# The challenges and opportunities of contemporary polymer mechanochemistry

Roman Boulatov, Chemistry Department, University of Liverpool, Liverpool, L69 7ZD, UK

Most polymeric materials are subject to mechanical loads throughout their lifetimes, from manufacture to recycling.[1-7] Stretching, compression, twisting or other distortions of the macroscopic shape of a material is accompanied by stretching of individual polymer chains or chain segments. The more a chain is stretched, the more the kinetic and thermodynamic stabilities of its constituent monomers changes. This coupling of a mechanical load, often acting at lengthscales >1 μm, and chemical reactivity localized within $nm^3$ volumes, is called mechanochemistry. In commercial polymers, such as polystyrene or vulcanized rubbers, a sufficiently large load – even a compressive one –leads to fragmentation of a fraction of the polymer chains. This fragmentation lowers the density of bonds across which the load distributes and thus the capacity of the material to withstand further loading, ultimately resulting in material failure. Conversely, it may be possible to exploit mechanochemical coupling to design polymeric materials that respond to mechanical loads in ways that prevent or at least inform the user of impeding catastrophic failure. These responses include self-strengthening[8] (i.e., the formation of multiple load-bearing bonds per each mechanochemically failed bond) and mechanochromism[9] (i.e., changes in local optical properties of the material proportional to either instantaneous or accumulated stress at a level of a single polymer chain). The role of mechanochemistry in facilitating material failure and (potentially) preventing it explains the contemporary interest in the field from materials scientists and engineers.[10]

Mechanochemical phenomena are of interest to organic and physical chemists thanks to their potential to expand our understanding of how external variables can affect and control chemical reactivity. A computationally and conceptually tractable model of localized reaction in a stretched polymer is an isolated reactive site with tensile force acting between the same pair of atoms which connect this moiety to the rest of the macrochain.[11-13] Consequently, chemists discuss polymer mechanochemistry in terms of effects of force on reactivity and contrasts are often drawn in the literature between force and other experimental variables that affect reaction rates, mechanisms and energies, including temperature and (more rarely) pressure, solvent or electromagnetic fields. An important, if underappreciated, aspect of this view of polymer mechanochemistry is that in it force is not a fundamental physical quantity but simply a convenient approach to making the system tractable by (in the words of Wilczek) "offering approximate, truncated description of the dynamics of matter [that] is easier to use and focuses on the relevant"[14] than the alternatives, thus "shielding us from irrelevant details" (e.g., atomic motions in parts of the macrochain far removed from the reacting site). This approach of modeling localized chemical reactivity in complex dynamic systems by representing a large number of molecular degrees of freedom by a single parameter with the physical meaning of an energy gradient (i.e., generalize force) acting on a fairly small reactive site may be useful beyond stretched polymers. If this view is correct then a general theoretically sound understanding of how force acting on a molecule changes its reactivity is potentially applicable to a broader range of phenomena than the often-unique reactivity of highly stretched macromolecules.

Stretching a macrochain can accelerate chain fragmentation enormously, by $10^{40}$-fold or more at 300 K. Qualitatively this acceleration is easy to rationalize. A strained reactant (a small molecule or a stretched macrochain) will react faster than its strain-free analog if the geometry of the rate-determining transition state allows (partial) relief of molecular strain. For such partial relief to occur, the rate determining transition state must be longer than the reactant along the pulling axis, in which case transition-state formation will correspond to atomic motion down the energy gradient (i.e., along the force vector). When the stretching force (gradient) is large (e.g., 5 nN = 31 eV/nm) even a small

elongation on the order of 1 Å lowers the barrier by 70 kcal/mol. This qualitative rationalization of polymer mechanochemistry dates back to Eyring[15] and is related to the framework of physical organic chemistry developed to rationalize the effect of molecular strain on chemical reactivity.

