

solvents. The researchers had previously shown that the extremely high dipole moment of merocyanine results in large dimerization constants ($K_{\text{dim}} > 10^6 \text{ M}^{-1}$) in low-polarity solvents. In addition, the chromophore's highly polarizable π system provides functionality.

While the substituted merocyanine dimers were shown by UV-vis absorption spectra to be stable in low-polarity solvents, even at low dilution levels, the substituted bis(merocyanine) dyes displayed absorption bands associated with three distinct species. In addition to the monomer band, two blue-shifted bands were observed, that is, their blue shift depended on the solvent. The researchers reported that observation of the less blue-shifted band indicated supramolecular polymerization by way of the two receptor sites in each molecule. Furthermore, observation of the bands that were more blue-shifted suggested to the researchers a further aggregation of the polymeric strands, which formed a more stable assembly. As dye concentration increased, a lyotropic mesophase formed, followed by a solvent-free film with an unusual liquid-crystalline texture. X-ray diffraction of the film revealed hexagonal columnar order with a lattice constant of 4.34 nm, which was in good agreement with rod size determined in a transmission electron microscope.

The researchers conclude that a hierarchical growth process occurs in the structures. As solvent polarity is reduced, each of the two chromophores in the bis(merocyanine) dye dimerizes with another dye in an antiparallel manner. The resulting randomly coiled fibrils fold into helical conformations. Six helices then intertwine to form a densely packed rod with the tridodecyloxybenzyl substituents on the outer, solvent-accessible surface, which is favorable in low-polarity solvents. At higher concentrations, interdigitation of the alkyl substituents leads to a decrease in the rod diameter as mesophases and gels are formed. The researchers said that the tubular structure of their dye aggregates is similar to chlorophyll dye rod elements in the chlorosomes of photosynthetic bacteria. In addition, they envision "fascinating possibilities [that] might arise for merocyanine dye assemblies, especially if their intermolecular arrangement could be changed."

STEVEN TROHALAKI

Functionalizable, Biodegradable, and Protein-Resistant Polymer Fabricated

Protein-resistant materials have wide applications in tissue regeneration, drug

delivery, and systems for both patterned cell cultures and high-throughput screening of proteins or cells. Poly(ethylene glycol) (PEG) as a main chain polyether has been shown to be a good candidate, except for its functionalization limits and non-biodegradability. Also, the involvement of carbohydrate moieties in self-assembled monolayers and polymeric materials has shown superior protein resistance. Combining these two merits, Z. Guan, M. Metzke, and J.Z. Bai of the University of California—Irvine designed a side-chain polyether constructed from the

carbohydrate-derived monomers. In addition, this polymer can be degraded by hydrolysis of the ester linkage between the repeating units. The researchers reported their work in the July 2 issue of the *Journal of the American Chemical Society*.

During preparation, the diol monomer was made from a commercially available reduced sugar. Its primary hydroxyl groups were protected with a trityl group, and its secondary hydroxyl groups were permethylated with iodomethane under a basic condition. Another diacid chloride monomer was then obtained from the diol



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monomer's further oxidations followed by treatment with thionyl chloride. The side-chain polyether was then formed by step-growth homogeneous solution polymerization. Its number-averaged molecular weight was 29,000 g/mol and its weight-averaged molecular weight was 44,000 g/mol. The measurement data from surface plasmon resonance spectroscopy showed the synthetic materials to have excellent protein resistance.

This carbohydrate-derived side-chain polyether material combines functionalizability, biodegradability, and protein resistance. Guan's group is now studying the influences of various structural permutations on the biocompatibility and biodegradability of this family of polymers.

