

Magnetic Levitation to Characterize the Kinetics of Free-Radical Polymerization

Supporting Information

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Experimental procedures

Calibration of the MagLev device

We used small drops (1-5 μL , ~ 1.2 - ~ 2.1 mm in diameter) of hydrophobic organic solvents and liquids of low-molecular-weight monomers with known densities to establish the calibration plots. Table S1 shows a list of suitable hydrophobic organic liquids for the purpose of calibration. Large standard glass beads (~ 4 mm in diameter) with precisely calibrated densities that we commonly used to establish the calibration plots are not preferred owing to their relatively large sizes and often non-spherical shapes, and thus a greater experimental uncertainties in determining the centroids of the beads.¹

Treatment of data

We used imageJ to analyze the images and manually determined the heights of the sample drops. Briefly, we drew a line across the centroid of the drop on the image and in parallel to the edge of the magnets, and read the height of the drop using the scale on the ruler (where the line intersects the scale) with a precision of ± 0.1 mm (one tenth of the smallest division on the ruler). We did not read h to a higher precision (the ultimate limit in this experiment is the size of a single pixel on the image, ± 0.025 mm) because the precision of the density values reported by the vendors is limited to $\pm \sim 0.001$, which translates to an estimated uncertainty in h of ± 0.1 mm (using an aqueous solution of 0.5 M MnCl_2).

Preparation of monomers, initiators, solvents, and paramagnetic medium

In general, inhibitors including 4-Methoxyphenol and O₂ dissolved in the liquids of monomers were removed by running the liquids of monomers through an Al₂O₃ column, and subsequently, performing freeze-and-thaw cycles (at least 3x). The purified monomer was stored at -4 °C under Ar until use. Dissolved O₂ in solvents and aqueous paramagnetic solutions were removed by purging the solvents or aqueous solutions by Ar for at least 30 min. All solvents and solutions were stored in a gloved box with a regulated gas environment (N₂ atmosphere, O₂ <0.5%, v/v%) at room temperature. In cases where the conversions of monomers at the endpoint (not kinetics) were concerned, the liquids of monomers were used as received without removing the inhibitors because the inhibitors would be consumed completely before polymerization initiates, and therefore, would not affect the net conversions of monomers.

Thermal initiators (benzoyl peroxide, sigma #179981, and azobisisobutyronitrile, sigma #441090) and photo-initiator (2,2-dimethoxy-2-phenylacetophenone, sigma #196118) were used as received.

Procedures for polymerization of PDMS prepolymers

PDMS base and catalyst (Dow Corning, Sylgard® 184) were mixed at a weight ratio of 10:1, and degassed using vacuum. A plastic pipette was used to transfer a small quantity of the mixture, and held above the cuvette containing an aqueous solution of MnCl₂, until a small drop (~10 µL) of the mixture dripped from the pipette tip. Once the drop entered the solution (before it floated and became trapped at the interface between the air and the aqueous medium), the cuvette was inserted immediately into the gap between the two magnets. The levitation height was measured and recorded. The

remaining mixture of the PDMS prepolymer and catalyst was allowed to crosslink at room temperature for 24 h. A small piece was cut from the crosslinked PDMS slab and placed into the same MnCl_2 solution for measurement of density.

Procedures for thermal polymerization including bulk and suspension

polymerization

Bulk polymerization was performed in small, sealed glass vials (~2 mL). A mixture including a liquid of a monomer and a thermal initiator was prepared in a glove box (N_2 atmosphere, $\text{O}_2 < 0.5\%$, v/v%), and small aliquots (200 μL) were sealed into small glass vials. The sealed glass vials were removed from the glove box and transferred to a chemical hood in which the samples were heated using a temperature-regulated oil bath. At the end of a specified time, the vials were immediately placed on ice to stop the reaction, and a small aliquot (~1 – 10 μL) of the reaction mixture was transferred using a laboratory pipettor to a MagLev device for density measurement. The sample drop reached equilibrium in ~1 s or less in the MagLev device used for density measurement.