Unfortunately, this framework, based on the ideas of strain energy and free energy relationships, is poorly suited[16] for quantitative understanding of polymer mechanochemistry. Quantitative models of mechanochemical reactivity aim at accurately extrapolating force-dependent activation barriers from strain-free values (which are considerably easier to obtain experimentally and computationally) or at inferring structural parameters of transition states from measured force-dependent kinetics. How to achieve these aims remains an outstanding question of contemporary polymer mechanochemistry. Reported extrapolations of force-dependent activation energies from strain free values vary from usefully approximate (estimated accelerations being within a factor of two of the explicitly calculated ones[17, 18]) to qualitatively incorrect (e.g., predicted inhibition of reactions that are accelerated by force[5]). The known reasons appear to reflect primarily strong and remarkably complex dependences of both the molecular geometries and reaction mechanisms[19, 20] on force.

Force-dependent kinetics at present can only be estimated from single-molecule force measurements, whereby an isolated polymer chain is stretched by an atomic force microscope, and the recorded force/extension curves contain information on the force at which the mechanochemical reaction occurred. These data are routinely fitted to empirical models that postulate a certain relationship (often simple proportionality) between the applied force and lowering of the apparent kinetic barrier. The number between ~0.15 and ~2.2 Å obtained from such fits is nothing more than an empirical parameter devoid of information about molecular structural differences between the reactant and the transition state(s). The narrow range of values simply reflects the fact that single-molecule force measurements are largely limited to reactions that occur on the 100 ms timescale in a chain stretched to $0.1 - 2.5$ nN. So far, the only successful inferences of the structural parameters of transition states from single-molecule force data were indirect, involving extensive quantum-chemical modeling of the measured force/extension curves, with the experimental data serving to validate the computed activation free energies and by extension, the computed geometries.[21, 22]

This focus on quantitative molecular interpretation of mechanochemical behavior of polymers is less than a decade old and regrettably remains somewhat of a niche of contemporary mechanochemistry. For most of its history, the field studied primarily fragmentations of simple commodity (e.g., polystyrene, polyamides) or biological (DNA, polysachirides) polymers.[23-26] This early work was plagued by poorly defined chemistry, such as load-accelerated homolysis of covalent bonds, which precluded not only quantitation of the underlying microscopic kinetics but even simple control of the fragmentation products or location along the polymer backbone. Perhaps the most consequential evolution of polymer mechanochemistry to date occurred at the turn of the century. At that time developments in single-molecule force spectroscopy (SMFS) allowed convincing demonstrations of force-induced accelerations of mechanistically and kinetically well-defined reactions at pre-determined polymer sites. SMF experiments on polymers comprised of two macromolecular chains linked end-to-end by a labile metal complex demonstrated site-specific mechanochemical dissociation of a chain.[27] Seminal studies[28] of single-chain micromechanics of azobenzene polymers demonstrated repeatable contraction and elongation of polymer contour length under force, arising from nearly simultaneous isomerization of multiple identical and non-interacting azobenzene moieties per chain. Further experiments[29] confirmed that the selectivity of mechanochemical reactions correlated broadly with that of the analogous reactions in the non-polymeric reactive sites. Collectively, this work suggested that the chemical response of polymers to mechanical loads could be controlled, with some degree of predictability, by

the chemical composition and molecular structure of one or more dissociatively labile reactive sites contained within a more "inert" polymer chain.

The subsequent decade has seen productive exploitation of these findings. Acceleration of over 20 distinct chemical reaction was demonstrated, with varying degree of experimental and sometimes computational support, in macrochains stretched by an AFM, in sonicated polymer solutions or in bulk solids under axial compression, stretching or shearing. Sonicating dilute polymer solutions is by far the most popular technique to induce polymer mechanochemistry, but such experiments are as challenging to interpret mechanistically or quantitatively as they are easy to do technically.[5] SMFS is the only technique that allows control of the force acting on a macromolecule and remains the only means of measuring force/rate correlations. Despite the technical complexity of SMFS, the limited substrate scope and the lack of spectroscopic characterization of the products, SMF measurements continue to impact disproportionately the development of polymer mechanochemistry.[22, 30] Load-induced accelerations of well-defined reactions in bulk polymer solids are probably closest to technologically important manifestations of mechanochemistry,[8, 31] but also are least amenable to quantitative or mechanistic characterization or molecular interpretation and so far remain largely empirical.

