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navigate the section

> Heart Cut

> Heart Cut Archive

> Patent Watch

> Patent Watch Archive

> HCPW Contributors

search

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quick find

-choose a page-

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Heart Cut

April 4, 2005

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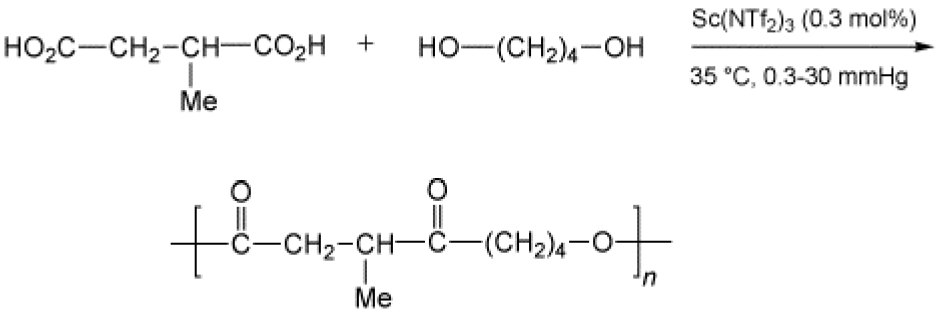
Epoxysilica nanoparticles can be used to cross-link polymers. A. Harwig*, M. Sebald, and M. Kleemeier of Fraunhofer-Institut für Fertigungstechnik und Angewandte Materialforschung, Bremen, Germany, report that silica nanoparticles that are surface-functionalized with epoxide groups can react with cycloaliphatic epoxides to produce cross-linked polymers. They first functionalized fumed silica with 3,4-epoxycyclohexylethyltrimethoxysilane to produce the reactive nanoparticles. Then they cationically polymerized cyclohexene oxide in the presence of 0–50 wt% of the epoxysilica.

As the silica level increased, the gel fraction of the product increased and the glass-transition temperature decreased. Polymer storage modulus generally increased with increased filler and cross-linking levels. The insoluble fraction of these nanocomposites comprised polymer-coated nanoparticles connected by 3-D polymer-bridged networks. (*Polymer* **2005**, *46*, 2029–2039; David A. Schiraldi) Go to top

This “green” polyester synthesis uses scandium catalysts. Aliphatic polyesters are useful industrial plastics that are environmentally benign because they biodegrade. However, their synthesis typically requires high temperatures (>250 °C) and very low pressures. A. Takasu and co-workers at the Nagoya Institute of Technology, Japan, report an elegant solution to this problem that allows the polycondensation to proceed at 35 °C and only moderately reduced pressure. The key to their method is the use of catalytic amounts of scandium trifluoromethanesulfonimide [$Sc(NTf_2)_3$] or scandium trifluoromethanesulfonate [$Sc(OTf)_3$].



$$HO_2C-CH_2-\underset{Me}{\underset{|}{CH}}-CO_2H + HO-(CH_2)_4-OH \xrightarrow[35\ °C,\ 0.3\text{-}30\ mmHg]{Sc(NTf_2)_3\ (0.3\ mol\%)} \left[-\overset{O}{\overset{\|}{C}}-CH_2-\underset{Me}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-O- \right]_n$$

1

A typical bulk (melt) polycondensation yielded 96% polymer with a molecular weight (M_n) of 12,200. The catalytic activity of $Sc(NTf_2)_3$ was greater than that of $Sc(OTf)_3$, as demonstrated in the preparation of poly(butylene methylsuccinate) (**1**), in which using $Sc(NTf_2)_3$ resulted in a polymer M_n of 12,000, compared with 5,900 using $Sc(OTf)_3$.

Both catalysts are easily recovered by water extraction and can be recycled for subsequent polyesterifications. The mildness of this polymerization method may allow the use of monomers having chirality, reactive functional groups, or biological activity. (*Macromolecules* **2005**, *38*, 1048–1050; W.

Jerry Patterson) Go to top

Direct laser writing gives 3-D spiral photonic crystals. H. Misawa and coauthors at Hokkaido University, Sapporo, Japan, and the University of Tokushima, Japan, have developed a two-photon direct laser writing method—a “top-down” approach as opposed to conventional layer-by-layer techniques—for making 3-D photonic crystals with “square-spiral” architectures. Most importantly, linear defects, which can serve as waveguides, could be created during fabrication.