Suspension polymerization was performed in either sealed glass vials or an open glass flask (50 – 200 mL, to facilitate continuous sampling and kinetic monitoring). To simplify the procedure, we used the same aqueous MnCl_2 solution both to suspend the reaction mixture in the glass flask, and to measure the densities of the reacting mixtures using MagLev. Aliquots of the reacting mixture (~0.5-1 mL) were periodically removed using a pipettor and a large-bore tip (we simply cut 1-mL pipette tips to enlarge the size the opening, and thus, to minimize clogging of drops at the pipette tips), cooled by a bath

of the same MnCl_2 solution used to suspend the reaction mixture, and measured in a MagLev device.

Procedures for photopolymerization

Photopolymerization was performed directly in a MagLev device by levitating a drop of reaction mixture containing a monomer and a photoinitiator in an aqueous MnCl_2 solution, and irradiating it with a UV lamp (365 nm, Blak ray, model UVL-21).

Briefly, a reaction mixture of a monomer, a photoinitiator, and a solvent (if used) was prepared in a glove box (N_2 atmosphere, $\text{O}_2 < 0.5\%$, v/v%), and a small aliquot (~1 - ~50 μL) was levitated in an aqueous solution of MnCl_2 (usually pre-saturated with the monomer). The cuvette (a standard, disposable UV-grade cuvette cut to 25 mm in height to fit the MagLev device, sigma #z188018) was then sealed using a double-side tape (Adhesive Research, #ARSEAL®90880) by pushing the cuvette firmly against the top magnet. The MagLev device along with the cuvette and the levitated drop of monomer liquid was transferred, with care not to allow the drop to stick to the cuvette, from the glove box to a chemical hood. A UV lamp (365 nm, Blak ray, model UVL-21) was positioned at a distance of 9 cm from the central axis of the MagLev device and used to initiate the photopolymerization. The airflow in the chemical hood helped stabilize the temperature of the paramagnetic medium and the polymerizing drop while they were continuously irradiated with a UV light.

Measurement of fractional conversion of the monomer using ^1H NMR

For this experiment of validation, we performed photopolymerization of methyl methacrylate in the open air (without removing inhibitors such as oxygen) initiated by 2,2-dimethoxy-2-phenylacetophenone (5%, wt%) and UV irradiation at 365 nm (UVGL-25, UVP LLC, Upland, CA) in the MagLev device. We repeated the same experiments four times, and removed the sample drops from the MagLev device using a glass pipet at the specified time points during the time course of photopolymerization (20, 40, 57, 80 min). We then dissolved the sample in deuterated chloroform (~0.5 mL), and recorded the ^1H NMR spectra on a 600 MHz NMR spectrometer. The characteristic shifts of protons in the methyl ester in methyl methacrylate appear at 3.76 ppm, which are well separated from the chemical shifts of the same protons in the polymer at 3.60 ppm. We integrated the areas of these peaks, and estimated the fractional conversion of methyl methacrylate during polymerization.

Measurement of temperature of a polymerizing drop

We inserted a small (diameter of the wire: 125 μm) thermocouple (#CHAL-005, Omega Engineering, CT) in the MagLev device to measure the temperature of a polymerizing drop. The thermocouple has a specified response time of <0.1 sec in still water, and the digital thermometer (#HH11C, Omega Engineering, CT) has a specified precision of 0.1 $^{\circ}\text{C}$. We placed a small drop containing methyl methacrylate and photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (5%, wt%) on the tip of the thermocouple, and also added a second drop that levitated in the MagLev device without physical contact. We initiated photopolymerization using 365 nm UV irradiation, and

measured the levitation heights of the nonadherent drop, and the temperature of the adherent drop over time.

Procedures for polymerization in the presence of solid materials

We performed all polymerizations in the presence of solid materials in a chemical hood at ambient conditions, and used the chemicals as received (without further purifications). The solid materials included the following three types in the form of thin, non-woven veils: aramid (Aramid tissue, ACP composites, Livermore, CA), carbon fiber (carbon-fiber tissue, ACP composites, Livermore, CA), and glass fiber (fiberglass tissue, ACP composites, Livermore, CA). We used 3-mm biopsy punches to make discs of these materials to facilitate the determination of the centers, and thus, the levitation heights, of the samples during polymerization.

For a typical experiment, we first dissolved benzoyl peroxide (5%, wt%) in a liquid of monomer methyl methacrylate, added 4,N,N-trimethylaniline (5 μ L) to a small aliquot (95 μ L) of the mixture, immediately mixed it on a vortex (and recorded the starting time of the polymerization), dipped a disc of a solid material in the reacting mixture, and quickly transferred the disc to a MagLev device for density measurements.

