

# A New Approach to Manufacturing with Frontal Polymerization to Generate Patterned Materials

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Using frontal polymerization to create controlled, programmable, and useful patterns in properties of a thermoset polymer without masks, molds, or printers.

In this issue of *ACS Central Science*, Lloyd et al. have shown how to use some unique characteristics of frontal polymerization to create mechanical, chemical, morphological, and optical patterns spontaneously.<sup>1</sup> They have created systems whose properties can be tuned spatially by adjusting the initial conditions of a self-propagating polymerization reaction. What makes this work so exciting is that the macroscopic property variations were achieved without the need for masks, molds, or printers that are used in traditional manufacturing.

Frontal polymerization was discovered in the early 1970s at the Institute of Chemical Physics in Chernogolovka, Russia.<sup>2</sup> Frontal polymerization is a localized reaction that propagates like a cigar burns—from the coupling of heat diffusion and the Arrhenius kinetics of an exothermic reaction. Heat from the reaction spreads and starts more reaction, which releases heat, and the reaction propagates throughout the sample. Instead of leaving behind ash, a polymerization front converts monomer into a polymer, often a solid one.

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Imagine that instead of a cigar burning smoothly as a moving plane of combustion, it burns like a corkscrew (helical pattern)



**Figure 1.** Visible image of a single-head spin mode in the frontal polymerization of a diacrylate with bromophenol blue as an indicator. The alternating green and yellow horizontal patterns in the wake of the spin head are the tracks left by the spiraling hot spot. Tube diameter = 125 mm.

or stops and starts, leaving patterns in the ash. These patterns had been observed in self-propagating high temperature synthesis (SHS) of inorganic compounds.<sup>3</sup> (The thermite reaction of iron oxide with aluminum is an example of SHS.) In **Figure 1**, a helix can be seen in a front performed in a test tube. The appearance of spin modes is strongly dependent on the kinetics of the polymerization and the geometry. The number of spin modes increases for larger tubes, and if the container is rectangular, then zigzag patterns arise.<sup>4</sup>

The sharp variation in temperature and composition caused by frontal polymerization also can cause spontaneous fluid motion (convection).<sup>5</sup> Such fluid motion has always been seen as an interference with using frontal polymerization for manufacturing. For example, unless the viscosity

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is sufficiently high, polymerization fronts will not propagate horizontally or upward. Also, only fluid motion caused by gravity or surface tension was considered and not fluid motion caused by the expansion of the solution from the large increase in temperature.

In this work, Lloyd et al. show how to use spin modes and convection to create well-controlled patterns in mechanical, chemical, and optical properties of an industrially relevant polymer. They use the frontal ring-opening metathesis polymerization of dicyclopentadiene and 1,5-cyclooctadiene, which Robertson et al.<sup>6</sup> showed could be used in an extremely energy efficient manner for preparing large composites. By tuning the reaction kinetics and the transport properties, they have created systems in which the properties of the final polymeric material can be programmed spatially on the centimeter scale. For example, the reaction rate was adjusted by changing the initial temperature of the resin/catalyst solution. Unlike other work with frontal polymerization, the surface of the liquid resin had a free interface to allow fluid motion, and they harnessed the interaction of the fluid motion and the fronts to create patterns.

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As the polymerization fronts propagate periodically, the front temperatures vary spatially, and these temperature variations can create large variations in glass transition temperature, stiffness, and sample thickness. The spatial variations in temperature altered the cis/trans ratio of 1,5-cyclooctadiene. Because the trans form tends to crystallize, patterns of amorphous and crystalline polymer were created. The undulations in temperature also created colored patterns with the incorporation of a phenylenediamine-based thermochromes.

This novel approach to manufacturing offers the possibility of making materials with desired periodic properties on the macroscopic scale by programming the patterns into the dynamics of the frontal propagation. The properties are then imprinted into the material by the self-organizing nature of the propagating front. Whether this method can be applied to industrial scale manufacturing of patterned materials remains to be seen, but there is no doubt this paper will motivate

more investigation into frontal polymerization and its possible use for manufacturing.

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#### Notes

The author declares the following competing financial interest(s): The author has a financial interest in QuickCure Clay.

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