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# Rapid Stiffening of a Microfluidic Endoskeleton via Frontal Polymerization

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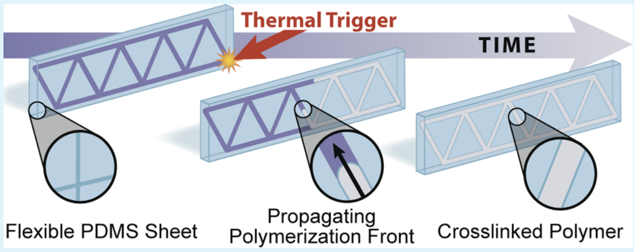
*Supporting Information*

**ABSTRACT:** Materials capable of rapidly modifying their physical properties in response to stimuli are desirable for on-demand deployment and adaptive engineering structures. Frontal polymerization is a self-propagating reaction that can quickly transform liquid reactants into solid products. In this contribution, we demonstrate that frontal polymerization enables facile, rapid stiffening of a vascular network embedded in a flexible matrix. Systematic variation of the vascular architecture shows that polymerization fronts in a polydimethylsiloxane (PDMS) matrix are self-propagating in channels as small as 838 $\mu$m and even when curves, branch points and converging geometries are present. After polymerization the composite structure was dramatically stiffened (up to 18 times the original Young's modulus) based on tensile testing results. This work demonstrates the use of frontal polymerization as an efficient methodology for transforming flexible materials into functional supports or surfaces through endoskeletal stiffening.



**KEYWORDS:** *frontal polymerization, microfluidic endoskeleton, rapid stiffening, shape fixing*

Autocatalytic or self-propagating reactions have widespread use in biological and synthetic systems as a means of amplifying small stimuli to effect dramatic change.[1] Self-propagating reactions, including combustion, base proliferation, frontal polymerization, and others, are advantageous for use in the chemical field because of their low energy requirements, because the initial stimulus is the only requisite input energy.[2−5] This stimulus ignites a self-sustaining reaction, perpetuating itself via the reaction's thermal energy release and chemical products. Frontal polymerizations are of particular interest because they engender a useful transformation of physical properties. In radical-based frontal polymerization, the stimulus is a localized heat or light source that activates an initiator dissolved in the monomer to produce a high local concentration of radical intermediates. The resulting chain growth polymerization is exothermic, thereby locally increasing the temperature of the unreacted solution, sustaining initiator homolysis, and enabling further chain growth. The result is a propagating polymerization wave or "front" that can travel at speeds greater than 30 cm/min.[6] Frontal polymerization of a liquid monomer into a solid polymer has been used to develop a number of functional materials such as fast-curing epoxy resins, thermochromic materials, hydrogels, and sensory materials.[7−16] To the best of our knowledge, frontal polymerization has not been used to stiffen flexible materials. In 2009, Chang et al. developed an approach for mechanical stiffening, where a reactive liquid embedded in channels within a flexible matrix was photopolymerized to yield a cross-linked solid.[17] However, the entire sample was required to be transparent and irradiation for 15 min was necessary to achieve the desired mechanical properties. We believe a self-propagating reaction wave employed in a similar fashion is a more facile and rapid means of reinforcing a flexible material.

Herein, we explore the versatility of frontal polymerization propagating through vascularized structures and demonstrate substantial material stiffening through the formation of reinforcing endoskeletons. Microfluidic vasculature enables the controlled penetration of the liquid monomer throughout the flexible matrix while minimizing the volume of reactants and retaining matrix flexibility until the triggered polymerization event (and substantial stiffening). Using this technique, we found that transformation of liquid monomer into solid polymer within microvascular networks embedded in a PDMS matrix is achieved within 1 min of a single, localized heating event (Figure 1).