Design of the device and alternative approaches

In this work, we assembled a MagLev device (Figure S1), rather than using the approaches (i)-(iii) discussed below, to perform polymerizations for one practical reason: to retain the operational simplicity of the standard configuration of MagLev to perform density measurements—we simply add a drop of the monomer, and then monitor polymerization (upon initiation), without requiring additional manipulations.

The standard configuration of MagLev cannot directly levitate hydrophobic organic liquids (including liquids of monomers, e.g. methyl methacrylate) having densities less than water. This shortcoming arises because of its relatively narrow range of accessible densities spanning from 1 to ~ 3 g/cm³ using aqueous solutions of simple paramagnetic salts (e.g. MnCl₂ and GdCl₃).¹

Three approaches we could (potentially) exploit based on the standard configuration or its variants include: (i) Tilted MagLev.² This variant of MagLev can measure the entire range of densities observed in matter at ambient conditions (from ~ 0 g/cm³ to ~ 23 g/cm³); it, however, requires tilting the standard MagLev device with respect to the vector of gravity, and rotating the sample container to minimize the impact of friction on density measurements (the sample, in this configuration of MagLev, is in physical contact with the sample container). The additional manipulations add operational complexity to the experimental protocol of density measurements. (ii) The use of dense solvents (or inert solids) to prepare the sample. We mix a light liquid with a dense liquid (or an inert solid, such as a glass bead with known volume, density, and mass) to tune the density of the mixture so that it falls in the accessible range of densities of the standard configuration of MagLev. While this approach offers a simple option to levitate light organic liquids, it uses additional components (i.e. solvents or solids) and also dilutes the change in density associated with the target liquid during, for example, polymerization. (iii) The use of light suspending medium. We prepare a light suspending medium using alcohols and other polar organic solvents (e.g. N,N-dimethylformamide or dimethylsulfoxide). While this approach works for solid samples of polymers,³ it may be

sub-optimal to study polymerization because of the compatibility of the solubilities of the participating components in polymerization with the suspending medium.

Given the shortcomings of these three approaches, we, therefore, developed a separate MagLev device with improved performance; this device has an expanded range of densities, and thus, can levitate—without additional manipulations—hydrophobic liquids with densities lighter than water (including methyl methacrylate). In the standard and other configurations that exploit the use of a linear magnetic field with the $B=0$ T in the middle point of the field, the theoretical range of density in these configurations of MagLev can be quantitatively described by eq S0:²

$$\Delta\rho = \frac{4\Delta\chi B_0^2}{\mu_0 g d} \quad (S0)$$

In eq S0, $\Delta\chi$ (unitless) is the difference in magnetic susceptibility between the levitated object and the suspending medium, B_0 (T) is the magnitude of the magnetic field at the center of the facing surfaces of the magnets, μ_0 ($4\pi \times 10^{-7} \text{ N}\cdot\text{A}^{-2}$) is the magnetic permeability of the free space, g (9.8 m/s^2) is the constant of gravitational acceleration, and d (m) is the distance of separation between the two magnets.

Eq S0 indicates that, for a given paramagnetic medium (e.g. an aqueous solution of MnCl_2) with a fixed $\Delta\chi$, the larger the ratio of B_0^2/d , the wider the range of density $\Delta\rho$. We, therefore, designed and assembled a MagLev that has a large ratio of B_0^2/d ($\sim 0.010 \text{ T}^2/\text{mm}$) than the standard configuration of MagLev ($\sim 0.003 \text{ T}^2/\text{mm}$). Figure S2 shows that plots of calibration for this MagLev device, validating the expanded range of densities using aqueous solutions of MnCl_2 .

Correlation of the concentration and the fractional conversion of monomer in the reacting mixture with the density of the mixture

For a typical polymerization experiment, we independently adjust the mass ratios of the starting materials: the mass ratio of an initiator to the monomer, k_2 , and the mass ratio of the solid material (if used) to the monomer, k_3 . The fractional conversion of the monomer in the reacting mixture is denoted as x ; the masses, densities, and the calculated volumes of all participating components are given in Table S2.

