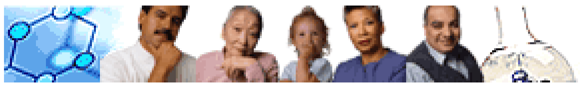

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Heart Cut

March 28, 2005

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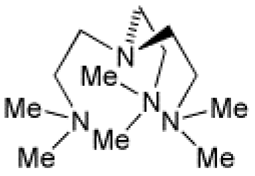
This polymerization technique controls molecular weight and tacticity. According to T. Kakuchi and coauthors at Hokkaido University, Sapporo, Nagoya University, and Mitsubishi Chemical, Yokkaich, all in Japan, the atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) provides highly syndiotactic polymers with very narrow polydispersity. Crucial features of this procedure were the use of methyl a-bromoisobutyrate, CuBr, and tris[2-(dimethylamino)ethyl]amine (**1**) as the ATRP initiating system and highly polar 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as the solvent.



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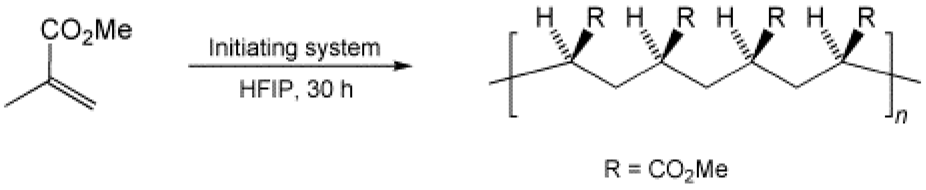
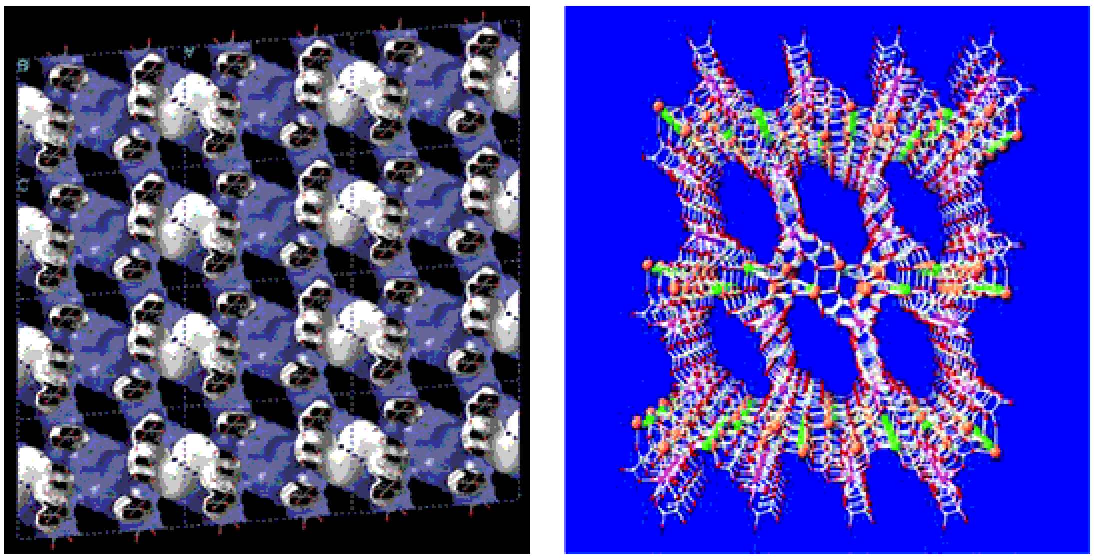


A 1:1 MMA/HFIP volume ratio allowed the polymerization to proceed smoothly for 30 h at − 78 ° C and to produce a polymer with molecular weight (M_n) 13,400 and a polydispersity of 1.31. A 24-h run at − 20 ° C gave a polymer M_n of 13,100 and a polydispersity of 1.17. The microstructure of the polymers, determined by ^{13}C NMR, showed a high degree of syndiotacticity, with polymerization runs at − 78 ° C providing the greatest stereocontrol. The authors noted that this is the first report of the synthesis of well-defined and stereoregulated PMMA based on radical polymerization. (*Macromolecules* **2005**, *38*, 1041 − 1043; W. Jerry Patterson) Go to top

Construct a supramolecular nanoporous architecture from a tetrahedral oxalato-uranium building unit. According to I. Imaz, G. Bravic, and J.-P. Sutter* of the University of Bordeaux, France, the reaction of $K_4U(C_2O_4)_4$ with Mg^{2+} in water yields single crystals of the composition $\{K_2Mg_2[U_2(C_2O_4)_7]\cdot 2H_2O\}\cdot 9H_2O$. X-ray diffraction data showed that the tetrahedral $U(C_2O_4)_4^{4-}$ units are joined by U − oxalate − U linkages in a ladderlike arrangement running along the *b* axis. The ladders are interconnected by the coordination of external oxalate ligands to K^+ and Mg^+ ions, forming a 3-D framework with 0.6- x 0.6-nm channels along the *a* axis, 1.2- x 0.8-nm channels along the *b* axis, and 0.55- x 0.55-nm channels along the *c* axis.

