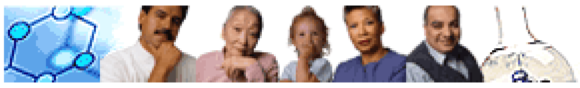

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Heart Cut

March 14, 2005

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- Stable, ultralow – dielectric constant organosilicate films
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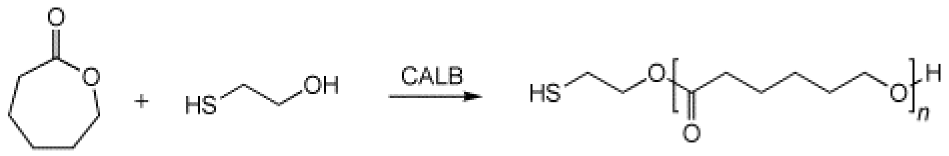
Polycaprolactone can be thiol-end-functionalized by lipase catalysis. M. Martinelle and co-workers at the Royal Institute of Technology, Stockholm, report that the ring-opening polymerization of e-caprolactone (**1**) at 60 ºC in the presence of mercaptoethanol and the enzyme *Candida antarctica* lipase B (CALB) produces poly(e-caprolactone) with thiol end groups (**2**). This structure is of interest because of the affinity of thiols to gold and other precious metals and the possibility of using this favorable interaction to create nanoscale devices for electronics and medicine.

