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Living dynamic polymeric materials

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Many materials exhibit static and functional properties. This article elaborates on how the last few decades of material research have demonstrated the apparent similarities between the equilibrium thermodynamics of static materials and the biological world utilizing non-equilibria biological processes. Dynamic polymer networks involving covalent and non-covalent multi-stimulus materials at nano-, micro-, and macro-scales and their biological counterparts at molecular, cellular, and species levels are addressed in the context of opportunities and challenges governing their development involving non-equilibria processes.

With few exceptions, the majority of materials exhibit static and functional properties. Traditional discovery of materials involves intentionally controlling functionality, performance, and durability, pursuing new or enhancing existing technological opportunities. Using thermodynamics and/or kinetics frameworks, traditional materials properties are identified, examined, and predicted. In contrast, the biological world senses, repairs, and responds (at the cellular level), learns (at the organism level), and evolves (at the species level). These biology assets are schematically depicted in Fig. 1A. The last couple of decades of material research have demonstrated the apparent similarities between the equilibrium thermodynamics of static materials and the biological world utilizing non-equilibria biological processes involving adapting,^{1–4} self-healing,⁵ learning,⁶ or self-replicating,⁷ to name a few.

Although the most significant scientific breakthroughs came from the desire to solve unsolved problems, forward-looking future materials are no exception. Incorporating unprecedented structural and compositional features that mimic biological systems, thus making materials stimuli-responsive, will enable active, reconfigurable, or adaptive attributes across multiple spatiotemporal scales (Fig. 1A).^{8–11} Creating materials with these biology-inspired properties, though, is challenging, but understanding the complex molecular processes responsible for these functions and their limitations can be particularly strenuous. Nevertheless, the richness of physicochemical processes developed in the last few decades undeniably changed the material world.¹² At the same time, new challenges have been raised; for example, how can inter- or intra-molecular signaling or the carrying of genetic information be implemented to introduce living functions?^{13,14} Furthermore, understanding principles governing the ability to signal, communicate, or grow

at nano-, micro-, macro, or higher scales (Fig. 1B) is an even greater challenge, but if successfully reached, will pave the way for the next generation of materials, thus opening technological opportunities.

While synthetic materials may have revolutionized engineering at some of these levels over the last century,^{15–17} have societal problems emerged from their success? materials, in particular polymers, save lives, but the issues associated with the environmental persistence of synthetic materials continue to be questioned.^{18,19} A shift of paradigms will require robust strategies for precise, scalable, engineerable quantities of precision materials that serve specific functions for a predictable time, ultimately minimizing the risk of producing high quantities of unsustainable or non-degradable materials. Given these considerations, if life functions require controlled active and functional longevity, how can these properties be achieved in materials?

As the central theme of many research efforts and socially justified concerns, preserving or salvaging functionality continues to emerge as the necessity.^{5,20,21} In general, there have been a couple concepts floating around: (1) sustain the existing functions of materials so their lifespan is extended,⁵ or (2) degrade the existing functional materials to the essential molecules and use the latter for the development of new higher-end materials (upcycling) or simply reprocessing.^{22,23} While the first opportunity leans towards developing commodity self-recuperating materials, the second option involves controllable reprocessing, requiring chemicophysical alterations. These approaches at industrial levels are in their infancy, and retooling existing or developing modern alternatives for precise tailoring may be required. Taking this step further, if additive manufacturing is an option, nano 3D printing should be of interest, or printing without a printer *via* nano-scale supramolecular self-organization.