An important emerging direction in contemporary polymer mechanochemistry is the design of cascades, whereby a mechanochemical reaction generates a catalyst or a reactant for a subsequent non-mechanochemical step[9, 32, 33] or one mechanochemical reaction controls the transmission of load to other reactive sites.[22] Such cascades are superior to simple one-step alternatives for exploitation in practical applications and fundamental studies of polymer behavior under load. While most practical applications of polymer mechanochemistry remain just proposals, few have been prototyped.[34-36]

Some argued[37] that chemistry occupies a privileged place among sciences because it has the tools and conceptual frameworks that are uniquely suited to benefit a broad range of highly interdisciplinary problems facing the humanity. Polymer mechanochemistry offers an organizing framework within which to exploit the sophisticated machinery of modern chemistry for designing molecules and reactions to develop broadly useful approaches for studying dynamics at lengthscales of $10 - 100$ nm. In this so-called "formidable gap", separating the domains of traditionally atomistic and continuum descriptions of matter, the existing tools to study the dynamic processes, or conceptual understanding of how to describe them quantitatively are particularly limited.[38] Such approaches will complement, among others, the ongoing effort to extend our understanding of mechanical properties of polymers to the molecular level.[6, 39]

The multiscale nature of mechanochemical phenomena in polymers makes studying and exploiting them conceptually and methodologically challenging. Yet long-term impact of overcoming these challenges seems equally substantial and is likely to extend beyond polymer science. While we are probably many years away from achieving this goal, partial solutions to a number of known mechanochemical problems[5, 12] are likely to have far ranging technological and fundamental implications.

[1] T. J. Kucharski, R. Boulatov *J. Mater. Chem.* **2011**, 21, 8237-8255.
[2] Z. S. Kean, S. L. Craig *Polymer*. **2012**, 53, 1035-1048.
[3] C. L. Brown, S. L. Craig *Chem. Sci*. **2015**, 6, 2158-2165.
[4] H. Zhang, Y. Lin, Y. Xu, W. Weng in *Mechanochemistry of Topological Complex Polymer Systems* (Ed. R. Boulatov), Springer, Cham, **2015**, pp.135-207.
[5] R. Boulatov, S. Akbulatov *ChemPhysChem*. **2017**, 18, in press.
[6] C. Creton, M. Ciccotti *Rep. Prog. Phys*. **2016**, 79, 046601.
[7] M. Naebe, M. M. Abolhasani, H. Khayyam, A. Amini, B. Fox *Polym. Rev.* **2016**, 56, 31-69.

[8] A. L. B. Ramirez, Z. S. Kean, J. A. Orlicki, M. Champhekar, S. M. Elsakr, W. E. Krause, S. L. Craig *Nat Chem*. **2013**, 5, 757-761.

[9] H. Zhang, F. Gao, X. Cao, Y. Li, Y. Xu, W. Weng, R. Boulatov *Angew. Chem. Int. Ed*. **2016**, 55, 3040-3044.

[10] J. F. Patrick, M. J. Robb, N. R. Sottos, J. S. Moore, S. R. White *Nature*. **2016**, 540, 363-370.

[11] J. Ribas-Arino, D. Marx *Chem. Rev.* **2012**, 112, 5412-5487.

[12] R. Boulatov *Nat Chem*. **2013**, 5, 84-86.

[13] G. S. Kochhar, G. S. Heverly-Coulson, N. J. Mosey in *Theoretical approaches for understanding the interplay between stress and chemical reactivity* (Ed. R. Boulatov), Springer, Cham, **2015**, pp.37-96.