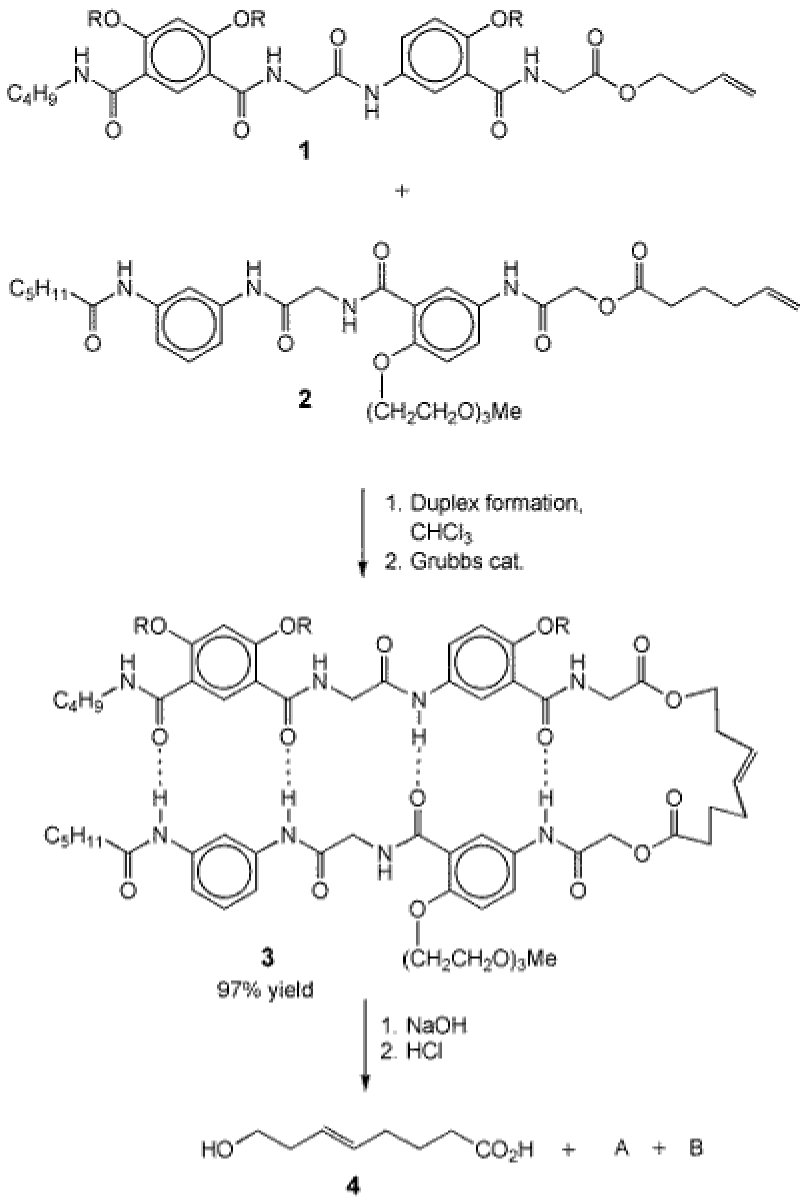


1 **2**

The authors demonstrated that in the absence of the sulfur compound, this reaction produces unmodified polycaprolactone. Other sulfur-terminated polymers were synthesized under similar conditions, producing polycaprolactone modified by mercaptopropionic acid, for example. The method appears to be capable of producing a wide range of potentially interesting polymers that are suitable for ligation to precious metals. (*Macromolecules* **2005**, *38*, 647 – 649; David A. Schiraldi) Go to top

Selectively alkylate secondary amines in the presence of primary amines. F. Laduron and co-workers at Johnson & Johnson (Belgium) selectively alkylated secondary amines in a one-pot process using methyl isobutyl ketone (MIBK) as solvent and as a temporary protecting group. For example, they heated 4-aminomethyl-3-hydroxypiperidine hydrochloride in MIBK with Na_2CO_3 and 1-chloro-3-methoxypropane to give, after hydrolysis, the alkylated secondary amine with a free primary amino group. The yield was 85%, and the purity (by gas chromatography) was 99%. Similarly selective *tert*-butoxycarbonyl protection of secondary amines can be achieved in high yield and purity. (*Org. Process Res. Dev*. **2005**, *9*, 102 – 104; Will Watson) Go to top

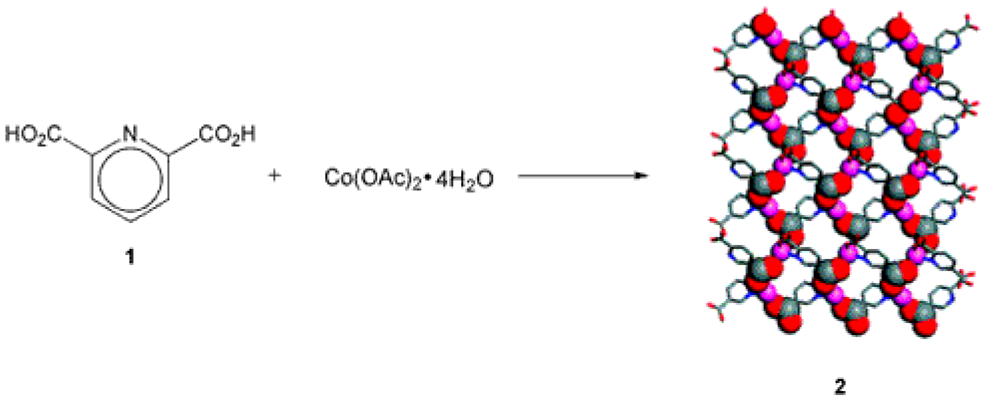
Control olefin metathesis reactions with hydrogen-bonded templates. Linear oligoamide strands can pair with complementary strands to form sequence-specific hydrogen-bonded duplexes. X. Yang and B. Gong* at the State University of New York attached olefin-bearing structures to the ends of separate A and B oligoamide strands to form structures **1** and **2**, which then generated the hydrogen-bonded duplex with the olefin units in close proximity. They treated the resulting template with the Grubbs catalyst to form the olefin metathesis reaction cross-product (**3**) in very high yield.



R is *n-octyl*. This method was used to synthesize the desired olefinic product 8-hydroxyoct-5-enoic acid (**4**), which was recovered by cleavage from the template by saponification. The authors found that the metathesis reaction occurred with extremely high selectivity, and no homodimeric products were observed. The original template strands could also be recycled for further reaction.