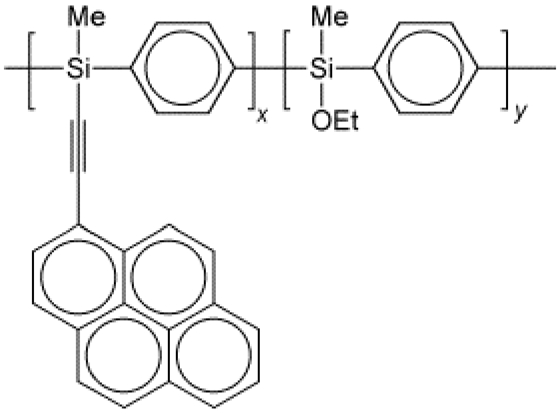


The figure shows a simulated view along the *b* axis that illustrates the van der Waals volumes of the atoms (left) and pore formation by the ladderlike structures (right). Thermogravimetric analysis showed that all of the coordinated water can be removed at 100 °C and that the structure is stable up to 230 °C. Such a robust open framework is significant in catalysis, membrane separation, and gas sorption and storage because it contains channels from which solvates are easily removed without affecting the chemical scaffolds. The authors also observed that the material retains its crystallinity during desorption–adsorption of small molecules, including water, MeOH, and EtOH. (*Chem. Commun*. **2005**, 993–995; George Xiu Song Zhao) Go to top

Here's how to synthesize peptides rapidly in solution. I. F. Eggen and co-workers at Diosynth, Oss, the Netherlands, describe a large-scale method for synthesizing peptides in solution that combines the advantages of classical liquid-phase synthesis with the generic character and amenability to automation inherent in the solid-phase approach. In most cases, the N-terminal amino acid is protected with a carbobenzoxy group (Cbz). If sulfur-containing amino acids are incorporated, 9-fluorenylmethoxycarbonyl (Fmoc), 2-(methanesulfonyl)ethoxycarbonyl (Msc) or 2-(4-nitrobenzenesulfonyl)ethoxycarbonyl (Nsc) protection can be used instead of Cbz. Side-chain functionality is protected with *tert*-butoxycarbonyl (Boc).

One cycle of the protocol consists of a coupling step, quenching of the residual activated carboxylic compound, an aqueous extractive workup, deprotection of the N-terminal amino function, and finally another aqueous extractive workup. One of the important modifications that makes this method so efficient is using an anion-forming amine such as a ß-alaninate ester to remove excess activated carboxylic compound. (*Org. Process Res. Dev*. **2005**, *9*, 98–101; Will Watson) Go to top

Use chromophore-containing polysilylenes for photoluminescence imaging. Luminescent images can be generated by changes in the color or photoluminescence (PL) efficiency of a polymer that are caused by external stimuli. The common approach to generating these images has involved the use of photoacid-sensitive dyes. J. Ohshita, A. Kunai, and coauthors at Hiroshima University, Higashi-Hiroshima, Japan, and Sumitomo Electric Industries, Osaka, Japan, have developed a series of polysilylenes that can be used to generate PL images directly.