[14] F. Wilczek *Physics Today*. **2004**, 57, 11-12.

[15] W. Kauzmann, H. Eyring *J. Am. Chem. Soc.* **1940**, 62, 3113-3125.

[16] Z. Huang, R. Boulatov *Chem. Soc. Rev.* **2011**, 40, 2359-2384.

[17] Y. Tian, R. Boulatov *Chem. Commun.* **2013**, 49, 4187-4189.

[18] M. Hermes, R. Boulatov *J. Am. Chem. Soc.* **2011**, 133, 20044-20047.

[19] Y. Tian, T. J. Kucharski, Q.-Z. Yang, R. Boulatov *Nat Commun*. **2013**, 4.

[20] P. Dopieralski, J. Ribas–Arino, P. Anjukandi, M. Krupicka, D. Marx *Nature Chem.* **2017**, 9, 164-170.

[21] S. Akbulatov, Y. Tian, R. Boulatov *J. Am. Chem. Soc.* **2012**, 134, 7620-7623.

[22] J. Wang, T. B. Kouznetsova, R. Boulatov, S. L. Craig *Nature Commun*. **2016**, 7, 13433.

[23] G. J. Price *Adv. Sonochem*. **1990**, 1, 231-287.

[24] T. Q. Nguyen, H.-H. Kausch *Adv. Polym. Sci.* **1992**, 100, 73-182.

[25] D. R. Tyler *J. Macromol. Sci. C*. **2004**, 44, 351-388.

[26] J. Sohma *Prog. Polym. Sci.* **1989**, 14, 451-596.

[27] M. Conti, G. Falini, B. Samori *Angew. Chem. Int. Ed.* **2000**, 39, 215-218.

[28] T. Hugel, N. B. Holland, A. Cattani, L. Moroder, M. Seitz, H. E. Gaub *Science*. **2002**, 296, 1103-1106.

[29] F. R. Kersey, W. C. Yount, S. L. Craig *J. Am. Chem. Soc.* **2006**, 128, 3886-3887.

[30] J. Wang, T. B. Kouznetsova, Z. Niu, M. T. Ong, H. M. Klukovich, A. L. Rheingold, T. J. Martinez, S. L. Craig *Nat. Chem*. **2015**, 7, 323-327.

[31] E. Ducrot, Y. Chen, M. Bulters, R. P. Sijbesma, C. Creton *Science*. **2014**, 344, 186-189.

[32] F. Verstraeten, R. Gostl, R. P. Sijbesma *Chem. Commun.* **2016**, 52, 8608-8611.

[33] J. M. Clough, A. Balan, T. L. J. van Daal, R. P. Sijbesma *Angew. Chem. Int. Ed.*. **2016**, 55, 1445-1449.

[34] Q. Wang, G. R. Gossweiler, S. L. Craig, X. Zhao *Nat. Commun.*. **2014**, 5, 4899.

[35] Q. M. Zhang, M. J. Serpe in *Responsive polymers as sensors, muscles and self-healing materials* (Ed. R. Boulatov), Springer, Cham, **2015**, pp.377-424.

[36] G. R. Gossweiler, C. L. Brown, G. B. Hewage, E. Sapiro-Gheiler, W. J. Trautman, G. W. Welshofer, S. L. Craig *ACS Appl. Mater. Interfaces*. **2015**, 7, 22431-22435.

[37] G. M. Whitesides *Angew. Chem. Int. Ed*. **2015**, 54, 3196-3209.

[38] G. R. Fleming, M. A. Ratner, Directing Matter and Energy: Five Challenges for Science and the Imagination. U.S. Department of Energy, **2007**.

[39] K. Chen, E. J. Saltzman, K. S. Schweizer *Annu. Rev. Cond. Matt. Phys*. **2010**, 1, 277-300.