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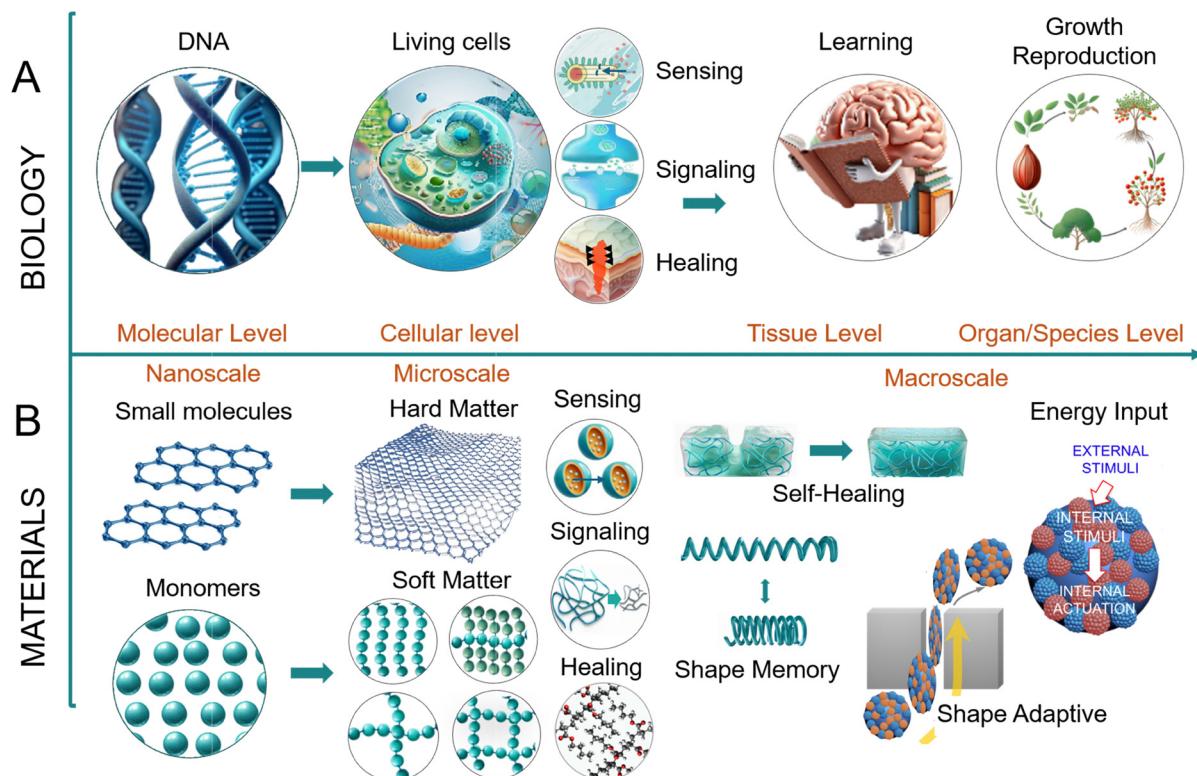


Fig. 1 Biological (A) and materials (B) responses at nano-, micro-, and macro-scale lengths.

Recent years have been particularly fruitful in fascinating discoveries resulting in material responses to physical, chemical, and biological stimuli.^{24,25} Taking these discoveries to another level may revolve around abiotic materials with dynamic functions that exhibit metabolic “life-like” behavior.^{26,27} An oversimplified version of anabolic-catabolic transitions governing biological processes has already been initiated by the development of macromolecules that fragmented into more straightforward segments to release (catabolic) and reform again, consuming energy (anabolic).^{28,29} Biology identified these processes as metabolism involving proteins, fat, carbohydrates, and nucleic acids.³⁰ If the hypothesis that the metabolic concept leads to a new generation of materials, controllable bonding and rebonding in creating sustainable materials requires fundamental knowledge of nanoscale processes. This process may involve covalent bond cleavage, which is typically responsible for the stability of a polymer backbone. Several strategies have emerged in recent years, including reversible-deactivation radical polymerization (RDRP), dynamic covalent chemistry, and metal complex- or enzyme-catalyzed depolymerization.^{31–34} These approaches offer pathways to recycle, repair, or reconfigure polymers while maintaining partial mechanical properties. However, reformed polymer chains often exhibit broader dispersity and partially altered conformations compared to their original state, making it challenging to recover their initial performance completely. Dynamic networks and their potential for chemical degradation may facilitate efficient end-of-life management when successful chemical degradation involves multifunctional amines. In this context, enaminones,³⁵ known

as vinylous amides, consisting of a conjugated system of an amino group linked through a carbon–carbon double bond to a carbonyl group, could play a critical role because they are highly reactive and can form intramolecular hydrogen bonds and different tautomeric components.

