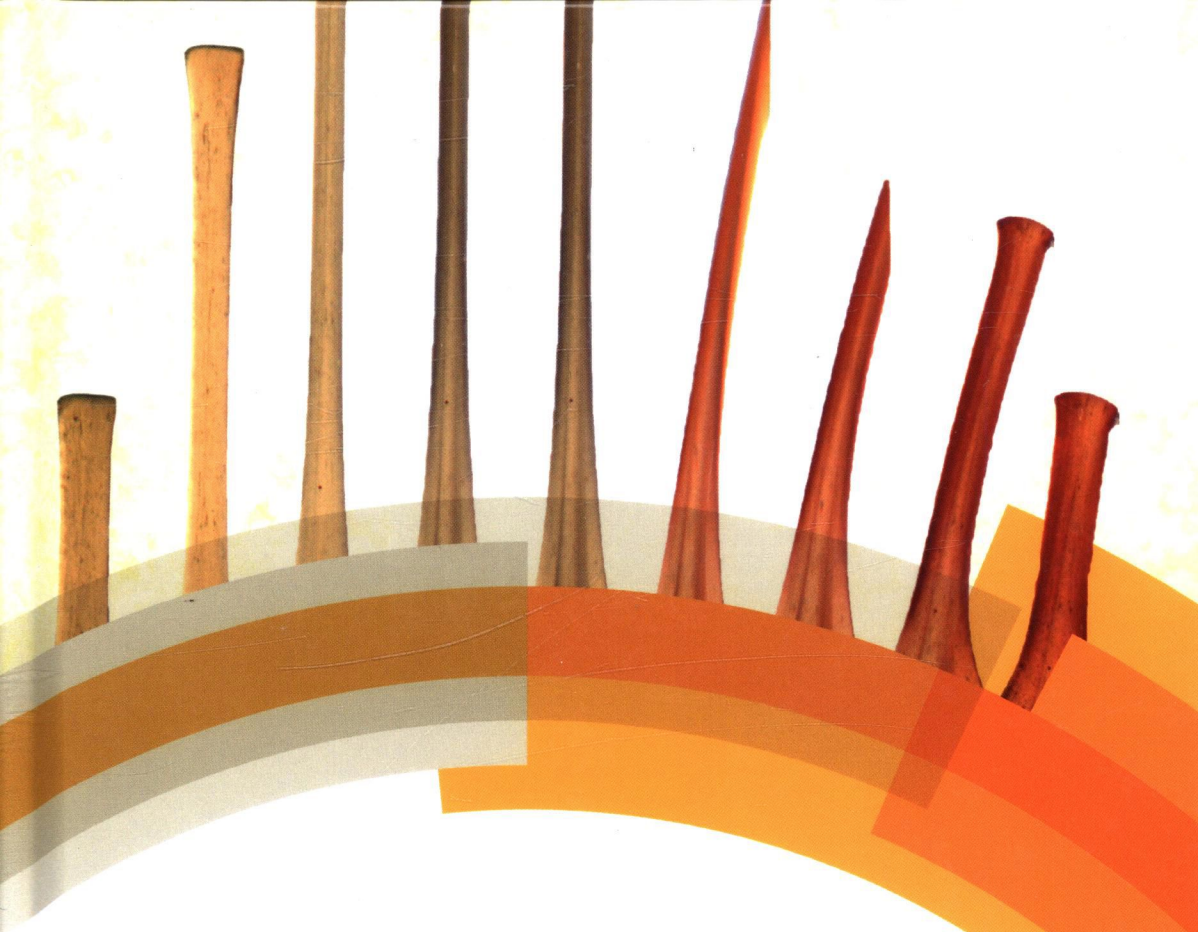

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Edited by Yoan C. Simon and Stephen L. Craig

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A spiropyran-linked poly(methylacrylate) changes colour in response to mechanical forces associated with tensile strain, image courtesy of Nancy Sottos. Background image © Shutterstock.

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Preface

Writing a preface is an opportunity to convince the reader (that would be you) of the importance of a monograph and the value of its content, but it is also a chance to frame the theme within a wider, maybe more entertaining, context. It is a central and somewhat stressful task. Conveniently, *stress* is at the center of the present manuscript, more specifically the relationship between stress and (polymeric) materials and the new strategies that have arisen in the past decades to harness mechanical energy and transduce it into useful chemistry in materials.

For many years, materials have been structural: a plush polyurethane foam to make a cushy seat, a glassy polycarbonate for plane windows, a rubbery vulcanized tire to attenuate the asperity of the road. Polymeric materials surround us. The last three decades have seen the unabated development of an ineluctable trend: we now want to impart some "wit" to our materials. Three decades ago a mechanically "smart" material was one whose properties were well suited to its intended use. Materials were designed to withstand a certain load or to allow a certain amount of deformation. The material had to resist or comply. In the intervening years, the moniker of smart materials came to refer to systems that are capable of responding in a predetermined manner to a given stimulus. Examples of smart materials include pH-responsive micelles for drug delivery, programmable shape-memory materials that can twist and tie or even materials that can move left or right depending on the polarization of incident light. It is now clear that mechanical response can be used as a similar stimulus-response mechanism.

