **CC9.3**

HYBRID MICRO-OPTICAL SENSORS VIA SOL-GEL SOFT LITHOGRAPHY. Michael J. Lochhead, Mark Clarner, 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 (MIMIC) or microcontact molding. These approaches are from a class of elastomeric stamping and molding techniques collectively known as soft lithography. Soft lithography and sol-gel 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 sol-gel 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 micro-optics and micro-chemical sensor applications. Patterned 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 ORMOCERS - INORGANIC-ORGANIC HYBRID MATERIALS. Michael Popall, Ralf Buestrich, Fraunhofer-Institut fuer Silicatforschung, Wuerzburg, GERMANY; Alexander Dabek, Thomas Stolle, Technische Universitaet, Berlin, GERMANY; Mats Robertsson, IMC-Microsystems, Ericsson Components AB, Kista-Stockholm, SWEDEN; Joacim Haglund, Sima Valizadeh, IMC-Microsystems, Linkoeping, SWEDEN; Lubomir Cergel, Motorola SPS, Geneva, SWITZERLAND; Daniel Lambert, BULL, VLSI Packaging, Les Clayes-sous-Bois, FRANCE; Matthias Schaub, W.C. Heraeus, Thickfilm, Hanau, GERMANY.

Photopatternable hybrid inorganic-organic polymers with negative resist behaviour have been developed and tested for evaluation in optical and electrical interconnection technology. They are composed of inorganic oxidic structures cross-linked or substituted by organic groups. The synthesis starts from organosilane precursors reacted by sol-gel-processing in combination with organic crosslinking of polymerizable organic functions. As a result of these functionalities the properties of the ORMOCERS are adjusted to the particular applications. Systematic variation of composition combined with 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 electrical systems and devices as well as core and cladding for optical applications enables e/o applications with high integration levels. - Postbaking at moderate temperatures (120°C - 170°C) enables processing on low-cost substrates such as FR-4. - Easily adaptable to thin film technology: spin-on with planarisation $>90\%$, via diameters down to $20\ \mu\text{m}$ and high aspect ratio for optical waveguides have been achieved. Synthesis, modification of the resins towards technological needs, their thin film technology and the resulting demonstrators will be discussed.

10:30 AM ***CC9.5**

CHEMICAL DESIGN OF NANOSTRUCTURED LUMINESCENT MATERIALS. Thierry Gacoin, Arnaud Huignard, Jean-Pierre Boilot, Laboratoire de Physique de la Matiere Condensee, CNRS UMR, Ecole Polytechnique, Palaiseau, FRANCE.

Inorganic luminescent materials have practical applications in almost any 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 has increased the demand for materials with always better characteristics in term of stability, brightness and industrial processing ability. The synthesis of new materials concerns less the research of new chemical compositions than 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 dependant on the development of

new methods of elaboration. In this context, colloid chemistry offers versatile routes for the synthesis of non-agglomerated nanoparticles with a surface accessibility for passivation treatments and an ability to 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 colloid chemistry for the synthesis of nanosized particles with optimized optical properties. The obtention of core-shell nanostructures or manganese doped particles has lead to a decisive improvement of their luminescence quantum yields, opening the way to their applications as original inorganic phosphors. Moreover, the obtention of highly concentrated solutions, formed of thiol stabilized particles, allows the extension of the sol-gel process to the non-aqueous synthesis of transparent chalcogenide materials. Now, our work is focused on the adaptation 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. Mayo, Eric Lochner, A.E. Stiegman, 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 the films that permits, among other things, organic monomers to be photopolymerized at the surface. Metal-silica films of approximately $1\ \mu\text{m}$ were made by spin-coating a sol containing the metal complex catalyst and tetramethylorthosilicate onto a fused quartz or stainless steel substrate. Dried films of this sol were placed in an evacuated chamber under a layer of condensed vinylidene fluoride and irradiated ($>366\ \text{nm}$) 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 $900\ \text{\AA}$ 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 CHELATE STRUCTURE. Anne-Christine Franville, Rachid Mahiou, Daniel Zambon, Universite Blaise Pascal and ENSCCF, Laboratoire des Materiaux Inorganiques, Aubiere, FRANCE.

