

# **Noteworthy Chemistry**

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Here are three ways to characterize a sonochemical reactor. The energy generated by acoustic cavitation has applications ranging from organic synthesis to wastewater treatment. Cavities produced in liquids by sonochemical reactors expand and collapse violently to generate high pressures and temperatures. Under these conditions, free radicals form that greatly enhance reaction rates. Because the spatial distribution of pressure is not uniform, active and passive zones, as defined by pressure intensity and cavitational activity, are generated.

A. B. Pandit and co-workers at Deemed University (Mumbai, India) report three methods for assigning the pressure distribution of a cleaning bath type of sonochemical reactor. The methods are based on hydrophone (pressure sensor) measurements, KI decomposition, and extraction of a natural dye from the bark of the Indian kino tree (*Pterocarpus marsupium*). The authors used data established for a specific reactor to define 150 (x, y, z) coordinates for evaluation (see figure).



Measurements of the local pressure field using a hydrophone showed high intensities just above the transducers. The highest local pressure intensity, and thus the best place to position the reaction mixture, was  $3\lambda/2$  from the transducer surface as a result of constructive interference of the combined waves from the transducers and the formation of standing wave patterns.

The decomposition of aqueous KI to form molecular iodine could be only partially correlated with pressure intensities, below a critical value specific to the reactor and the reaction. The relationship between the measured pressure and the physical effect of cavitation was evaluated by extracting a dye from *Pterocarpus marsupium* bark using MeOH as solvent. The same locations used for KI decomposition were chosen, and the results correlated with those of the KI test. Although the KI decomposition and dye extraction processes are quite different, both are governed by the dynamics of the cavity and show similar general behavior. (*Ind. Eng. Chem. Res.* 2009, 48, Article ASAP DOI: 10.1021/ie801467n; José C. Barros)

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**These asymmetric hybrid colloidal particles consist of metal nanoparticles and polymer beads.** Y. Xia and coauthors at Washington University (St. Louis) and Hokkaido University (Sapporo, Japan) used a modified precipitation polymerization method to generate asymmetric metal–polymer hybrid colloidal particles. They created metal nanoparticles by adding gold or silver colloids to the styrene polymerization system after the polymerization had proceeded for 2 min.

Scanning electron microscopy results showed that each polymer particle contains one metal nanoparticle partially embedded in its surface. The authors note that the time of adding colloidal metal particles and the amount of monomer added are critical factors in the formation of the asymmetric particles. (*J. Am. Chem. Soc.* **2009,** *131,* **1352–1353**; George Xiu Song Zhao)

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**Multiple stimuli can reorganize block copolymers in solution.** Researchers at Southern Methodist University (Dallas) have developed boronic acid block copolymers that respond to changes in pH, temperature, and sugar concentration. D. Roy, J. Cambre, and B. S. Sumerlin\* used reversible addition–fragmentation chain transfer to synthesize poly(3-acrylamidophenylboronic acid) (PAPBA)-*b*-poly(*N*-isopropylacrylamide) (PNIPAM) [28.1 kDa, polydispersity 1.15], in which the PNIPAM is thermally responsive, and PAPBA is regulated by sugar content (esterification with a sugar diol) and pH.

At pH ~11 and room temperature, PAPBA and PNIPAM are water-soluble; they form unimers with a hydrodynamic radius of 8 nm. Lowering the pH to 8.7 (below the  $pK_a$  of PAPBA) results in the formation of

reverse micelles (55 nm), which revert to the dissociated unimer state with an increase in pH or addition of a sugar diol. Heating the molecularly dissolved unimers at pH ~11 above the critical aggregation temperature (42 °C) of PAPBA-*b*-PNIPAM yields micelles (78 nm) with PNIPAM cores and PAPBA coronas. The hydrated or dehydrated state of the PAPBA and PNIPAM blocks can be probed by variable temperature NMR. This process may have wide applicability for designing multi-responsive copolymer systems. (*Chem. Commun.* **2009**, *11*, Advance Article DOI: 10.1039/b900374f; LaShanda Korley)

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**Catalyzed cycloadditions of ketenes with nitroso compounds form oxazetidinones that yield α-hydroxy carboxylic acids.** One approach to enantioenriched α-hydroxy carboxylic acid derivatives is ring opening



1,2-oxazetidin-3-ones, which can be formed by the [2 + 2] cycloaddition of a ketene with a nitroso compound. However, no studies report the use of catalysis to enhance the efficiency of these transformations. M. Dochnahl and G. C. Fu\* at MIT describe [2 + 2] cycloadditions mediated by planar-chiral 4dimethylaminopyridine catalysts (e.g., 1) to form the target 1,2-oxazetidin-3-one intermediates (2) with high enantiomeric excesses.

The authors observed that unsubstituted phenyl groups on the nitroso compound result in unfavorable regioselectivity of the heterocyclic ring. They improved the reaction efficiency by introducing electron-withdrawing substituents such as  $CF_3$  in the ortho position of the phenyl ring of the nitroso reactant. This reversed the regioselectivity in the heterocyclic ring to provide a high yield of **2** with as much as 98% ee.