Free radical polymerization is the most common mode of frontal polymerization due to its high exothermicity, low reactivity at room temperature, and high rate of reaction. Research by Pojman et al. has shown that the frontal velocity, i.e., the rate at which the reaction wave travels, correlates to the number of reactive double bonds per molecular weight of the monomer.[18] Rapid curing is desirable, so we sought a system that maximizes the speed of the reaction wave. For an initial investigation, we chose a combination of the low volatility

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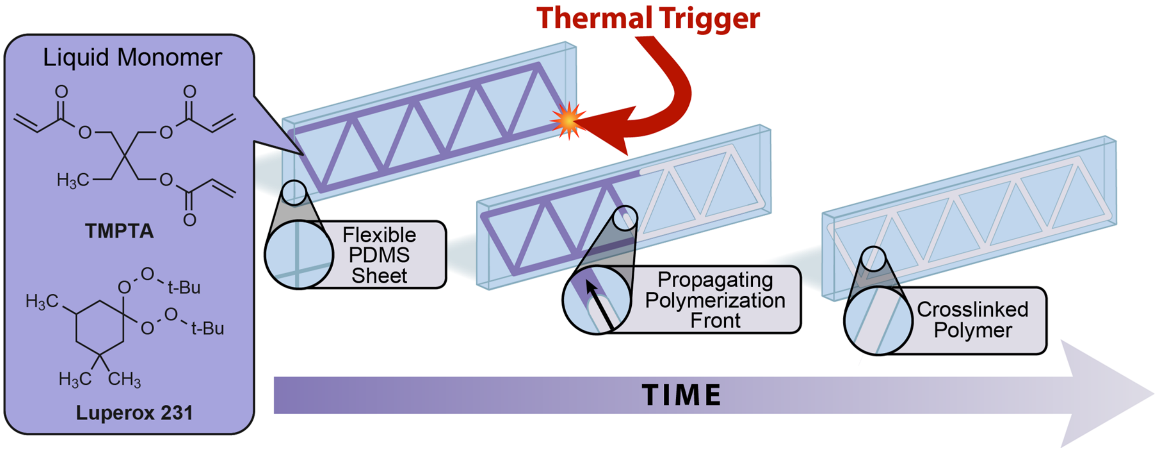

**Figure 1.** Schematic illustration of frontal polymerization within a microchannel endoskeletal network. Before frontal polymerization is initiated, the material is a highly flexible PDMS sheet encapsulating microchannels filled with reactive liquid monomer and initiator, shown in purple. A concentrated source of thermal energy initiates a polymerization front that quickly spreads throughout the microvascular network, effectively reinforcing the entire sample with rigid, cross-linked polymer, shown in gray.

**Table 1. Assessment of the Limitations of Front Propagation Imposed by Microchannel Size**

| channel diameter ($\mu$m) | average propagation distance (mm) | percentage complete propagation[c] | average frontal velocity[d] (cm/min) |
|---|---|---|---|
| 723 | 1[a] | 0 | |
| 762 | 6[a] | 12.5 | 15.9 ± 1.5 |
| 838 | 16[a] | 62.5 | 17.4 ± 0.4 |
| 1120 | 50[b] | 100 | 21.0 ± 0.2 |
| predicted adiabatic front | | | 30 |

[a] Calculated from 20 to 25 initiation events. Includes samples that did not propagate. [b] Calculated from 10 initiation events. [c] Calculated from 8 samples. Defined as the fraction of samples that polymerized all available monomer with one initiation event. [d] Calculated from samples that showed propagation greater than 10 mm. $N$ = 3, 5, 10 for 762, 838, and 1100 $\mu$m, respectively.

trimethylolpropane triacrylate (TMPTA) (99 g/mol per double bond) monomer and Luperox 231 initiator, which has been well-studied and demonstrated to sustain high frontal velocities.[18−20]

Performing a frontal polymerization on the microscale presents unique challenges. In microchannels, the surface-area-to-volume ratio is notably higher than in previously studied cm-scale vessels; thus, a significant portion of the reaction's thermal energy is transferred into the surrounding matrix rather than effectively captured for homolysis of the initiator. Any factor that further impedes direct transfer of heat from the reaction zone to the unreacted monomer leads to quenching of the polymerization. Convection and bubble formation are the two main factors that inhibit frontal propagation in microscale vessels. Convection of the monomer solution at the frontal boundary causes the heat of reaction to disperse into a larger volume than conduction alone, preventing monomer from reaching the requisite temperature for propagation.[21] As the fronts for this system typically reach temperatures ca. 300 °C, dissolved gases, volatile liquids, or gaseous reaction products will expand dramatically during propagation. Gas formation presents a particularly acute problem in a microchannel where avenues for gas escape are limited. Any bubbles formed will expand, accumulate at the front, and form an insulating barrier, thereby lowering the front temperature and effectively halting frontal propagation. Pojman et al. have shown that the addition of fumed silica as a thixotropic filler allowed fronts to propagate in thin layers by impeding convection.[21] The filler also has the benefit of minimizing bubble expansion and transport because of the increased viscosity of the polymerizing medium.