Non-covalent bonding and rebonding in polymeric materials always involve the interplay of side groups containing polar or dipolar bonding characteristics. While hydrophobic components often participate in the van der Waals (vdW) interactions, hydrophilic groups contribute more polar characteristics. The interplay of these interactions at the atomic levels are driven by atom electronegativity; for example, oxygen and nitrogen tend to draw the electron cloud toward themselves through the covalent bond from the less electronegative attached neighboring atoms. This dipolar nature creates a charge dispersion, forming partial positive ($\delta+$) and negative ($\delta-$) charges within the same macromolecular entity. Suppose dipolar groups within one or more adjacent macromolecular chains generate charge fluctuations, relatively weak energy interactions ($0.5\text{--}1.2\text{ kcal mol}^{-1}$) of a nonionic distance-sensitive nature are expected. These weak interactions established between opposite charges ($\delta+$ and $\delta-$) are ubiquitous, thus governing many properties, and their multiple characters control many biological processes. Inorganic materials science has begun exploring entropic contributions,³⁶ but until recently, only a few polymeric materials have exploited this concept.^{37,38} By creating ergotropically favorable non-equilibrium gradient states and manipulating polar and dipolar interactions, new properties, include electrical circuit elements or energy storage devices can be developed.³⁹ Along these lines,

Polymeric memristors are exalted candidates for low-power edge computing. One of the promising candidates are thiophene-quinoxaline polymers with donor-acceptor pairs, but the most challenging is to achieve crystalline uniformity. Also, precisely designing new and redesigning existing systems will enhance sustainability by controlled copolymerization which has led to key-and-lock,⁴⁰ ring-and-lock,⁴¹ and sigma-lock⁴² self-healable copolymers. Also, crystallinity and phase separation in polymeric materials can significantly influence self-healing and reformation processes.⁴³ For example, phase-separated polycaprolactone-polyurethane fibrous thermoplastic polymers form stable interfacial regions between hard and soft segments, enabling multiple damage-repair cycles.⁴⁴ These structural changes often arise from dynamic bonding or segmental rearrangements, forming time-dependent morphological features that affect mechanical properties⁴³ or phase reorganizations responding to electric fields.³⁹

In the search for materials with new properties and sustainability being a part of the equation, several classes of materials at different scale lengths are of particular significance. At nanoscales, metamaterials involve artificially engineered structures composed of repeating subwavelengths, which can be fashioned from metals, dielectrics, or organics.⁴⁵ The key challenge is controlling electromagnetic wave interactions by designing these quantum-like structures with specific geometric patterns including (1) the negative refraction that does not follow Snell's law of traditional light bending,⁴⁶ (2) focusing light by overcoming the diffraction limits, allowing imaging and sensing at much higher resolutions and potentially enabling nanoscopic or more advanced photonic circuits,^{47,48} (3) focusing light with no distortion, overcoming the capabilities of conventional lenses made from glass or other natural materials,⁴⁹ or (4) cloaking which involves bending of light around an object, making the object invisible, or reducing the visibility of objects by manipulating how light interacts with them (plasmonic resonance).⁵⁰ These properties will enable the light to reverse in a specific direction, thus enhancing the interaction between light and the material at the nanoscale, offering sensing, imaging, and enhanced nonlinear optical responses with harmonic generation, optical switching, and optical modulators.⁵¹ It should be pointed out that the definition of metamaterials has been broadened, and often well-ordered nanonetworks composed of periodic patterns, such as block copolymers, are considered in the category where shape memory enables structural reconfigurations.⁵² However, gain-enhanced metamaterials and nano-plasmonics are still the exciting frontiers at the nanoscale, where actively integrated precursors or quantum nano-optics may enable manipulating and shaping the emission spectra of fluorescent elements at scales below a few tens of nanometers.⁵³

At the microscopic or cellular scales (Fig. 1), combining or embedding different components into various environments may provide an opportunity for interactive structures enabling communication between modular components, each containing and constraining individual metabolic networks.⁵⁴ This hypothesis could be tested in the context of dynamics of interactions of hydrophobic domains in hydrophilic environments, where the

formation of microdomains may be critical when scaling up to macroscale levels, leading to the development of architecturally or kinetically different, self-contained metabolic materials. The grand challenge of creating materials with adaptability, responsiveness, and sustainability will require a molecular understanding of principles that govern life-like functions involving signaling, communications, growth to higher scales, replication, and anabolic-catabolic transitions. Although there are striking differences between biological and synthetic materials, there are similarities. The ability to self-assemble and create functionalities across a broad spectrum of length scales by sequential arrangements of nucleotides and amino acids at nanoscales is analogous to controlled monomer copolymerization forming random, alternative,⁵⁵ or block topologies,⁵⁶ ultimately dictating what assemblies of morphologies will be formed.