This approach has the advantage of being combinatorial, so that simply mixing a group of five olefins tethered to the A strand with five different olefins tethered to the B strand leads to 25 combinations. This contrasts with covalently linked olefins in which all 25 combinations must be synthesized first before they can be tested. (*Angew. Chem., Int. Ed*. **2005**, *44*, 1352−1356; W. Jerry Patterson) Go to top

Build helical coordination polymers from achiral reagents. Helicity is an important structural motif used by nature to assemble chiral molecules into helical polymers, as illustrated by the famous DNA double helix. Generating helical polymers in the laboratory is of great interest to scientists, but the building blocks, the auxiliaries, or the environment must be chiral. The accepted principle has been that helicity cannot be created from achirality. However, G. Zhu, S. Qiu, and co-workers at Jilin University, Changchun, China, and Y. Wei at Drexel University, Philadelphia, report a seemingly impossible system in which a helical strand is generated from achiral materials under achiral conditions.



When a mixture of pyridine-2,5-dicarboxylic acid (H$_2$PDC, **1**) and Co(OAc)$_2$•4H$_2$O suspended in deionized water was heated in a sealed autoclave at 180 ºC for 3 days, a 2-D coordination polymer, Co (PDC)(H$_2$O)$_2$•H$_2$O (**2**), was formed. Although no chiral reagents, solvents, or auxiliaries were used in the synthesis, the resultant crystalline polymer contained helical chains with preferred handedness, as evidenced by the strong signals in its vibrational circular dichroism spectrum. The authors reasoned that the organic ligand may have acted as a structure-directing agent to induce the coordination polymer chain to rotate helically in a screw sense. (*Chem. Commun*. **2005**, *11*, 1396–1398; Ben Zhong Tang)

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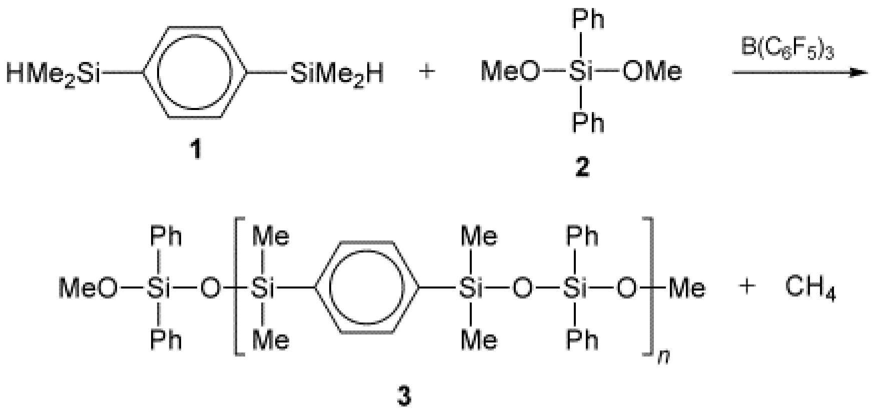
Make ultralow–dielectric constant organosilicate films with the help of ethyl acrylate–capped thermally labile porogens. Low (*k* ≤ 2.5) and ultralow (*k* ≤ 2.0) dielectric constant materials are desirable in high-performance integrated circuits because they lower line-to-line noise in interconnect conductors and minimize power dissipation by reducing the capacitance between the interconnects. Unfortunately, wholly organic materials with low *k* suffer from poor thermal and mechanical stability.

Polysilsesquioxanes make up a family of composite materials that have organic species periodically incorporated into a silicate matrix. These materials have relatively low dielectric constants (*k* ~ 2.7), minimal moisture uptake, and good thermal stability (>400 °C). One strategy to lower the *k* value further is to create air holes in the bulk materials.