We define ρ as the density of the polymerizing mixture – the experimental parameter we measure directly using MagLev (by measuring the levitation height of the polymerizing drop). Eq S1 describes the fractional conversion of the monomer and eq S2 describes the concentration of the monomer in the polymerizing sample:

$$x = \frac{\rho_m \rho_p}{\rho_p - \rho_m} \left[\left(\frac{1}{\rho_m} + \frac{k_2}{\rho_2} + \frac{k_3}{\rho_3} \right) - \frac{1 + k_2 + k_3}{\rho} \right] \quad (S1)$$

$$[M] = \frac{\rho_m \rho_p}{M_w (\rho_p - \rho_m)} \left[1 - \frac{\frac{1}{\rho_p} + \frac{k_2}{\rho_2} + \frac{k_3}{\rho_3}}{\frac{1 + k_2 + k_3}{\rho}} \right] \quad (S2)$$

In eq S2, M_w (g/mol) is the molecular weight of the monomer (see Table S2 for definitions of the rest of the parameters). When deriving these equations, we assumed that the volumes of participating components, including the monomer and polymer, are simply additive in the sample – i.e. no volume change occurs simply as a result of mixing

Theoretical model to calculate the average rate of polymerization of a spherical drop

The general formula for the rate of polymerization of a radical polymerization system has been established previously:⁴

$$R_p = -\frac{d[M]}{dt} = k_p[M] \left(\frac{R_i}{2k_t} \right)^{0.5} \quad (S3)$$

In eq S3, R_p ($\text{mol L}^{-1}\text{s}^{-1}$) is the rate of propagation, $[M]$ (mol/L) is the concentration of the monomer, k_p ($\text{L mol}^{-1}\text{s}^{-1}$) is the rate constant of radical propagation, R_i ($\text{mol L}^{-1}\text{s}^{-1}$) is the rate of initiation, and k_t ($\text{L mol}^{-1}\text{s}^{-1}$) is the rate constant of radical termination.

We will use eq S3 as the basis to derive the average rate of photopolymerization of a polymerizing drop. We specifically made the following assumptions when deriving the equations: (i) we did not account for the inhibitory effects of O_2 (the residual amount present in the aqueous solution and in the drop) or from other sources, such as the presence of an aqueous phase surrounding the drop, and (ii) we assume that the incident UV light did not refract at the interface of the aqueous solution and the drop.

The rate of photochemical initiation per unit volume is given by

$$R_i = 2\phi I_a \quad (S4)$$

In eq S4, ϕ (unitless) is the quantum yield for initiation, and I_a ($\text{mol L}^{-1}\text{s}^{-1}$) is the intensity of absorbed light. I_a is derived using the Beer-Lambert law (Figure S5A) which states:

$$\frac{I}{I_o} = 10^{-\varepsilon[A]x} \quad (S5)$$

In eq S5, I ($\text{mol cm}^{-2}\text{s}^{-1}$) is the intensity of light at the position x (cm) into the light-absorbing medium, I_o ($\text{mol cm}^{-2}\text{s}^{-1}$) is the intensity of the incident light, ε ($\text{L mol}^{-1}\text{cm}^{-1}$) is the molar absorptivity (or extinction coefficient), and $[A]$ (mole L^{-1}) is the concentration of the initiator. Rearranging the equation using the natural base (to facilitate integration in ensuing steps), and defining $\alpha = \ln 10 \varepsilon = 2.3\varepsilon$, we obtain eq S6:

$$I = I_o e^{-\ln 10 \varepsilon [A] x} = I_o e^{-\alpha [A] x} \quad (S6)$$

We, therefore, obtain the local I_a at the position x :

$$I_a = -\frac{dI}{dx} = 10^3 I_o \alpha [A] e^{-\alpha [A] x} \quad (S7)$$

In eq S7, the term 10^3 is included to convert the unit of I_a from $\text{mol cm}^{-3} \text{s}^{-1}$ to $\text{mol L}^{-1} \text{s}^{-1}$.