Growing up as kids, judo was a somewhat popular sport and while neither of us practiced it one of the elementary tenets of that martial art is the utilization of the force of one's opponent to one's own advantage. One can draw an analogy between mechanochemistry and this creed. Indeed, after many

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years of designing materials to fight the effect of mechanical action (which thankfully we still do for certain structural components), it is now clear that mechanical force can be used to one's advantage. The present treatise looks at the contribution from various researchers from around the world towards that direction. The range of scientists from different backgrounds is necessary, given the intrinsic interdisciplinary nature of this work. Chemists, surface scientists, materials specialists and engineers alike bring important contributions to the field.

Going back to natural systems, adaptability and feedback loops in living organisms are crucial for their survival. Of particular relevance to our topic of interest are the multiple examples in nature that make use of a graduated or adaptive response to mechanical stimuli such as actin polymerization, stem cell differentiation, or response to an edema, *etc*... Understanding the solutions that Nature has evolved in response to these challenges is therefore a good starting point for the present monograph. The first chapter of this book is therefore concerned with this biological inspiration, taking a look at various instances where Nature needs to respond in mechanical force, looking (in awe) at the sophistication of said systems.

Early in the quest for mechanically responsive systems, it was realized that the conversion of mechanical energy into a useful chemical potential could only be realized through the careful design of functional groups capable of preferentially activating in response to mechanical forces, *ergo* generating a desired chemical function. The second chapter focuses especially on the design of such functional groups, or mechanophores, classifying them according to their ultimate purpose, *e.g.* creation of reactive species, catalytic activation, chromatic change. Scientists worldwide have indeed shown incredible resource to devise and synthesize systems with diverse natures (organic, organometallic), geometries (linear, cyclic) or end goals.

Among the obvious and promising technological outlook for these polymers lies the ability to sense stress. Much like somatosensory cells are able to inform you of a pleasant touch or a painful pinch, it is often crucial to be able to evaluate the stress state of a material, *e.g.* to forestall fatigue or, worse, failure. Optical cues are especially attractive for their sensitivity, spatial and spectral resolution and maybe more importantly their facile observation. Chapter 3 goes over some of the methodologies that have been developed for sensing, including those based on chain scission, aggregation, isomerization, *etc.* These detection strategies require a combined understanding of both chemistry and stress-transfer phenomena.

The latter are explained in greater details in Chapter 4, which focuses on the design principles to effectively transduce mechanical force. In fact, while chemists have found interesting ways to probe new mechanophores through elongational flow, the veritable challenge of mechanochemistry probably lies in the aptitude to transfer as efficiently as possible a macroscopic force to the judiciously designed mechanophores. This section aptly presents the mechanics background to explain transfer of load from the matrix down to the mechanophore level, taking into account experimental

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conditions, the nature of the matrix and kinetics considerations pertaining to the mechanophore.

Along these lines, it is interesting to evaluate the influence that other chains can have on the overall mechanoresponsiveness, especially *via* the introduction of directional non-covalent interactions. Chapter 5 goes over the recent developments in the field of supramolecular chemistry, rightfully acknowledging that the introduction of strong secondary interactions will have a tremendous impact on the microstructure of a material and, eventually, the ability to transfer stress. Of particular interest to that section are the series of materials that contain supramolecular motifs both in the bulk and as the mechanoresponsive unit.

Understanding what governs force transfer in the bulk is crucial to create materials that respond in a desirable manner to stress. Yet, one easily recognizes that surface and interfacial properties are often as important as, if not more important than, bulk behavior. With that in mind, Chapter 6 highlights some of the most recent findings in the area of polymer brushes and how swelling behaviors and chain conformation have a tremendous impact on coating stability. It goes over some of the compositional considerations that affect the overall resistance of the brush and its attachment to the substrate.

Finally, Chapter 7 highlights the premises of a novel concept in the field of chemo-mechanical transduction converting the energy of an alternating reaction to generate gels that throb autonomously but that are also capable of detecting a force being applied. This adaptability opens up the road for the fabrication of systems that are capable of computing and to respond in an appropriate manner to a given stimulus. As such, the strategies described help move mechanically "smart" materials from being merely obedient, to being capable of adapting their properties to reach endpoints that might not have been specifically designed by the scientist.

It is often acknowledged (and rightfully so) that "a professor is only as good as his students". As editors of this monograph, we gratefully acknowledge that one should extend this to say that a book is only as good as its contributors. We are very fortunate to have convinced some of the leaders in the field to take some of their precious time to contribute to this book. We fully appreciate their patience, involvement and dedication towards the realization of this monograph.

Yoan C. Simon and Stephen L. Craig

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