There is considerable interest in the optical properties of luminescent organic species in sol-gel glasses for applications as laser materials, waveguides or chemical sensors. Until now, very few is however reported on sol-gel derived organic-inorganic hybrid materials usable as luminophors for lamps or screens. In a previous paper¹, we have shown that stable and highly luminescent rare earth hybrids could be obtained by covalent grafting Eu^{3+} organic chelates to a siloxane based inorganic network. Suitable design of organic ligands allows to shield Ln^{3+} ions from their environment, to prevent clustering and also to improve absorption efficiencies of the derived compounds. Tailoring optical properties of these hybrid materials 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 sol-gel 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 ratio and synthesis conditions were previously used to modify the morphology, the 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 those of the corresponding organic complexes. 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 ^{29}Si 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 Gd^{3+} samples. As a result of ligand modifications, the absorption efficiency or the ability of the ligand to transfer the absorbed energy to Eu^{3+} and consequently the emission quantum yields are modified. In one particular case, hybrid materials exhibit different behavior ascribed 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 ORMOCERS FOR DIELECTRICAL AND OPTICAL INTERCONNECTION TECHNOLOGY. Ralf Buestrich, Frank Kahlenberg, Michael Popall, Fraunhofer-Institut fuer Silicatforschung, Wuerzburg, GERMANY; Joacim Haglund, Mats Robertsson, IMC-Microsystems, Linkoeeping, 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 in order to achieve reproducible low cost materials which are photo-patternable even in higher layer thickness 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: 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 and characterization (IR, ^{29}Si -NMR, (UV)-DSC, TG-MS, CTE) as well as photo-lithographic processing of ORMOCER materials will be presented.

SESSION CC10: BIOMATERIALS AND BIOGELS

Chairs: Shawn H. Phillips, Richard M. Laine and Albert E. Stiegman
Thursday Afternoon, April 27, 2000
Metropolitan III (Argent)

1:30 PM ***CC10.1**

SiO₂ ENTRAPMENT OF ANIMAL CELLS FOR BIO-ARTIFICIAL ORGANS. Giovanni Carturan, Dept of Materials Engineering, Trento, ITALY; Renzo Dal Monte, I.R.B., Altavilla, ITALY; Maurizio Muraca, Dept of Medical and Surgical Sciences, Padua, ITALY.

The Biosil method involves the sol-gel silicon oxide deposition directly on the surface of living cells by reaction of silicon alkoxides in gas 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/or to cells, (ii) a definite increase of the mechanical resistance and (iii) a valuable protection of encapsulated allogenic or xenogenic cells vs. immunological reaction. 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 Me_xSiH_yO_{2-1/2(x+y)} (x=0.3-0.5, y=0.1-0.2) resulted in the encapsulation of gels. 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 diffusion coefficients proper of the sol-gel hybrid silicon oxide were also calculated for proteins with different bulkiness. The specific functions of collagen-SiO₂ encapsulated hepatocytes were tested in the case of monoconjugated bilirubin production, ammonia removal, urea and diazepam metabolite productions. The kinetics of these hepatocyte-assisted reactions indicated maintenance of functions which in some cases is exalted after encapsulation. The biocompatibility of the Biosil membrane was tested performing *in vivo* experiments which indicate the possible extension of this encapsulation process to xenogenic biomass for permanent grafts. The definition of intrinsic mechanical properties was performed by flow experiments with different liquids at various speeds. Collected data concerning the features demanded to bioartificial organs may be useful to design operative devices.

2:00 PM **CC10.2**

SOL-GEL ENTRAPMENT OF ENZYMES. Laurie Bergogne, Souad Fennouh, Cecile Roux, Jacques Livage.

This text report on the encapsulation of two enzymes within a sol-gel silica matrix. The matrix have been synthesized from pure TMOS alcoxide by the two step sol-gel proces without adding alcohol and with different amount of water. The first enzyme entrapped has been a lipase. Both enzymatic activities have been studied hydrolysis and transesterification of esters. For a large amount of water, the kinetic parameters (Km, Vmax) are not very affected by the lipase encapsulation within a wet gel. But the enzymes loose their catalytic activity after the drying. An opposite effect is observed when the amount is little. Then enzyme-substrate affinity is better in wet and dried gel than in solution. More over, in 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 transesterification. The second example correponds 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 The enzymatic activity of B-galactosidase is mesured using p-nitrophenyl-B-D-galactopyranoside as a substrat. In the wet gel transmission electron microscopy of entrapped cells show that bacteria are randomly dispersed within the silica gel and retain their integrity. The Michaelis constant is Km=0.25 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 bacteria entrapped within a dried gel loose their integrity and then their catalytic activity.