Inserting eq S7 and eq S4 to eq S3, we obtain eq S8 that describes the local rate of polymerization at a distance x into the sample:

$$R_p = k_p [M] \left(\frac{\phi 10^3 I_o \alpha [A] e^{-\alpha [A] x}}{k_t} \right)^{0.5} \quad (S8)$$

Integrating the local rate of polymerization over the entire volume of the block (Figure S5A) and normalizing it to the total volume, we obtain the average rate of polymerization (eq S9) – i.e. the average rate of polymerization over the entire distance D shown in Figure S5A:

$$\overline{R_p} = \frac{\int R_p dv}{V_{total}} = \frac{\int R_p dx}{D} = 2k_p [M] \left(\frac{\phi 10^3 I_o}{\alpha [A] k_t} \right)^{0.5} \left(\frac{1 - e^{-\frac{\alpha [A] D}{2}}}{D} \right) \quad (S9)$$

We apply the same approach over the entire sphere to obtain the average rate of polymerization of a drop. In this case, we treat the sphere as a stack of coaxial cylindrical shells with the axis aligned with the incident light (Figure S5B, only one shell is shown).

For each shell,

$$D = 2R \cos \theta \quad (S10)$$

$$\overline{R_p} = k_p [M] \left(\frac{\phi 10^3 I_o}{\alpha [A] k_t} \right)^{0.5} \left(\frac{1 - e^{-\alpha [A] R \cos \theta}}{R \cos \theta} \right) \quad (S11)$$

$$dv = \pi 2R \sin \theta d(R \sin \theta) 2R \cos \theta = 4\pi R^3 \sin \theta \cos^2 \theta d\theta \quad (S12)$$

We, then, obtain Eq S13 that describes the average rate of polymerization of a sphere:

$$\begin{aligned}
\overline{R_p^s} &= \frac{\int \overline{R_p} dv}{V_{total}} \\
&= k_p [M] \left(\frac{\phi 10^3 I_o}{\alpha [A] k_t} \right)^{0.5} \frac{3}{R} \int_0^{\frac{\pi}{2}} (1 - e^{-\alpha [A] R \cos \theta}) \sin \theta \cos \theta d\theta \\
&= k_p [M] \left(\frac{\alpha [A] \phi 10^3 I_o}{k_t} \right)^{0.5} \left[\frac{3}{\alpha [A] R} \left(\frac{1}{2} + \frac{e^{-\alpha [A] R}}{\alpha [A] R} + \frac{e^{-\alpha [A] R} - 1}{(\alpha [A] R)^2} \right) \right] \quad (S13)
\end{aligned}$$

In eq S13, superscript s to denote a sphere and α is defined as $\ln 10 \epsilon$. Eq S13 is an exact equation to describe average rate of polymerization of a drop; it will – under certain conditions as discussed below – reduce to a form that is independent on the radius of the sample drop, R, and help simplify the experimental procedures with which to study the kinetics of polymerization.

We define K' as the term in the bracket in eq S13

$$K' = \frac{3}{\alpha [A] R} \left(\frac{1}{2} + \frac{e^{-\alpha [A] R}}{\alpha [A] R} + \frac{e^{-\alpha [A] R} - 1}{(\alpha [A] R)^2} \right) \quad (S14)$$

We show that eq S14 will approach one when $\alpha [A] R$ is sufficiently small. Let $y = \alpha [A] R$, we obtain Eq S15:

$$\lim_{y \rightarrow 0} \frac{3}{y} \left(\frac{1}{2} + \frac{e^{-y}}{y} + \frac{e^{-y} - 1}{y^2} \right) = \lim_{y \rightarrow 0} \frac{3y^2 + 6ye^{-y} + 6e^{-y} - 6}{2y^3} \quad (S15)$$

Eq S15 is in an indeterminate form – i.e. 0/0 when y approaches zero; its limit can be calculated following the L'Hospital's rule.

$$\lim_{y \rightarrow 0} \frac{(3y^2 + 6ye^{-y} + 6e^{-y} - 6)'}{(2y^3)'} = \lim_{y \rightarrow 0} \frac{(1 - e^{-y})'}{y'} = \lim_{y \rightarrow 0} e^{-y} = 1 \quad (S16)$$

We, therefore, obtain Eq S16 that describes the average rate of polymerization of a drop when the term $\alpha[A]R$ is sufficiently small.

$$\lim_{\alpha[A]R \rightarrow 0} \overline{R}_p^s = k_p[M] \left(\frac{\alpha[A]\phi 10^3 I_o}{k_t} \right)^{0.5} \quad (S17)$$

Eq S17 is identical to the formula shown in eq S9 when the term $\alpha[A]D$ is sufficiently small. This result indicates that neither a thin film nor a small drop would show a dependence of the average rate of polymerization on their physical sizes when the light traversing them is minimally attenuated.

