



Latest News

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PHYSICAL CHEMISTRY

Macromolecules Self-Destruct

Adsorption induces carbon-carbon bonds in brushlike macromolecules to break

[Michael Freemantle](#)



PHOTO
COURTESY
SERGEI S.
SHEIKO

Iconoclasts

**Sheiko (left),
Ph.D. student
Frank C. Sun,
and
coworkers
show that
adsorption-
induced
forces can**

**exceed the
strength of a
covalent bond.**

Covalent carbon-carbon bonds in organic molecules are considered tough and difficult to break. It's therefore counterintuitive that the relatively weak attractive forces at play when molecules adsorb to a surface would be strong enough to break these bonds.

But break they do, according to new research—at least in macromolecules with highly branched architectures. Associate professor of chemistry [Sergei S. Sheiko](#) at the University of North Carolina, Chapel Hill; [Krzysztof Matyjaszewski](#), professor of natural sciences at Carnegie Mellon University, Pittsburgh; and their coworkers used atomic force microscopy (AFM) to show the covalent bonds that make up the backbones of brush-like macromolecules spontaneously rupture after adsorption on a substrate (*Nature* **2006**, 440, 191).

The researchers used atom-transfer radical polymerization to prepare polymer backbones with more than 2,000 2-hydroxyethyl methacrylate units and polymeric "bristles" containing as many as 140 or so *n*-butyl acrylate units. They then deposited the brushlike molecules on the surfaces of various liquid and solid substrates. AFM revealed that the molecules break apart and that the fragmentation rate increases with increasing length of the bristles and the ability of the substrate to attract the side chains.

"Our findings call into question the generally accepted belief that the chemical structures of macromolecules synthesized in solution remain intact after deposition onto a substrate," Sheiko tells C&EN.

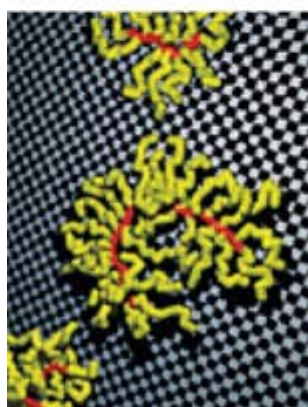
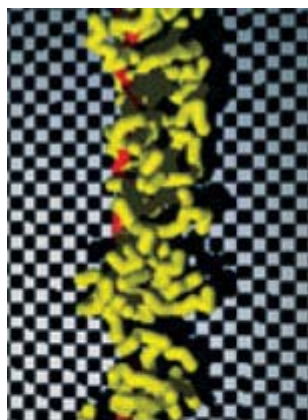


IMAGE
COURTESY
SERGEI S.
SHEIKO

Dwindling Discovery

Fatal Attraction
A
macromolecule
adsorbed on a
substrate is
under tension
(top), with the
yellow side
chains
engaged in a
tug-of-war that
breaks the red
backbone
(bottom).

He explains that when the molecules adsorb, the side chains

spread unevenly over the substrate, predominantly along the polymer backbone. The physical interactions of the side chains with the substrate consequently induce tension that concentrates along the backbone, stretching and eventually snapping it.

"The macromolecule struggles to reconfigure and maximize the number of contacts with the substrate," Sheiko says. "By engaging in this intramolecular tug-of-war, the macromolecule opts to incur the large cost of breaking covalent bonds to reduce the overall free energy of the system."

The rupture of strong, covalent carbon-carbon bonds by the commonplace process of adsorption is a seemingly heretical notion according to professor of materials science and engineering [Steve Granick](#) and research scientist Sung Chul Bae at the University of Illinois, Urbana-Champaign, writing in the same issue of *Nature*.

They suggest the work could provide a general model for designing materials that have an architecture better able to cope with mechanical stress. The general proof of concept that slow or even forbidden chemical reactions can be activated by mechanical stress is "even more exciting," they add.

In light of the discovery, the surface-induced scission of covalent bonds will need to be carefully considered when complex molecular architectures for surface applications are designed, Sheiko and coauthors note. The phenomenon also opens up "intriguing opportunities" for designing architectures that break at predefined sites, they add.

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