The force of mechanochemistry

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Mechanochemical phenomena are all around us. They affect the generation, growth and propagation of microcracks that are responsible for catastrophic failure of polymeric materials, behavior of impact-resistant materials (e.g., bulletproof vests) and tires, stabilities of surface-anchored polymers in microfluidic diagnostics and high-performance chromatography. Exploiting mechanochemistry may yield remarkable new materials and processes, including polymer photoactuation, efficient capture of waste mechanical energy, materials capable of autonomous reporting of internal stresses and self-healing, and tools to study polymer dynamics at sub-nm scales. The recent remarkable advances in empirical polymer mechanochemistry, evidenced by the proliferation of designer polymer that undergo specific chemistry when loaded demands a conceptual framework within which to rationalize and systematize such observations and to develop systematic approaches to identifying new mechanochemical phenomena without extensive trial-and-error effort. I'll describe one such framework we have developed and will illustrate its capabilities by demonstrating successful (a) quantitative predictions of mechanochemical behavior of isolated polymer chains from the force-dependent reactivity of a single monomer and (b) mapping of force distribution along a single polymer chain in elongational flow using specially designed small-molecule force "gauges".