The polymerization mixture used for all experiments described herein was composed of 2.5 wt % Luperox 231 and 10 wt % fumed silica in TMPTA. This mixture could still be initiated 24 h after initial mixing. We also recorded the maximum temperature ($T_{\max}$) of the frontal polymerization, and the values of $T_{\max}$ did not deviate significantly over the course of 7.5 h. Results from both of these experiments show that the level of incident (nonfrontal) polymerization was minimal. The polymerization mixture was viable for frontal polymerization in microchannel systems for approximately 2 h after mixing. After that time, bubbles from decomposing initiator began to form in the channels and block propagation. Because all experimental samples were initiated <30 min after mixing, the effect of incident polymerization is negligible in our studies.

Because microchannel diameter impacts heat transfer and front quenching based on the surface-area-to-volume ratio of the channel, we anticipate a minimum channel size through which a front will propagate for a given reaction and matrix composition. To test the limitations of the chosen chemistry, a series of straight, cylindrical channels ranging from 723 to 1120 $\mu$m in diameter and 50 mm in length were fabricated by embedding nylon monofilament in PDMS and removing it after curing. Channels of each diameter were initiated with a concentrated heat source. The results were recorded on video and the average propagation distance, percentage complete propagation, and average front speed were calculated (Table 1). On the basis of these data, the limiting size for the chemistry reported here was between 762 and 838 $\mu$m, where the propagation reached the critical diameter allowing >50% of the samples to completely propagate. Initiating polymerization in the 762 $\mu$m channels rarely led to propagation, and for those that successfully propagated, the front usually traveled a distance no greater than 20% of the channel length. The majority of 838 $\mu$m channels allowed propagation through the

Figure 2. Array of accessible geometries for frontal polymerization in vascular structures. Features investigated included curvature and branching. All microchannels shown here were fabricated using the catalyzed depolymerization of laser-cut polylactide sheets, approximately 600 $\mu$m in thickness. Channel widths range from 1 to 2 mm. Propagation through the entire sample with one initiation was observed in most cases. All scale bars are 1 cm.

entire sample. Below 762 $\mu$m, there were no instances of propagation, and above 838 $\mu$m, propagation through the entire sample was almost always observed. At 1120 $\mu$m, the frontal velocity was observed to be approximately 20 cm/min. Therefore, a 5 cm sample could be stiffened in as little as 15 s.

Goldfeder et al. developed a mathematical model for adiabatic frontal polymerization that predicts frontal velocity based on the kinetic and thermodynamic parameters of the system.[22] By applying parameters consistent with the formation of polyTMPTA, the calculations predict a frontal velocity of ca. 30 cm/min under adiabatic conditions. In the 762 $\mu$m channels, the frontal velocity was nearly 50% lower than this theoretical adiabatic value. As channel size was increased, the frontal velocity approached the predicted rate. The highest experimental frontal velocity for the chemistry used here was recorded at ca. 22 cm/min in a 1 cm test tube. The significant deviation from the calculated ideal was a result of factors such as heat lost to the matrix and bubble formation, which were not included in the model. Both of these factors had higher impact with decreased channel diameters and increased surface-area-to-volume ratio, leading to the observed reduced frontal velocity.

Given the wide variety of microfluidic structures found in the literature,[23−25] we explored the scope of frontal propagation by investigating the effects of channel geometry. To determine the limitations imposed by channel shape, frontal polymerization of TMPTA was performed in samples containing multiple branches, converging fronts, and curves. (Figure 2). Fronts were initiated from a single point (an open channel location) and allowed to propagate. Most geometries did not impede propagation. Perpendicular branching geometries presented an interesting challenge, where propagation typically proceeded only through one branch of the channel. The unreacted channels were still reactive when initiated from the opposite end, suggesting the monomer solution was not the cause of this reaction termination. We speculate that small bubbles accumulate at the front and are shunted to one side as the propagating wave reaches the branching points. As a result, these bubbles direct the front to travel through one path over the other. To achieve simultaneous propagation into split channels, we modified the perpendicular junctions to include a triangular shape so that the increased volume would trap bubbles at the junction without disrupting the polymerization (Figure 2, middle row, left).