2:15 PM **CC10.3**

BIOFUNCTIONALITY OF ENCAPSULATED BIOPOLYMERS IN INORGANIC MATRICES. Dae-Sung Yoon, Dean-Mo Liu, I-Wei Chen, Dept of Materials Science & Engineering, University of Pennsylvania, Philadelphia, PA.

Sol-gel methods have been used to encapsulate biopolymers in inorganic 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 alkoxide route. Instead, direct gelation of colloidal particles at room temperature and nearly neutral pH has proved to be effective for this purpose. Using different nanosized ceramic particles, we have also demonstrated an important size effect: the inter-ceramic-particle pores should not be much larger than the biomolecules; otherwise the latter's structural stability can not be preserved. Lastly, using inorganic sols 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 biomolecules will be discussed.

2:30 PM **CC10.4**

POROUS INORGANIC SUBSTRATES FOR HIGH DENSITY DNA ARRAYS. Curt Frank, Marc Glazer, Dept of Chemical Engineering, Stanford Univ, Stanford, CA; Jacqueline Fidanza, Glenn McGall, 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 1999) we demonstrated the concept of using a porous inorganic support to increase the density of probes for a given "2-D" area. A phase-separating sodium borosilicate glass was etched in a "subtractive" approach and stained with a fluorescent dye. Here we use a 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 (tetramethoxysilane) 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 order of magnitude 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 assays. 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. Jenna 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 biomolecule-doped sol-gel materials to biomedical sensor 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 L-glutamate at 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 encapsulation of streptavidin, 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 biotechnology applications because of the many biotinylated 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 BIODEGRADATION OF POROUS GELATIN-SILICATE HYBRIDS. Lei Ren, Kanji Tsuru, Satoshi Hayakawa, Akiyoshi Osaka, Okayama Univ, Dept of Bioscience and Biotech, Okayama, JAPAN.

Porous gelatin matrices have a 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 sol-gel process and freeze-drying techniques. Under stirring, 3-(glycidoxypentyl)trimethoxysilane (GPSM) was added into a gelatin and calcium nitrate solution to attain several GPSM/gelatin and Ca(II)/GPSM mass ratio. After gelation, the wet gels were soaked into an ammonia-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, TF-XRD and SEM. Biodegradability was evaluated by weight loss after the hybrids were soaked in a Tris(hydroxymethyl)aminomethane buffer solution. SEM observation demonstrated a network structure of heterogeneous pores with an average inner-diameter 250 micron for hybrids having GPSM/gelatin ratio=1. TF-XRD 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 GPSM content. Nevertheless, the biodegradation rate decreased with the concentration of the ammonia-formaldehyde solution at the same mass ratio of GPSM/gelatin. These results were discussed in terms of gelatin-GPSM-gelatin bridging.

4:00 PM CC10.7

THE SYNTHESIS AND CHARACTERIZATION OF DAM-1 TYPE MATERIALS. Kenneth J. Balkus, 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 important anti-oxidant 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 silica phase referred to as DAM-1 (Dallas Amorphous 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

THE U.S. ARMY REACTIVE TOPICAL SKIN PROTECTANT (RTSP): CHALLENGES AND SUCCESSES. Stephen T. Hobson, Erich K. Lehnert, Ernie H. Braue, Drug Assessment Division, U.S. Army Medical Research Institute of Chemical Defense, Aberdeen Proving Ground, MD.

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 (rTSP's). 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 include organic polymers, organic/inorganic hybrid materials, polyoxometallates (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 sulfur mustard (HD) and a representative nerve agent, soman (GD), using a penetration cell model coupled to a continuous

air monitor and also by in vivo testing. Composite materials with optimum reactive compounds exhibit a 97% reduction of GD vapor break-through after 20 hours (from 9450 ng to 317 ng) and a 3.6 fold increase (from 162 min 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 break-through after 20 hours (from 4040 ng to 16 ng), a 2.3 fold increase (from 524 min to >1200 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...)