We generated two theoretical plots (Figure S6) of photopolymerization of methyl methacrylate, describing the dependence of (i) the correction term K' (Eq S18), and (ii) the average rate of polymerization (Eq S19) on the concentration of photoinitiator, $[A]$, and the size of the drop, R :

$$K' = \frac{3}{\alpha[A]R} \left(\frac{1}{2} + \frac{e^{-\alpha[A]R}}{\alpha[A]R} + \frac{e^{-\alpha[A]R} - 1}{(\alpha[A]R)^2} \right) \quad (S18)$$

$$\overline{r}_p^s = [A]^{0.5} \left[\frac{3}{\alpha[A]R} \left(\frac{1}{2} + \frac{e^{-\alpha[A]R}}{\alpha[A]R} + \frac{e^{-\alpha[A]R} - 1}{(\alpha[A]R)^2} \right) \right] \quad (S19)$$

In eq S19, we focused specifically on the effects of $[A]$ and R on the average rate of polymerization, and used \overline{r}_p^s , instead of \overline{R}_p^s , to make the distinction (\overline{r}_p^s scales linearly with \overline{R}_p^s , for the same concentration of monomer and irradiation conditions).

These plots are a useful guide to select appropriate range of parameters for experimental validation. We plotted the volume of the drop from 1 μL to $\sim 1 \text{ mL}$, a range over which the volume of the drop is easily transferred using typical laboratory pipettors and the size of the drop is compatible with standard plastic cuvettes (with a path length of

1 cm) used for density measurements. We plotted the concentration of the photoinitiator from \sim mM to sub M, a range over which the kinetics of polymerization of a drop is not too slow to be monitored or not overly complicated by nonlinear photoinitiations at high concentrations of photoinitiators.

Table S1 Hydrophobic organic solvents and monomers that could be used as density standards

Name	Density reported by the vendor or in literature	Density measured using a balance and a gas-tight syringe	Reference
hexyl methacrylate	0.863	0.878	sigmaaldrich.com
n-octadecyl methacrylate	0.864	0.858	
toluene	0.865	--	sigmaaldrich.com
1,2,3,4-tetramethylbenzene	0.9052	--	5
methyl methacrylate	0.936	0.932	sigmaaldrich.com
4,N,N-Trimethylaniline	0.937	--	sigmaaldrich.com
4-methylanisole	0.969	--	sigmaaldrich.com
anisole	0.993	--	sigmaaldrich.com
fluorobenzene	1.025	--	sigmaaldrich.com
3-chlorotoluene	1.072	--	sigmaaldrich.com
chlorobenzene	1.107	--	sigmaaldrich.com
2-nitrotoluene	1.163	--	sigmaaldrich.com
nitrobenzene	1.196	--	sigmaaldrich.com
dichloromethane	1.325	--	sigmaaldrich.com
1,1,2-trichlorotrifluoroethane	1.575	--	sigmaaldrich.com
1,2-dibromoethane	2.180	--	sigmaaldrich.com
dibromomethane	2.477	--	sigmaaldrich.com
tribromomethane	2.8910	--	5

Table S2 Calculating the density of a polymerizing sample

Component	Density ¹	Mass ²	Volume
Monomer	ρ_m	$(1 - x)m_1$	$\frac{(1 - x)m_1}{\rho_m}$
Polymer	ρ_p	xm_1	$\frac{xm_1}{\rho_p}$
Initiator	ρ_2	k_2m_1	$\frac{k_2m_1}{\rho_2}$
Solid ³	ρ_3	k_3m_1	$\frac{k_3m_1}{\rho_3}$

1: For a given experiment, all density values are assumed to be known (on the basis of the reported values in the literature or by the vendor, or the experimental values measured independently using MagLev), and used for calculations.

2: m_1 is the starting mass of the monomer. x is the fractional conversion of the monomer during polymerization. k_2 and k_3 are mass ratios of the corresponding component to the monomer, and are experimentally adjustable.

3: Solid materials used in this study were aramid, glass fiber, and carbon fiber. This calculation applies equally to solvents when used to dissolve the reactants. $k_3 = 0$ for polymerization in the absence of a solid material or a solvent.