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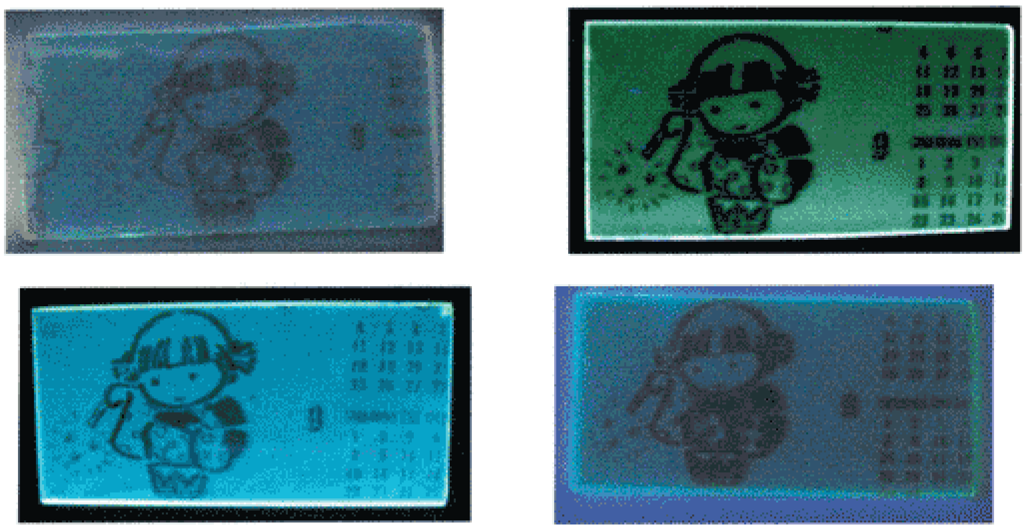
The authors synthesized poly(silylene-*p*-phenylene)s with anthrylethynyl, pyrenylethynyl, and ter(2,5-thienylidene) substituents; the pyrenylethynyl-substituted polymer is shown. These polymers are photoluminescent and photoactive. Direct irradiation of their films in air with a low-pressure mercury lamp made them almost nonemissive. This PL “bleaching” process generated the patterned images shown in the figure.



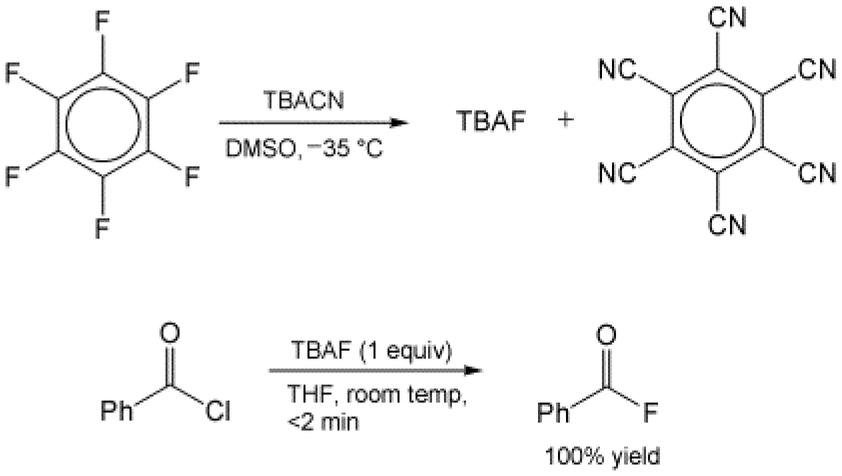
(*Macromolecules* **2005**, *38*, 730－735; Ben Zhong Tang) Go to top

Study the Brønsted acid sites in a zeolite with high-field NMR techniques. Brønsted acid sites in zeolites account for their catalytic properties, so understanding these sites is important. Using three ^{17}O－^{1}H double-resonance NMR techniques, C. P. Grey and coauthors at the State University of New York, Stony Brook, and Virginia Tech, Blacksburg, observed ^{17}O resonance signals attributed to oxygen atoms directly bonded to Brønsted acid sites [Si－O(H) －Al].

- A ^{1}H－^{17}O cross-polarized (CP) magic-angle spinning (MAS) NMR technique was used to study the proximity between oxygen and hydrogen atoms. A signal at －6 ppm in the 17.6-T ^{1}H－^{17}O CP-MAS-NMR spectrum represented the oxygen atoms in the Si－O(H) －Al linkage.
- The authors also used a ^{17}O－^{1}H rotational echo double resonance (REDOR) NMR technique to differentiate oxygen atoms. The REDOR difference spectrum was obtained by subtracting the double-resonance spectrum from the control spectrum. The difference spectrum contained a resonance signal from oxygen sites close to protons.
- Finally, the authors probed the Brønsted oxygen sites by using a ^{1}H－^{17}O transfer of population double resonance (TRAPDOR) NMR technique. This method can track any change to the Brønsted acid site local environment that occurs on gas sorption.

The authors predicted that extensions of these methods could be used to study the changes in the surroundings of specific atoms during catalytic reactions. (*Nat. Mater.* **2005**, *4*, 216－219; George Xiu Song Zhao) Go to top