Chairs: Michael Popall, Bruce S. Dunn and

Thierry Gacoin

Friday Morning, April 28, 2000

Metropolitan III (Argent)

8:30 AM *CC11.1

PREPARATION OF ORGANIC-INORGANIC NANOCOMPOSITES (NANOMERS) FOR OPTICAL APPLICATIONS. M. Mennig, P.W. Oliveira, P. Rogin, A. Gier, H. Schmidt, Institute for New Materials, Saarbruecken, 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 hydrolysis 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 ligands (methacrylic acid, organosilanes). These nanoparticulate 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 these 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 stampers and subsequent UV-curing. The patterns can be cladded 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 abraser test and therefore can be useful for product protection.

9:00 AM CC11.2

PATTERNING OF PHOTOACTIVE THIN FILM SILICA MESOPHASES. Dhaval A. Doshi¹, Nicola Huesing², Hongyou Fan¹, Alan J. Hurd³, C. Jeffrey Brinker^{1,3}, 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 mesostructured materials with tunable pore sizes and arrangements and good compositional control. A variety of macro- and microstructures have been synthesized such as powders, fibers, monoliths, thin films, hollow and transparent hard spheres and aerosol particles. Thin films are one of the most promising applications of so-called mesostructured materials, and the ability to build hierarchical structures and functionality is the key to their successful implementation in future micro-systems. Recently, so-called micro-contact printing (μ CP) 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 1-step negative resist process) and allows patterning of thin film mesostructure, refractive index, and wetting behavior. The process involves incorporation of a photoacid generator in the coating sol. Dip/spin coating results in the formation of a photoactive mesostructured thin film. Selective UV exposure through a mask results in localized photoacid generation. We exploit the pH sensitivity of supra-molecular self-assembly by affecting the silica condensation kinetics and also the mesophase formation, 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 is of interest for sensor arrays, nano-reactors, photonic and fluidic devices, and low dielectric constant films.

9:15 AM CC11.3

Abstract Withdrawn.

9:30 AM CC11.4

CROSSLINKED ORGANIC-INORGANIC HYBRID THIN FILMS FOR CORROSION RESISTANCE: SPECTROSCOPIC AND SALT SPRAY CHARACTERIZATION. Tammy Metroke, 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 2024-T3 aluminum. Solid state ^1H - ^{13}C CP/MAS NMR results indicate that primary aliphatic amines and super acids are effective crosslinkers for epoxide groups in ormosils. Accelerated salt spray and filiform tests have been conducted in order to study the corrosion resistance behavior of ormosil thin films before and after crosslinking. The choice of curing agent was found to influence the film structure and corrosion resistance properties. Amine cured thin films were hard and highly adherent to the aluminum alloy substrates, exhibiting good bare and filiform 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

PREPARATION AND CHARACTERIZATION OF PHOTO-PATTERNABLE BaTiO_3 /POLYMER COMPOSITES. R. Popielarz, C.K. Chiang, R. Nozaki and J. Obrzut, Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD.

Feasibility of preparation and photopolymerization of high dielectric constant BaTiO_3 /acrylic resin composites has been evaluated. A series of the photocurable resin formulations were prepared and photocured into thin wafers. Up to 45 vol% (82 wt%) of BaTiO_3 loading into the resin has been achieved. It was found that up to 100 μm thick wafers of highly crosslinked BaTiO_3 /polymer composites can be prepared by the photopolymerization technique within the entire range of BaTiO_3 loadings. Dielectric permittivity of the materials was investigated at frequencies from 100 Hz to 10 GHz and temperatures from -140°C to $+140^\circ\text{C}$. The dielectric constant of the photopatternable composites based on an acrylic resin exceeded 30 at highest BaTiO_3 loadings. An empirical relationship between the BaTiO_3 content and dielectric constant of the composite has been established.