Figure S1 A MagLev device used in this study. A pair of like-poles facing magnets (Length x Width x Height: 25.4 mm x 25.4 mm x 50 mm, face-to-face separation: 25.0 mm) were mechanically secured using 3D-printed plastic parts and stainless steel rods and nuts (both interact weakly with magnets, and thus, minimally disturb the magnetic field between the two like-poles). A drop of 3-chlorotoluene stably levitated in an aqueous solution of 0.5 M MnCl_2 , and did not physically touch the wall of the plastic cuvette. A ruler with mm scale markings was placed on the side to measure the levitation height of the drop.

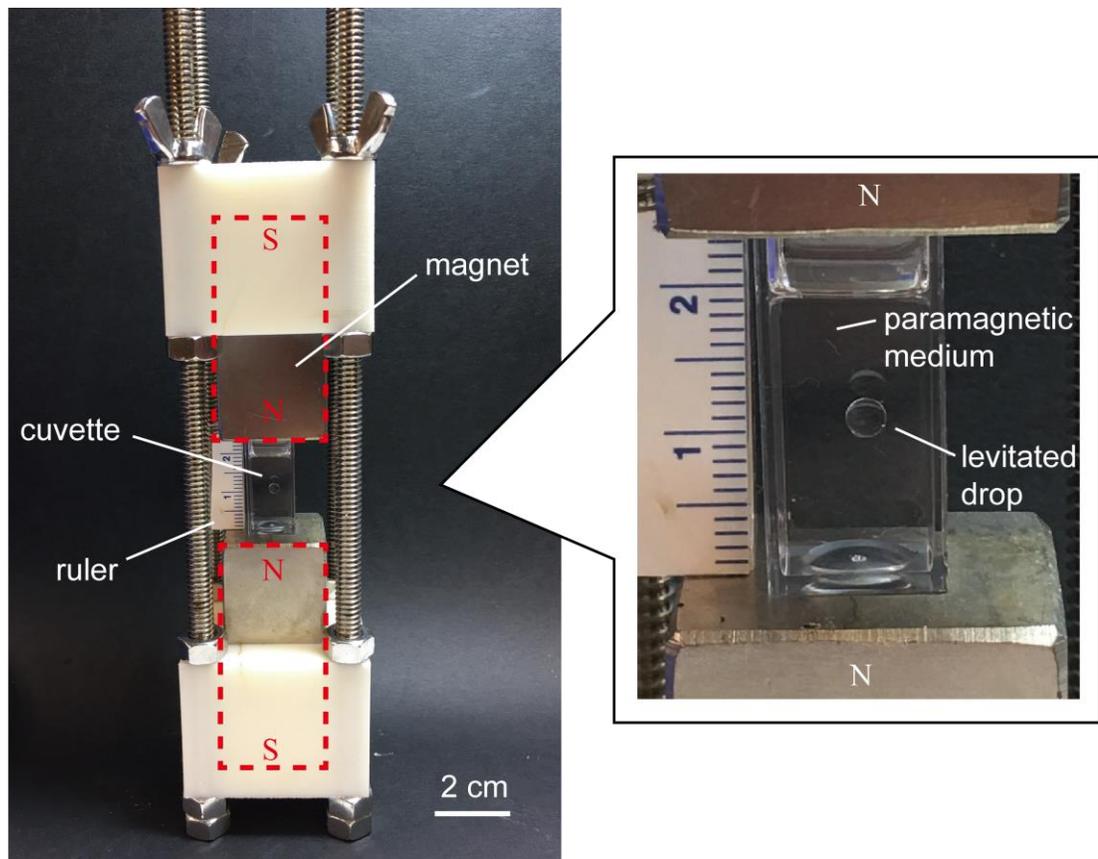


Figure S2 Plots of calibration using organic solvents and monomers. A list of hydrophobic organic liquids that could be used as density standards are included in Table S1.

