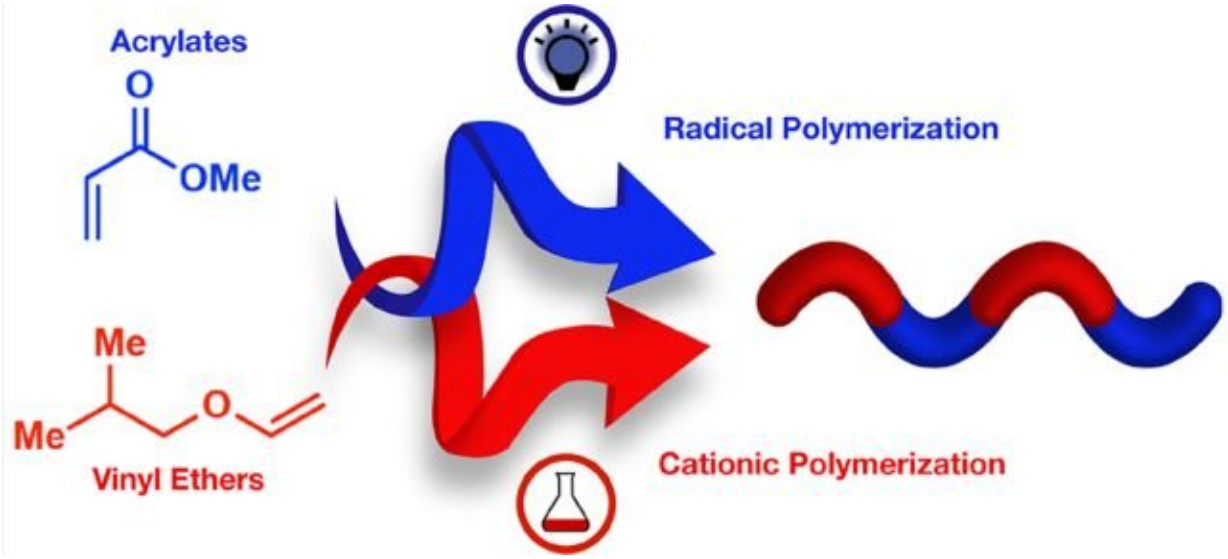
Designer polymers on demand

August 8 2018



Credit: American Chemical Society

When jewelers create a necklace, they control the order and number of each bead or jewel they use to form a desired pattern. It's been challenging for scientists to do the same thing when designing polymers—until now. In *ACS Central Science*, researchers report a new method using light and chemical reactions to control how subunits come together to form polymers with precise properties.

Laboratory-made polymers as influential to modern life as Teflon, nylon and polyvinyl chloride (known as PVC) are made up of repeating units of just one kind of molecule that collectively give the polymer its unique

physical properties. But nature is full of designer polymers like DNA and proteins, which are made up of differing subunits strung together that can encode information or structural features. In previous research, Brett Fors and colleagues had taken steps toward mimicking nature's variety in the lab to create designer polymers using two photocatalysts that worked when either blue or green light was shone on them. The method wasn't very selective, so the researchers set out to optimize the strategy.

The team used blue light to make one type of monomer bind, and a chemical stimulus (an oxidant) to make another type of monomer bind. By toggling between the light or the chemical additive, the researchers could selectively choose which subunit was added to the growing polymer molecule. They showed that they could create different patterns of polymer blocks along the chain, the length of which was dependent on how long the stimulus was applied.

The researchers suggest that this approach will improve on-demand control over sequence, structure and architecture for many different polymers.

More information: "On Demand Switching of Polymerization Mechanism and Monomer Selectivity with Orthogonal Stimuli" *ACS Central Science* (2018). pubs.acs.org/doi/full/10.1021/acscentsci.8b00401

Abstract

The development of next-generation materials is coupled with the ability to predictably and precisely synthesize polymers with well-defined structures and architectures. In this regard, the discovery of synthetic strategies that allow on demand control over monomer connectivity during polymerization would provide access to complex structures in a modular fashion and remains a grand challenge in polymer chemistry. In

this Article, we report a method where monomer selectivity is controlled during the polymerization by the application of two orthogonal stimuli. Specifically, we developed a cationic polymerization where polymer chain growth is controlled by a chemical stimulus and paired it with a compatible photocontrolled radical polymerization. By alternating the application of the chemical and photochemical stimuli the incorporation of vinyl ethers and acrylates could be dictated by switching between cationic and radical polymerization mechanisms, respectively. This enables the synthesis of multiblock copolymers where each block length is governed by the amount of time a stimulus is applied, and the quantity of blocks is determined by the number of times the two stimuli are toggled. This new method allows on demand control over polymer structure with external influences and highlights the potential for using stimuli-controlled polymerizations to access novel materials.

Provided by American Chemical Society