Because of the low refractive index contrast of the SU-8 photoresist material and other limitations, the authors could not achieve a full photonic bandgap in the material. However, the thermal stability of the SU-8 photoresist (up to 380 °C) allowed the 3-D spiral architecture to serve as a template into which high-refractive-index materials could be infiltrated by techniques such as the sol–gel method, low-temperature chemical vapor deposition, and the double templating method. (*Adv. Mater*. **2005**, *17*, 541–545; George Xiu Song Zhao) Go to top

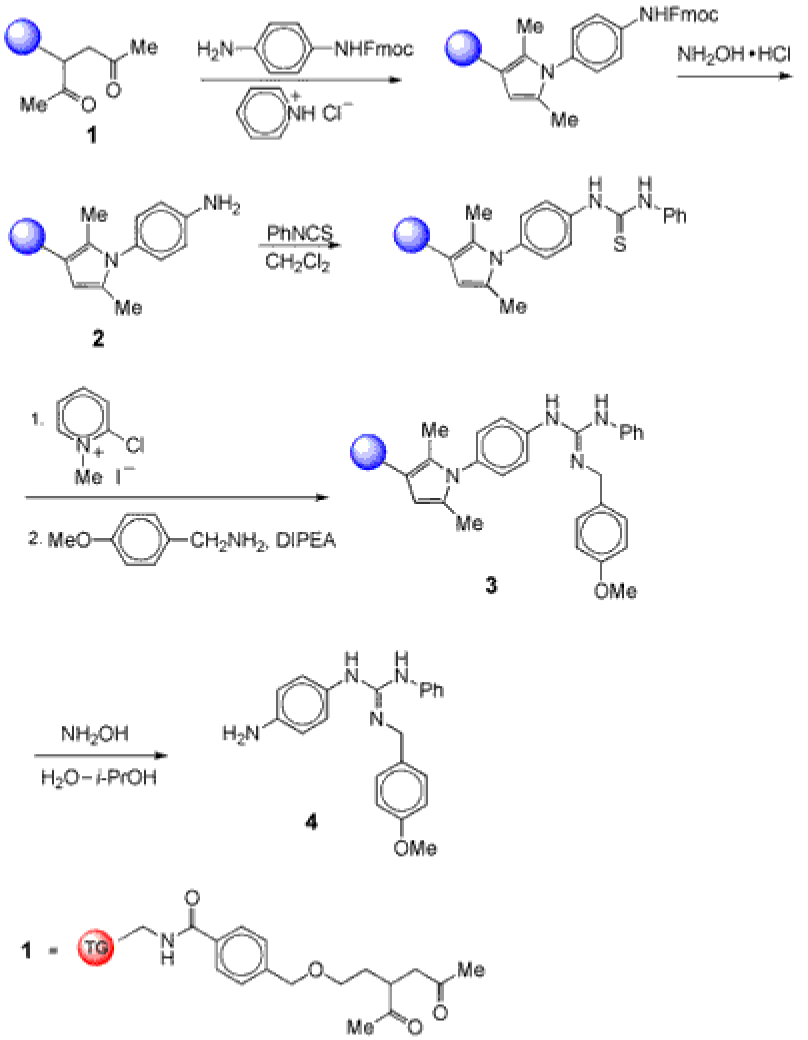
Transparent polymer–clay gels can have significant mesoscopic structure. G. Schmidt and coauthors at Louisiana State University, Baton Rouge, the National Institute of Standards and Technology, Gaithersburg, MD, and Technion-Israel Institute of Technology, Haifa, combined aqueous solutions of poly(ethylene oxide) and synthetic hectorite to produce hydrogels. The gels were optically transparent, but the authors showed that they have structure on the micrometer scale, presumably because the indexes of refraction of the two phases match each other.

Scanning electron microscopy of freeze-fractured surfaces of the gels showed an extended lacelike network in which the clay platelets are covered with 1.5-nm polymer coatings. The gels can be drawn into meter-long fibers, which apparently obtain structural strength from the aggregation of clay platelets into fibrous polymer-enclosed bundles. (*Macromolecules* **2005**, *38*, 2047–2049; David A. Schiraldi) Go to top

A diketone linker masks primary amines on a solid support. In their studies of biologically active guanidine derivatives, M. Botta, F. Corelli, and co-workers at the Università degli Studi di Siena, Italy, developed a polymer-supported reagent that protects primary amines as pyrroles, thereby allowing subsequent functionalization steps. The authors selected the pyrrole ring in part because it is non-ionizable, non-nucleophilic, and stable in the presence of strong bases and reducing agents. The pyrrole structure could be easily cleaved to recover the free amine.