To evaluate these polyTMPTA channels as on-demand endoskeletons, we assessed the mechanical reinforcement this reaction imparts on a flexible matrix. Composite samples were fabricated consisting of Sylgard 184 PDMS with zero to five frontally polymerized, unidirectional polyTMPTA rods, provid-

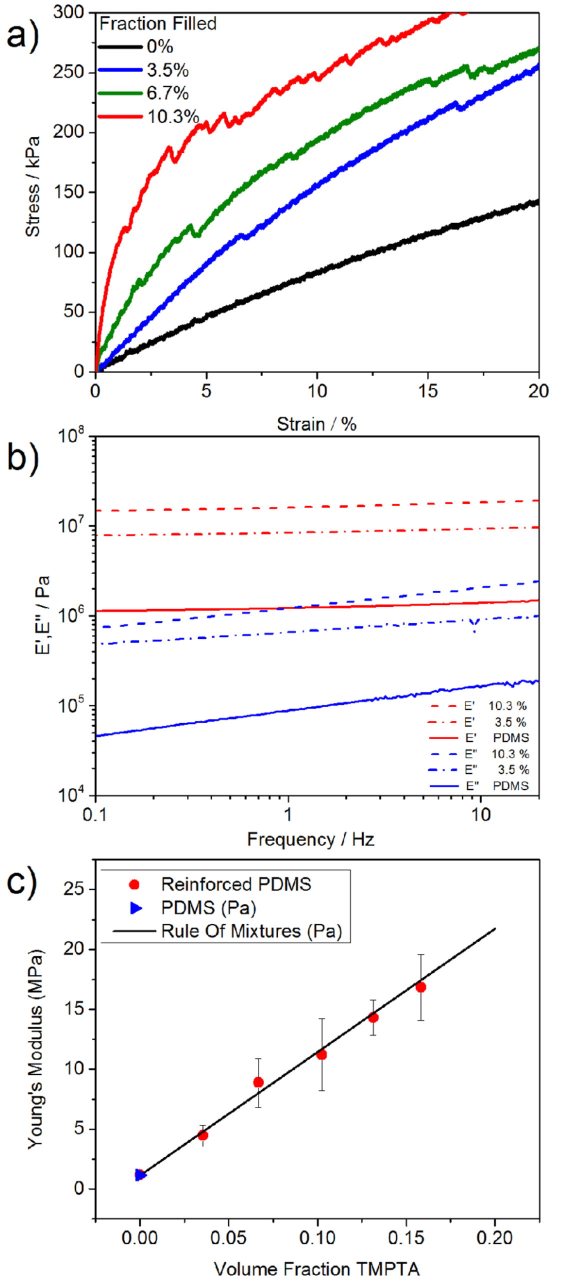

**Figure 3.** Effect of frontally polymerized channels on the mechanical properties of PDMS composites. (a) Representative stress−strain curves for Young's modulus measurements up to 20% strain. The fracture of polyTMPTA reinforcement at large strains results in rapid drops in the stress response. (b) Frequency response of the storage and loss moduli of the composite samples with increasing polyTMPTA volume percent. (c) Young's moduli for samples with 1−5 channels. The modulus increases with increasing vol % and is in agreement with the rule of mixtures. Error bars represent one standard deviation ($n$ = 3).

