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FIRST REACTIONS

Next-Generation Materials via Orthogonal Stimuli

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A novel and user-friendly synthetic platform enables enhanced control over polymer design and synthesis by exploiting the orthogonality between chemical and photochemical stimuli.

One of the grand challenges in modern polymer chemistry is the development of increasingly facile synthetic strategies that enable access to next-generation polymeric materials. In this vein, the advent of "living" polymerization techniques has had a central role across numerous scientific endeavors ranging from biomedical[1] to self-healing materials.[2] These user-friendly strategies have empowered scientists, synthetic and non-synthetic experts alike, with the ability to imagine, design, and realize polymeric materials with unprecedented levels of control over molar mass, architecture, chain-end functionality, and overall chemical composition.[3,4] Drawing inspiration from advanced synthetic methodology, well-defined materials can now be realized with exceptional levels of control using a variety of stimuli, including photochemical, mechanochemical, chemical, and electrochemical systems,[5] to regulate the growth of macromolecules in "living" polymerization techniques.

Through the synergistic combination of two fundamentally different stimuli, Fors and co-workers introduce an elegant way to exert on-demand control over two distinct polymerization mechanisms in an orthogonal manner.[6] Contrary to other systems that offer orthogonal control within a single stimulus (i.e., two different wavelengths of light[7] or two different electrochemical potentials)[8] or through sequential activation (i.e., light and then heat),[9] this work is particularly unique in that the ultimate polymer architecture is dictated by divergent photochemical and chemically mediated pathways (Figure 1). Simply put, when light is applied, radical polymerization ensues, and when light is turned off, an appropriate chemical reagent can be added to commence the cationic pathway. The beauty of this methodology lies in the way it harnesses the synergy of two fundamentally distinct stimuli to engender complex materials that are otherwise inaccessible via either stimulus alone. This is best exemplified by the capacity to synthesize unique architectures like alternating tetrablock polymers in one pot solely governed by when and how long the desired external stimulus is applied (Figure 2). To realize this impressive achievement, the authors drew inspiration from Kamigaito and co-workers who pioneered the concept for concurrent copolymerization proceeding through the reversible activation of a common dormant species by two different stimuli.[10] These methods afford the opportunity to study the influence of monomer sequence on polymer properties more precisely, which brings us closer to understanding sequence control in polymer synthesis.

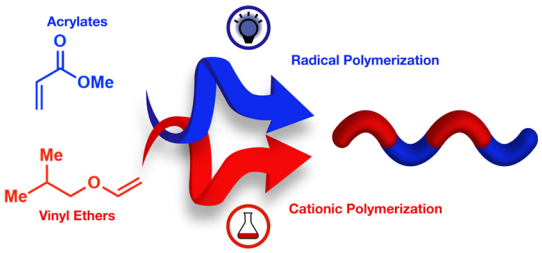

Figure 1. Representative schematic illustrating a method to control monomer addition orthogonally based on photochemical and chemical stimuli in one pot. Reprinted with permission from ref 6. Copyright 2018 American Chemical Society.

> The beauty of this methodology lies in the way it harnesses the synergy of two fundamentally distinct stimuli to engender complex materials that are otherwise inaccessible via either stimulus alone.

The concept of enhancing control over polymer design and architecture by exploiting the orthogonality between chemical and photochemical stimuli represents the forefront

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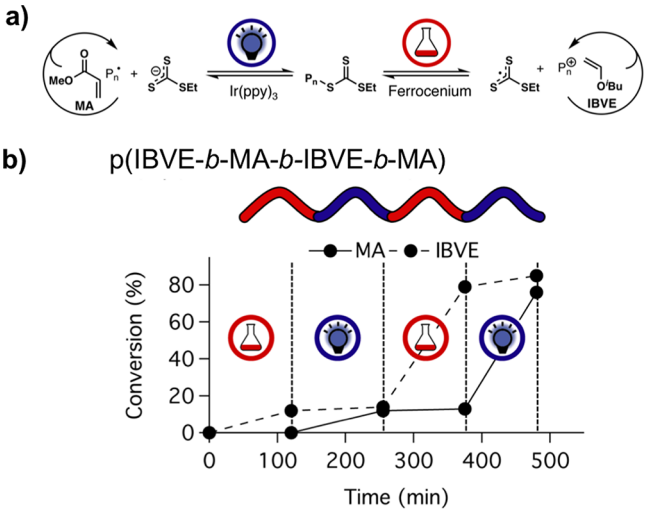

Figure 2. (a) Chemical schematic highlighting polymerization pathways dictated by the application of a photochemical (radical polymerization) or chemical (cationic polymerization) stimulus. (b) Plot tracking the conversion of methyl acrylate (solid line) and isobutyl vinyl ether (dotted line) upon application of appropriate stimulus for the preparation of tetrablock copolymers. Reprinted with permission from ref 6. Copyright 2018 American Chemical Society.

of synthetic polymer methodology. It is without doubt that the synthetic community will continue to research and discover new ways to advance available tools needed to push the boundaries of materials synthesis, while synchronously ensuring broader access to unique materials for use by both synthetic and nonsynthetic experts. As this field grows, one aspect that could be further explored is the design of tunable functional groups that exhibit highly selective activation in increasingly complex environments such as hyperbranched or star polymers. These reactions must proceed efficiently in the presence of the multitude of functional groups found in complex materials and would benefit from activation using highly accessible stimuli such as sunlight or heat.

Moving a step further, could three or four different stimuli be utilized in a single system? Intuitively, the more knobs there are to tune, the greater the control and complexity of the resulting materials. In this manner, the community will not only increase the breadth of accessible materials, but also garner fundamental insight regarding the compatibility of multiple stimuli in a single reactive system. The grand challenge will be to achieve this while balancing it with the need to keep it "simple" for widespread use. It is also essential to keep in mind that along with expanding the accessibility of interesting and diverse macromolecules, there needs to be a concomitant push for identifying and characterizing the usefulness of these new materials in application-driven settings. Only through these collaborative research efforts will we be able to bridge the gap between synthetic materials design and end utility. In this way, the true potential of fundamental synthetic discoveries such as these can be fully appreciated.

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