At higher-level scales, cells can organize themselves into ordered architectures using encoded genetic instructions in their genome that control and orchestrate cell differentiation. Copolymers constructed by integrating synthetic components will convert into different forms by structural rearrangements, resulting in the ability to recognize other confirmations, mechanical stability, conductivity, or adhesion.^{57,58} The growing field of hybrid living materials engineered by integrated living cells and artificial materials forming porous silica structures enables hosting single diatom cells to provide the organism with robust metabolic processes involving chlorophyll synthesis.⁵⁹ Along these lines, microbially induced calcium-carbonate precipitation in bacteria-containing bricks, which, through the aggregation of separate inorganic particles, results in the formation of bricks with high mechanical strengths, thus self-healing cracked concrete.⁶⁰

One of the challenges at macroscale levels is to design materials that, upon approaching an obstacle, a mechanical force experienced by the micro-object upon contact induces non-uniform deformations and strains, generating rapid softening and shape adaption, thus enabling a narrow space passage.⁶¹ If shape recovery follows, the return to the initial physical state/shape/behavior is expected. The challenging aspect is using other stimuli (e.g., light radiation, temperature, chemical environments) embedded into materials, which cannot be achieved in conventional strain-softening (ductile) materials because their moduli decrease gradually with the increasing strain in an irreversible manner. Since self-configurable, self-healing, or self-adaptable properties are inherently associated with structural rearrangements, understanding fundamental physico-chemical processes governing shape adaptations and recovery modes is essential.

The field of stimuli-responsive materials continues to be an active and potent area of research. Multi-stimulus responses may be orthogonal, competitive, or synergistic and governed by the redefined polymer science principles, with signaling and communications, encoding phenotypic properties with precisely defined sequences, programmable assembly/disassembly, and recognition attributes.¹² Traditional synthetic approaches resulting in controllable responses to engineered biological cells involving microbial colonies to generate or remodel material structures or the cell-free design of synthetic materials using



organic/inorganic hybrid building blocks are only recent advances.⁶² Seeking to harness these capabilities to match nature's intricacy, integrating anabolic–catabolic transitions to synthesize and controllably break down complex macromolecular structures into simple building blocks offers paths for materials sustainability with compartmentalized structural features capable of reversible remodeling at macroscopic scales.⁶³ These efforts will require enhanced analytical tools at all scale lengths (Fig. 1) integrated and not isolated computational methods to understand living functions further and connect them to tunable sustainability. In this context, thermoplastic and thermoset polymers as two distinguished groups slowly vanish as the last couple of decades have witnessed extensive bridging of this gap in a new class of covalent adaptable networks (CANs) that utilize dissociative or associative exchange reactions for reprocessing.^{64,65} Dissociative CANs contain reversible covalent bonds that, under various stimuli, establish an equilibrium between open (dissociated) and closed (associated) states. During bond-breaking crosslinks cleavage, the network contains the released reactive components capable of diffusion that can react again, thus regenerating crosslinks. These dynamic crosslinks form covalent bonds that undergo exchange with one another, offering an exceptional combination of mechanical performance, recyclability, and many applications.

The recent growth of machine learning (ML) and artificial intelligence (AI) are highly promising aids if sufficient databases are available. Large structural and crystallographic databases have been successfully utilized in the fast composition-based structural screening of inorganic hard materials,^{66,67} but despite advances in reprocessable and sustainable soft matter, including thermoplastics^{68,69} and thermosets,^{70–76} at this point there are limitations. With many compositional and structural variables, reliable data platforms can be developed. While ML and AI can effectively address societal needs and offer practical solutions, advances in developing living and dynamic soft materials are still limited. Although these tools can be powerful when databases are reliable, at this stage, they need more materials science than materials science needs ML and AI.

Data availability

This opinion article does not contain experimental data; it only has cited references.

Conflicts of interest

There are no conflicts to declare.

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