The diketone linker reagent (**1**) was formed in five steps starting from the commercial resin TentaGel S-NH_2 (TG). The efficiency of this method was demonstrated by reacting **1** with Fmoc-protected *p*-anisidine to form the pyrrole, then regenerating the free amine (**2**) with $NH_2OH \cdot HCl$. Pure *p*-anisidine was recovered quantitatively.

The authors then converted **2** to guanidine derivatives (**3**) of the protected amine. The desired guanidine-substituted primary amine (**4**) was recovered in 90% yield by opening the pyrrole ring.

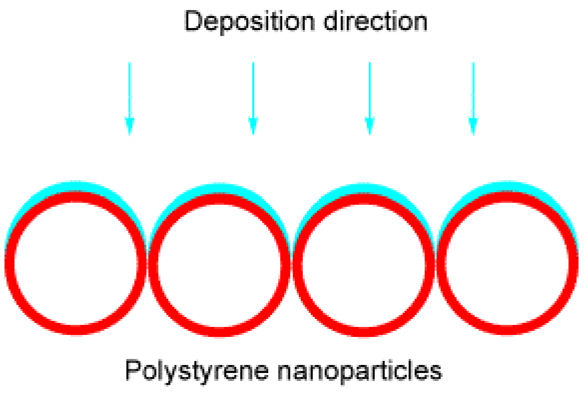


Fmoc is 9-fluorenylmethoxycarbonyl; DIPEA is diisopropylethylamine. The authors extended this method to preparing small libraries of compounds by parallel synthesis. (*Org. Lett.* **2005**, *7*, 565–568; W. Jerry Patterson) Go to top

What is the best route to *cis*-3-methylamino-4-methylpiperidines? D. H. Brown Ripin and coworkers at Pfizer considered several routes to this useful drug intermediate and selected two for further investigation. Their initial work centered on an electrochemical approach starting from 4-methylpiperidine carbamate. The yield over three steps was acceptable at 35%, but the lack of suitable intermediates for purification meant that the final product required chromatographic separation.

The successful alternative strategy was the reduction of the methyl carbamate of 3-amino-4-methylpyridine by catalytic hydrogenation. It was used to produce multikilogram quantities of *cis*-*N*-benzyl-3-methylamino-4-methylpiperidine in 55% overall yield over four steps. (*Org. Process Res. Dev*. **2005**, *9*, 51–56; Will Watson) Go to top

Magnetic multilayer films on nanospheres have unusual, and advantageous, properties. M. Albrecht and coauthors at the University of Konstanz, Germany, and the Hitachi San Jose Research Center, CA, demonstrate that a substrate with a curved surface can impart unusual properties to thin films. For example, they deposited magnetic multilayer Pd–Co films (blue in the figure) onto a topographic pattern formed from spherical polystyrene nanoparticles (red) and discovered that the resulting magnetic material has several advantages over flat films.



The nanostructures are monodisperse, magnetically isolated, and single-domain; and they have uniform magnetic anisotropy with an unexpected switching behavior that is induced by their spherical shape. In addition, changing the deposition angle with respect to the particle ensemble makes it possible to tailor the orientation of the magnetic anisotropy, resulting in “tilted” nanostructured materials.

The authors anticipate that their work will lead to further manipulation of curved surfaces in materials science. Any material with strongly thickness-dependent properties (e.g., superconductors and optical materials) is a potential candidate for magnetic multilayer deposition. (*Nature Mater*. **2005**, *4*, 203－206; George Xiu Song Zhao) Go to top

Here is a demonstration of the similarity between the solution and solid-state structures of crystalline materials. It may seem intuitive that during crystallization, the solid-state structure should be similar to the structure of the dissolved material that immediately precedes it, but this is a difficult concept to demonstrate unambiguously in an experiment. R. J. Davey and co-workers at the University of Manchester, U.K., studied tetrolic acid ($MeC{\equiv}CO_2H$), an alkynecarboxylic acid that can crystallize into two different polymorphs.

Crystallizing tetrolic acid from $CHCl_3$ produces the a form of the material, whereas EtOH solutions produce its ß form. IR spectroscopy can be used to differentiate between the two forms. When IR was used to characterize nearly saturated solutions of tetrolic acid in each solvent, the spectra clearly showed bands consistent with the crystalline form that would eventually precipitate from that solution; the alternate structure was completely absent. Thus, this work demonstrates a direct link between the solution and solid-state structures of crystalline materials. (*Chem. Commun*. **2005**, 1531－1533; David A. Schiraldi) Go to top

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