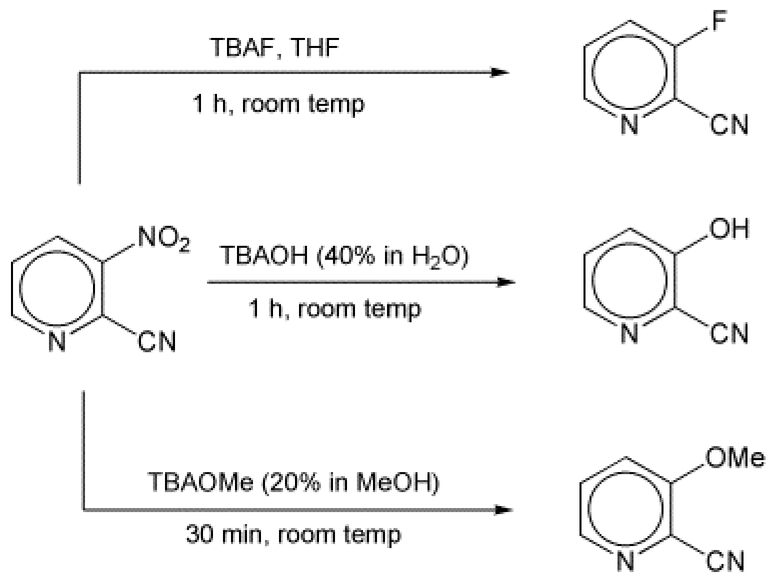
Use anhydrous tetrabutylammonium fluoride for fluorination reactions. Bu_4NF (TBAF) is a potentially useful nucleophilic fluorinating reagent, but it is uncertain whether the reagent has previously been successfully prepared as an anhydrous or “naked” organic fluoride salt. H. Sun and S. G. DiMagno* at the University of Nebraska, Lincoln, report a new method for preparing truly anhydrous TBAF using a low-temperature nucleophilic aromatic substitution (SNAr) reaction that involves treating hexafluorobenzene with Bu_4NCN (TBACN).



Solid anhydrous TBAF prepared by this method was stable under nitrogen at －35 °C for weeks and for >24 h as a solution in DMSO at 25 °C. Several substrates (e.g., benzoyl chloride, as shown) were typically fluorinated in minutes at －40 °C or at room temperature, resulting in quantitative yields of the monofluorinated products.

TBAF can be prepared conveniently in situ in polar aprotic solvents and used without isolation or purification. The self-dehydrating nature of the S_NAr preparative method provides an unusually forgiving synthetic route to TBAF. (*J. Am. Chem. Soc.* **2005**, *127*, 2050－2051; W. Jerry Patterson) Go to top

Fluorodenitrate efficiently with tetrabutylammonium fluoride. Methods for fluorinating aromatic rings are always of interest to synthetics chemists because the fluorine atom can dramatically alter the chemical and biological properties of a molecule. S. D. Kuduk*, R. M. DiPardo, and M. G. Bock of the Merck Research Laboratories, West Point, PA, report a new fluorination technique that fluorodenitrates nitropyridines with Bu_4NF (TBAF) under mild conditions. The authors extended this method to treat the same substrates with Bu_4NOH (TBAOH) or Bu_4NOMe (TBAOMe) to form hydroxypyridines and methoxypyridines, respectively.



Pyridines with nitro groups at the 2- or 4-positions reacted smoothly at room temperature, whereas 3-nitropyridines required electron-withdrawing groups for the reaction to proceed efficiently. The authors point out that anhydrous conditions are not necessary for this reaction, and they used commercially available TBAF solutions that contained ~5% water.

This method could be used to readily convert aniline-substituted nitropyridine substrates to the desired fluorinated products without protecting (and subsequently deprotecting) the aniline nitrogen. The hydroxy- and methoxydenitrations were typically carried out at room temperature with fair-to-good product yields. (*Org. Lett.* **2005**, *7*, 577−579; W. Jerry Patterson) Go to top

Photonic double heterostructures provide ultrahigh-*Q* nanocavities. S. Noda and co-workers at Kyoto University, Japan, and Sumitomo Electric Industries, Hyogo, Japan, found that an electric-field distribution described by a gaussian function is one of the most promising approaches to achieving ultrahigh−quality factor (*Q*) nanocavities. By forming a photonic double heterostructure, the authors experimentally achieved nanocavities with *Q* values of 600,000, >1 order of magnitude higher than reported previously.

It has been shown theoretically that *Q* >20,000,000 may be realized by optimizing nanocavity structures. As a result, extremely strong light−matter interactions can be obtained. The authors believe that their results will accelerate developments in fields such as designing single-photon emitters for quantum communication and computing, zero-threshold nanolasers, ultrasmall photonic chips, and high-accuracy environmental monitors, as well as for atom trapping and biosensing. Furthermore, integrating high-*Q* nanocavities into photonic chips may make it possible to stop light. These findings will stimulate further developments in the area of photonic-crystal heterostructures, because structural modifications could be made to extend the scope of devices for photon control and manipulation. (*Nature Mater*. **2005**, *4*, 207−210; George Xiu Song Zhao) Go to top

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