M. Ree and co-workers at the Pohang University of Science and Technology, Republic of Korea, show that ethyl acrylate–capped polypropylenimine dendrimers are fully miscible in any proportion with a polymethylsilsesquioxane (PMSSQ) precursor. When the dendrimer porogens are thermally decomposed, closed spherical pores of <2.0 nm radius and narrow size distribution are created. The pore size and distribution are the smallest and the narrowest, respectively, ever achieved in spin-on dielectrics. The thin films produced from these materials had *k* values as low as 1.66. Thus, this method delivers low- and ultralow-*k* PMSSQ dielectric films that should be useful in advanced integrated circuits. (*Nature Mater*. **2005**, *4*, 147–151; George Xiu Song Zhao) Go to top

Make polysiloxanes from silanes and alkoxysilanes. Polysiloxane polymers are generally produced by ring-opening reactions of cyclic monomers or by polycondensation of silane with unsaturated siloxane monomers. The latter reaction is highly efficient but requires significant amounts of precious metal catalysts. S. Rubinsztajn* and J. A. Cella of General Electric report the facile synthesis of polysiloxanes (**3**) from bissilanes (**1**) and bis(alkoxy)silanes (**2**) in the presence of the Lewis acid catalyst tris(pentafluorophenyl)borane.

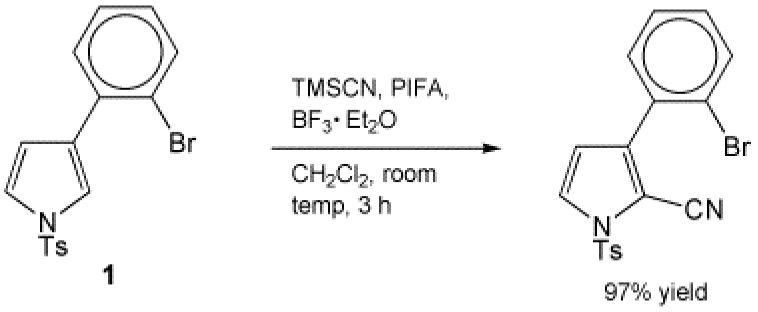


The reactions typically were carried out at 0 °C for 2 h, then at 50 °C for 1 h to complete the polymerization. The authors produced a wide range of polysiloxane structures with molecular weights in the 12,000–53,000 range. (*Macromolecules* **2005**, *38*, 1061–1063; David A. Schiraldi) Go to top

Functionalize mesoporous silica using free-radical polymerization. The functionalization of mesoporous materials by in situ synthesis or post-synthesis modification has been researched extensively. The primary objectives are to create high-performance catalysts and adsorbents on one hand, and improve the thermal stability of the materials on the other. R. Ryoo and co-workers at the Korea Advanced Institute of Science and Technology, Daejeon, describe an alternative route to functionalization.

Free-radical polymerization of a vinyl monomer (e.g., styrene, *p*-chloromethylstyrene, 2-hydroxyethyl methacrylate, and methacrylic acid) inside mesoporous silica yields a composite material with a layer of polymer coated onto the internal surface of the silica. Such a composite displays enhanced adsorption capacity toward hemoglobin. Further modifying the composite material by sulfonation produces an acid catalyst that shows remarkably enhanced activity and selectivity for esterifying benzyl alcohol with hexanoic acid, compared with bulk polymer resins. (*J. Am. Chem. Soc*. **2005**, *127*, 1924–1932; George Xiu Song Zhao) Go to top

This iodine reagent promotes a range of cyanation reactions. Y. Kita and co-workers at Osaka University, Japan, have used the remarkable oxidizing features of hypervalent iodine(III) to mediate the cyanation of electron-rich aromatic substrates such as pyrroles, thiophenes, and indoles. In a typical reaction, they treated *N*-*p*-toluenesulfonylpyrroles (**1**) with phenyliodine bis(trifluoroacetate) (PIFA), using trimethylsilyl cyanide (TMSCN) as a CN^- source.



Cyanation occurred primarily at the 2-position. Protecting the pyrrole nitrogen as the tosylate was crucial because attempts to cyanate the unprotected pyrrole gave only biaryl coupling products. Monosubstituted pyrroles generally gave excellent yields of the cyanation product, whereas di- and trisubstituted pyrroles gave somewhat poorer results. Cyanation of thiophene and indole substrates also occurred exclusively at the 2-position, but gave reduced product yields compared with pyrrole. This method offers a useful solution to the difficult synthesis of 2-substituted 3-arylpyrroles, and the cyano group can be converted to other functionalized structures. (*Org. Lett*. **2005**, *7*, 537 − 540; W. Jerry Patterson) Go to top

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