In addition to forming the potentially useful bioactive structure **2**, variants of this intermediate open a synthetic pathway to  $\alpha$ -hydroxy carboxylic acids (**3**) and 1,2-diols (**4**); Cy is cyclohexyl. Compounds such as **3** and **4** are useful intermediates for synthesizing more complex organic structures. (*Angew. Chem., Int. Ed.* **2009**, *48*, **2391–2393**; **W. Jerry Patterson**)

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**Polymer nanocomposites reinforced with cellulose nanowhiskers form percolating networks.** C. Weder and coauthors at Case Western Reserve University (Cleveland) and the Louis Stokes Cleveland DVA Medical Center report the development of polymer nanocomposites derived from microcrystalline cellulose (MCC) nanowhiskers (length ~260 nm, width ~23 nm) and cotton cellulose nanowhiskers (length ~210 nm, width ~20 nm). Their research probed the reinforcing effect of cellulose nanowhiskers on an ethylene oxide– epichlorohydrin (EO-EPI) copolymer matrix.

Transmission electron microscopy studies showed that the MCC nanowhiskers form small fibrillar structures in the absence of net surface charge, whereas the cellulose nanowhiskers exist as individual fibers because of repulsive forces from surface sulfate groups. Using a solution casting process, the authors produced EO-EPI– nanowhisker composites with 0–35% filler content. At ~25 vol%, the cotton nanowhisker composite displays a ~27-fold increase in shear storage modulus ( $G_c$ ') compared with neat EO-EPI;  $G_c$ ' increases by a factor of ~11 for the MCC-derived nanocomposites.

The authors determined that the cotton nanowhiskers form a percolated network, but the percolation model does not adequately describe the reinforcing behavior of the MCC nanowhiskers at lower filler concentrations, mainly because of nanowhisker aggregation effects. The researchers used a previously reported template-based method (*Nat. Nanotechnol.* **2007**, *2*, 765–769) to enhance the dispersion characteristics of the fractionated

MMC-EO-EPI nanocomposites.

These composites are well described by a percolation model: They exhibit about twofold enhancement in  $G_c$ ,

compared with the solution-cast MMC polymer nanocomposites at 25 vol% and have shear storage moduli similar to the cellulose nanowhisker composites. This study gives insight into the interplay of processing, fractionation, and templating on mechanical enhancement and percolating network formation in polymer nanocomposites. (*Biomacromolecules* 2009, *10*, Article ASAP DOI: <u>10.1021/bm8010903</u>; <u>LaShanda Korley</u>)

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**Electrophosphorescence device based on a porphyrin–platinum complex** efficiently emits in the near infrared. The development of organic light-emitting diodes (OLEDs) that luminesce in the long-wavelength region is desirable because of the OLEDs' potential use in telecommunications, IR signaling, and wound healing.



Organolanthanide complexes have been used as near-IR luminophores, but the OLEDs based on these complexes have low quantum efficiencies—the highest are only  $\sim 0.5\%$ —because of the low intrinsic photoluminescence quantum efficiency of the metal-centered F states.

J. R. Reynolds, J. Xue, K. S. Schanze, and co-workers at University of Florida (Gainesville) used a phosphorescent (tetraphenyltetranaphtho[2,3]porphyrin)platinum(II) complex (1) to fashion OLEDs. The device, with an active layer of 4,4'-bis(carbazol-9-yl)biphenyl doped with 1, emits near-IR light at ~900 nm, with a bandwidth of ~100 nm. The maximum external quantum efficiency of the device reaches 3.8%, which is the highest efficiency reported to date for an OLED that emits at a wavelength >800 nm. (*ACS Appl. Mater. Interfaces* 2009, *1*, 274–278; Ben Zhong Tang)

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**Versatile aziridine building blocks form new cyclic dihydroxazines.** W.-J. Xiao, Y.-G. Zhou, and coauthors at the Chinese Academy of Sciences (Dalian) and Central China Normal University (Hubei) found that N-protected substituted aziridines can be treated with propargyl alcohols in the presence of *t*-BuOK to promote a tandem ring-opening–closing reaction yielding dihydroxazine derivatives.



The initial goal of the study was to form a simple ring-opening product. However, the authors observed that the aziridine ring (1) opened with the propargyl alcohol (2), then reclosed to form good yields of the six-membered dihydroxazine ring (3)—all with high atom economy.

The authors illustrated the usefulness of this method by creating an efficient route to bioactive morpholine derivatives. They accomplished this by reducing **3** to give highly diastereoselective (>95:5 dr) morpholines (**4**). When isopropyl-substituted dihydroxazines were used, only *cis*-morpholine derivatives were produced. The *p*-toluenesulfonyl (Ts) protecting group on **4** was easily removed to liberate chiral 3,5-disubstituted morpholine **5**. (*Org. Lett.* **2009**, *11*, **1119–1122**; **W. Jerry Patterson**)

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