POLY 62: Controlling the evolution of frontal photopolymerization waves for 3D polymeric patterning

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In this work we describe a general, simple and exceptionally well-controlled patterning approach for photocurable monomers based on frontal photopolymerization (FPP). FPP is a significant case of photopolymerization reaction, where illumination results in the development of a solidification front which propagates in the form of a planar wave, invading the monomer bath. The factors governing the planar solidification process, including front position, profile shape, diffusion and thermal effects, are explicitly investigated and quantified. We find the FPP process to be controlled by tuning selected photopolymerization parameters, such as monomer chemistry, optical properties, temperature, time and intensity of irradiation, in a remarkably general and simple fashion. A minimal descriptive model accurately describes the frontal solidification kinetics, and model extensions were developed accounting for different phenomena occurring during FPP, such as diffusive mass transport, swelling, heat generation and transport, optical attenuation. The predictive capability of the model is applicable to the fabrication of 3D patterned materials from representative radical photopolymerizing systems, showing prescribed dimensions and controlled mechanical properties and stress development.

Schematic of the FPP experimental setup showing the photopolymerization front propagation from the UV illuminated surface and examples of 3D patterns obtained by FPP. The extent of monomer-to-polymer conversion $\phi$ within the network has a sigmoidal shape profile, while the sample thickness $z_f$ increases logarithmically with exposure dose $d$. 