Supplementary Information - Modeling of Oxygen-Inhibited Free Radical Photopolymerization in a PDMS Microfluidic Device

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1 Determination of the knee of the conversion curve

An accurate method is required to determine the critical particle height, γ_c which occurs at the knee of the particle height versus time curves. The knee is defined as the point of minimum radius of curvature of such a curve (Fig. 1). Discrete data points from the model were interpolated to find a smooth curve whose first and second derivatives were then used to find the minimum radius of curvature. The point of minimum radius of curvature was then used to find the critical particle height, γ_c from which the critical thickness of the oxygen inhibition layer was found as $\delta_{i,c} = (1 - \gamma_c)/2$.

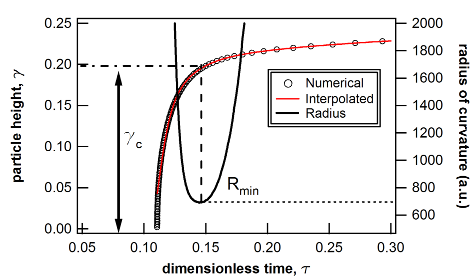

Figure 1: Calculation of the knee of the conversion curve. The knee is defined as the point where the radius of curvature of the curve is at its minimum value. Model data points (black circles) are first used to obtain an interpolated curve (red). The radius of curvature (solid black line) is then calculated from the interpolated curve using the formula $R = d^2y/dx^2/(1 + (dy/dx)^2)^{3/2}$

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2 Sensitivity of results on the value of ξ_c

We have focused on two important variables to present our results and validate our model experimentally. These are the induction time, τ_i and the critical thickness of the oxygen inhibition layer, $\delta_{i,c}$. We find that the particular value of critical conversion, ξ_c chosen does not significantly alter the values of these variables. This can be seen by examining the plots of particle height, γ vs. time, τ at different values of the critical concentration, ξ_c. The data in Fig. 2 were obtained using the parameter values in Table 2 of the manuscript and are typical of the results reported. Changing the critical conversion through a very wide range (90-99%) results in values of τ_i that range from 0.045-0.051 and values of $\delta_{i,c}$ that range from 0.29-0.31.

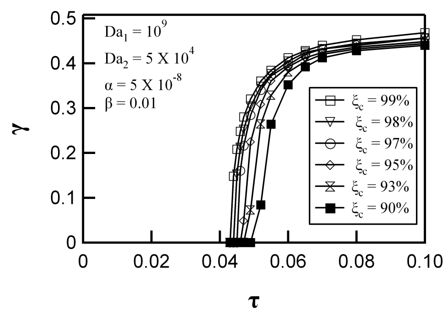

Figure 2: Sensitivity of τ_i and $\delta_{i,c}$ to changes in the value of the parameter ξ_c. xi_c was varied between 90-99% and curves of particle height vs. time were obtained at the values of the parameters shown in Table 2 of the manuscript.

3 Control experiment to prove Oxygen inhibtion

The apparatus used to prove the necessity of oxygen for the occurrence of the inhibition layer that permits flow lithography is shown in Fig. 3. The apparatus was fashioned by encasing the microfluidic device inside a sawed-off plastic tube whose top and bottom were sealed with 24 × 60 mm glass slides and sealed with epoxy. Three holes were punctured in the plastic - one to permit the entry of gas (Argon/air), one to permit the exit of gas (air/Argon) as required and the third to allow for the entry of oligomer solution. Fluid entry was facilitated through 1 ml syringes attached to a 22 gauge needle as seen in Fig. 3b. Each time a new gas was exchanged for the existing gas, 30 minutes were allowed for the gas to saturate the atmosphere inside the apparatus before the effects were observed.

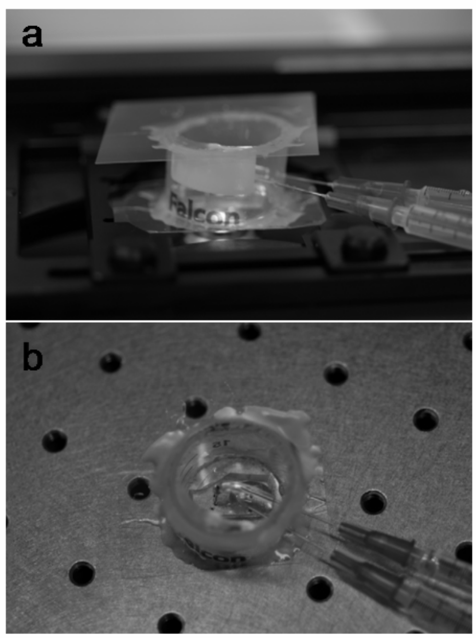

Figure 3: Chamber used to prove the oxygen inhibition effect. The all-PDMS microfluidic device was surrounded by a plastic ring and capped and sealed by glass slides on the top and the bottom. Two inlet ports were drilled into the plastic ring surrounding the PDMS device. Argon or air was flown through one port while PEG-DA solution flowed through the other. a)Side view.b)Top view