YUE HU

Mesostructured Silica Thin Films with Spherical Voids Organized in a BCC Array Achieved

In the development of the microelectronics industry, device physics is not the only limiting factor for continued performance improvements in systems. Challenges remain in carrying electric power, and distributing clock signals that control the timing and synchronize the operation. The propagation velocity of electromagnetic waves will become increasingly important due to their unyielding constraints on interconnect delay. The introduction of Cu and low- κ dielectrics has incrementally improved the situation, as compared to the conventional Al/SiO₂ technology, by reducing both resistivity and capacitance between wires. Silica materials composed of nanometer-scale isolated, but ordered, pores, exhibiting low dielectric constants and good mechanical properties, are highly desirable for future semiconductor devices. In the January issue of *Advanced Functional Materials* and September issues of *Langmuir*, K. Yu of the National Research Council Canada, C.J. Brinker of Sandia National Laboratories, and their colleagues have published a series of articles on the synthesis and comprehensive characterization of mesostructured methyl-

silica (CH₃-SiO_{3/2}) thin-films consisting of isolated spherical voids organized in a body-centered cubic (bcc) array. The closed porosity and controlled hydrophobicity should yield low dielectric constant values for these thin film materials.

The films were synthesized on silicon substrates using solvent evaporation-induced sol-gel and self-assembly processes (EISGSA), with polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) as a structure-directing agent and MTES (CH₃-Si(OCH₂CH₃)₃) as the silica precursor. Afterwards, pyrolysis in argon was performed carefully to remove the template. This synthetic approach was designed to suppress the condensation of the inorganic network allowing co-self-assembly of the silica and the amphiphile PS-*b*-PEO, followed by retraction of the PEO chains from the silica matrix and matrix consolidation to occur unimpeded. The researchers proposed a solvent-mediated formation mechanism for the absence of microporosity.

An unusual transmission electron microscopy (TEM) approach was developed to resolve the mesostructure. This approach involved sample tilting to obtain different zone axes, simulation, as well as the calculation of plane spacings and angles for comparison of the experimental values with corresponding theoretical ones. The mesostructure was conclusively found to be body-centered cubic (bcc) rather than face-centered cubic (fcc). In addition, the bcc mesostructure with a slight distortion was assigned to a body-centered tetragonal (bct) structure with $a = 13.5$ nm and $c = 13.0$ nm. Two types of dislocations were observed by TEM: an edge dislocation and a dislocation dipole. The development of the edge dislocation was argued to partially relieve the tensile strain developed during the film shrinkage in the fabrication process; the researchers proposed a new concept, namely critical mesostructure thickness for the occurrence of the stress relaxation, which was computed using an elastic strain energy argument. The bcc mesostructure

was also confirmed by grazing incidence small-angle x-ray scattering (GISAXS).

In addition to the mesostructure, the researchers characterized the microstructure thoroughly, using nitrogen sorption and gas permeation measurements, in addition to TEM and GISAXS. The GISAXS study indicated that there was essentially no microporosity in the calcined film. The absence of microporosity was also in agreement with surface acoustic wave nitrogen sorption thin film measurements, a technique suitable for the characterization of pore sizes larger than 0.4 nm. Magic angle spinning solid-state ²⁹Si and ¹³C nuclear magnetic resonance and the GISAXS experiments proved the maintenance of Si-CH₃ bonds in the film after pyrolysis in argon. The presence of the methyl ligands after calcination was also in agreement with the contact angle measurement of ~115°.

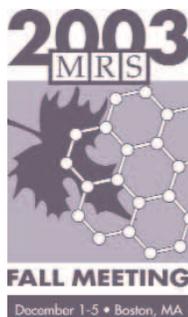
The self-assembled MTES-derived silica thin film with isolated bcc-arranged voids provides a conceptual route to the fabrication of materials with nanosized voids arranged in a cubic array as well as with controllable hydrophobicity. The researchers said that "concerning the utilization of porous materials as low- κ dielectric insulators, cubic arrangements of isolated spherical pores are expected to maximize the modulus for a given porosity. Thus, the PS-*b*-PEO-templated films and related ordered closed porosity films should be of general interest to the microelectronics community."

MAXIM NIKIFOROV

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