10:30 AM CC11.6

CONTROLLED SYNTHESIS OF PERFLUOROARYL FUNCTIONALIZED HYBRID MATERIALS FOR OPTICAL APPLICATIONS BASED ON NMR SPECTROSCOPY AND MOLECULAR MODELING. Frank Kahlenberg, Ralf Buestrich, Michael Popall, Fraunhofer-Institut fuer Silicatforschung, Wuerzburg, 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 organoalkoxysilanes by ^{29}Si -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

ELECTRICAL CHARACTERISTICS OF METAL-SELF-ASSEMBLED-MONOLAYER-STRUCTURES. Martin Rittner, Frank Buckel, Markus Schuetz, Steffen Seifritz, Franz Effenberger, Heinz Schweizer, Universitaet Stuttgart, 4. Physikalisches Institut, Stuttgart, GERMANY.

Self-assembling of molecular monolayers offers an effective and simple tool to get very thin films on different substrates. New application fields can be opened up by introducing these new materials in electronic devices like transistors or sensors. Under examinations are the electrical characteristics of capacity test structures consisting of a mesoscopic ($200\ \mu\text{m} \times 200\ \mu\text{m}$) metal contacts on the self-assembled monolayer (SAM). One group of monolayers is formed by Trichlorosilanes bonded on silicon dioxide. Two types of silicon dioxide are used: Native silicon dioxide on Si (100) wafers made in Piranha-solution and plasma deposited silicon dioxide on silicon wafers made by ECR-PECVD process. The second group of monolayers is formed by Aldehydes with and without functionalized endgroups on hydrogen terminated Si (111) Wafers. The metalization is formed by standard photolithographical processes including e-gun evaporation of gold and aluminum. Octadecyl-Trichlorosilane (OTS) improves the isolation behavior of the native oxide. The current density is reduced by two orders of magnitude and the breakdown voltage is increased. Strong non-linear current-voltage-characteristics of the metal-insulator-semiconductor (MIS) structure are observed using phenoxy-functionalized Aldehydes on highly doped p-silicon. Less marked non-linear behavior is found using doped and highly doped n-silicon. From our results we expect new transistor-devices with high transconductance consisting of self-assembled monolayers on silicon substrates and silicon dioxide substrates.

11:00 AM CC11.8

STIFFNESS IMPROVEMENTS AND MOLECULAR MOBILITY IN EPOXY-CLAY NANOCOMPOSITES. Xavier Kornmann, Lars Berglund, Lulea Univ, Div of Polymer Engineering, Lulea, SWEDEN; Henrik Lindberg, Lulea Univ, Div of Wood Material Science, Skelleftea, SWEDEN.

Intercalated and delaminated nanocomposites based on a glassy epoxy matrix and an organophilic clay were synthesised 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 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 of 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 T_g of 20°C towards lower temperature was observed for the epoxy-clay nanocomposites cured at 160°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 Shu-Jen 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 triethoxysilane, phenyl triethoxysilane, and Titanium(IV) *n*-butoxide. The prepared hybrid materials show excellent thermal stability and without phase separation. The AFM study suggests that the prepared hybrid thin films have excellent planarization. For the PMMA-silica hybrid thin films, the refractive indices of the prepared hybrid thin films at 190-900 nm can be controlled by the side 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 off-resonant refractive indices of the PMMA-titania hybrid thin films were in the range of 1.505 to 1.553, which linearly increase with the titania content. The shift of the absorption maximum of the prepared hybrid thin films from 230 nm to 310 nm can be correlated with the titania content. The hybrid polymer films have the abbe numbers all above 30. The prepared hybrid films show very high optical transparency in the visible region. These results suggest that the prepared hybrid films have potential applications for optical devices.

11:30 AM CC11.10

NEW MICROPOROUS CATALYSTS FROM MOLECULAR ENGINEERING AND CO-POLYMERISATION. Bruce W. Manson,

Paul-Alain Jaffres, Russell E. Morris. School of Chemistry, University of St. Andrews, St. Andrews, Fife, UNITED KINGDOM.

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 $(R_3SiO_3/2)_8$ 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 hydrosilylation 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 Swearingen, 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 unreactive 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. Trimethylchlorosilane, which can be used to derivatize silica, would not react with the titania. Alkylalkoxysilanes, such as dimethyldimethoxysilane, 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