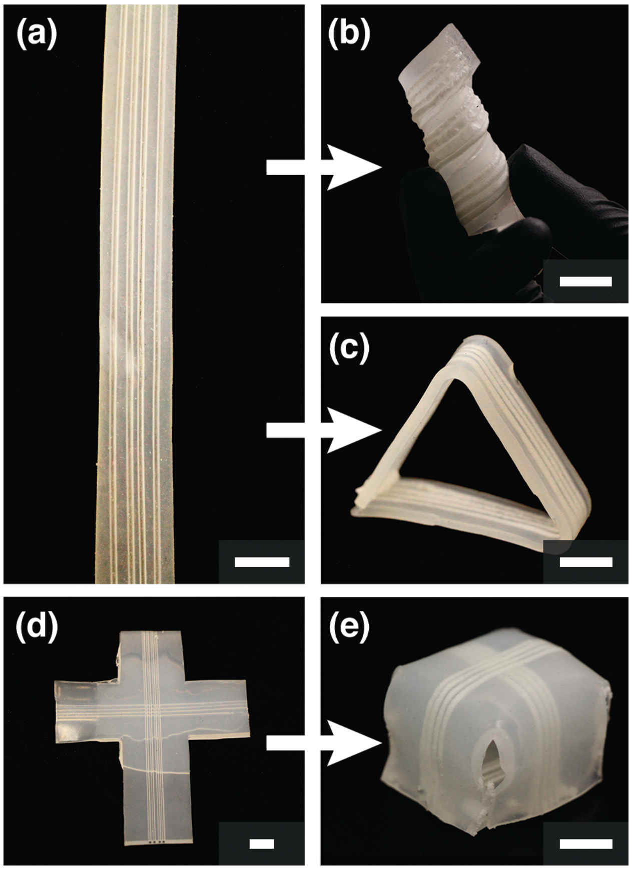

**Figure 4.** Embedded microchannels used to flash-cure PDMS into a variety of shapes. (a) Several straight segments of Ecoflex PDMS with four linear 1120 μm channels were fabricated. (b) One segment was wrapped around a 3/4 in. rod into a helical shape. Frontal polymerization was spot-initiated at one end and propagation through the whole channel was complete in approximately 1 min. The helix retains its shape after being removed from the rod. (c) Similar 4-channel segment of Ecoflex PDMS was flash-cured into a free-standing triangle. (d) A layer-by-layer fabrication introduced 2 sets of channels into a t-shaped piece of PDMS. (e) This pattern allowed for the formation of a cube, which retained its shape after polymerization was performed within the channels. All scale bars are 1 cm.

ing samples with 0−16 vol % reinforcement. The Young's moduli were determined by tensile testing the samples in the longitudinal direction of the microfluidic channels and calculating the slope from the initial linear region of stress−strain curves. Representative stress−strain responses of these samples (Figure 3a) illustrate the impact of the endoskeletons on mechanical behavior. Dynamic mechanical analysis was also performed for the composite (Figure 3b) and supports the tensile test results. The frontally polymerized endoskeleton increased the stiffness of the PDMS composite by up to 18 times at 16 vol % compared to the matrix alone (Figure 3c). To assess the performance of the system as a unidirectional composite, we compared the results to the rule of mixtures (eq 1).

$$E_{\mathrm{c}} = V_{\mathrm{f}}E_{\mathrm{f}} + V_{\mathrm{m}}E_{\mathrm{m}} \qquad (1)$$

The model depends on the volume percent of matrix ($V_{\mathrm{m}}$) and reinforcing material ($V_{\mathrm{f}}$) in the composite, as well as the individual moduli of the matrix ($E_{\mathrm{m}}$) and reinforcing material ($E_{\mathrm{f}}$). The Young's moduli of Sylgard 184 PDMS and polyTMPTA were determined independently to be 1.14 and 104 MPa, respectively. The experimental data agree well with the rule of mixtures predictions for Sylgard 184 PDMS reinforce with polyTMPTA.

The presence of stiff polyTMPTA channels provides mechanical support to the PDMS matrix, and frontal polymerization offers a unique approach to shape control of flexible materials. To demonstrate the utility of this approach, we filled several samples with linear channels 1120 μm in diameter with reactive monomer and initiator, deformed them into different shapes and subsequently spot-initiated. The frontal polymerization flash-cured the system in less than 1 min. After the maintaining force was removed, the samples retained their shapes, reflective of enhanced rigidity (Figure 4). The ability of frontal polymerization to propagate through many microchannel geometries will allow it to solidify a three-dimensional reinforcing structure, such as a set of struts, in much the same manner. The development of mechanically robust frontally polymerizable sheets will facilitate packing and transportation of deployable objects that are quickly transformed into the final form needed for a variety of aerospace and military applications.

In summary, this work demonstrates rapid stiffening of vascularized materials that change their properties in less than a minute. This effect is either localized or propagated throughout a microvascular system of potentially unlimited size. If the initiating stimulus is applied to multiple points throughout the network, the time required for reinforcement is reduced dramatically to provide a stiffening effect in a matter of seconds. Our approach is applicable to any heat-resistant, flexible microvascular system and useful for flash-curing flexible sheets into mechanically robust supports or surfaces. Furthermore, the heat generated by the reaction may activate other components embedded in the matrix to further reinforce the material.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Microchannel fabrication details, parameters for frontal polymerization and mechanical testing, and calculations for experimental and theoretical front characteristics. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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