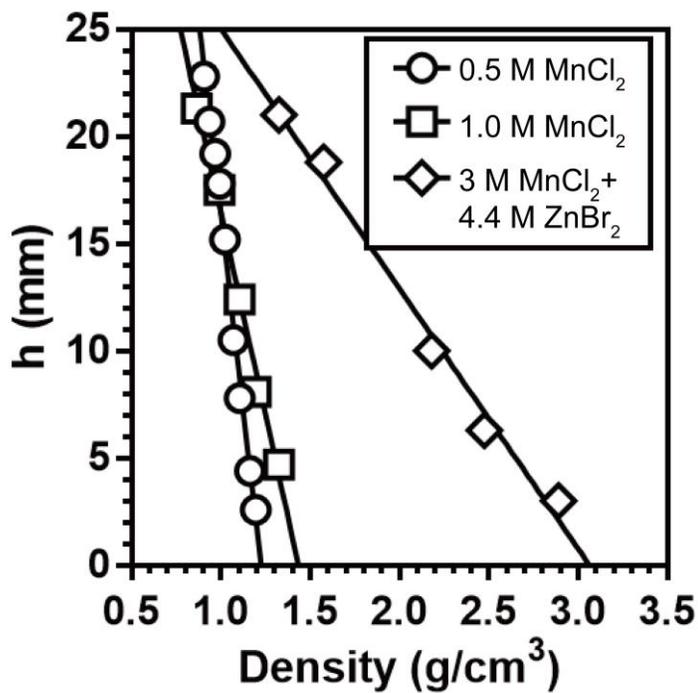


Figure S3 A demonstration of the use of MagLev to monitor the reaction progress of suspension polymerization of benzyl methacrylate. We carried out suspension polymerization in a 50-mL flask equipped with a magnetic stir bar and controlled the reacting temperature using an oil bath. We used 1% (wt%) of poly(vinyl alcohol) in water to help stabilize the monomer drops. To monitor the progress of reaction, a small aliquot of the suspension ($\sim 500 \mu\text{L}$) was periodically removed (sample was carried out with a laboratory pipettor), cooled, and transferred to a MagLev device for density measurement. We used the standard MagLev device described in our previous studies¹ to perform this demonstration (two indistinguishable NdFeB magnets, Length x Width x Height=50.8 mm x 50.8 mm x 25.4 mm, placed with like-poles facing at a distance of 45.0 mm). The density – and also the drop size – increased as polymerization reaction proceeded. Occasionally, small air bubbles were trapped in the polymeric particles (e.g. the particles towards the center of the cuvette at 25 min and 30 min), and thus, decreased the apparent densities of these particles.

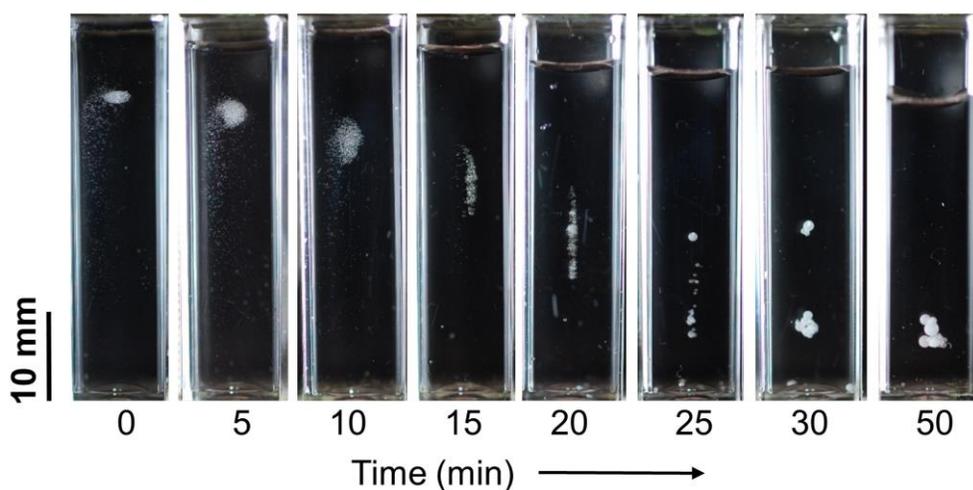


Figure S4 (A) Spectrum of UV irradiation. (B-C) Spectra of absorption of the paramagnetic medium, the liquid of monomer (methyl methacrylate, MMA), the photoinitiator dissolved in the MMA (0.05%, wt%), anisole, and the photoinitiator dissolved in anisole (0.05%, wt%). We performed the measurements using standard-sized quartz cuvettes with a 10-mm light path in a UV/vis spectrometer.

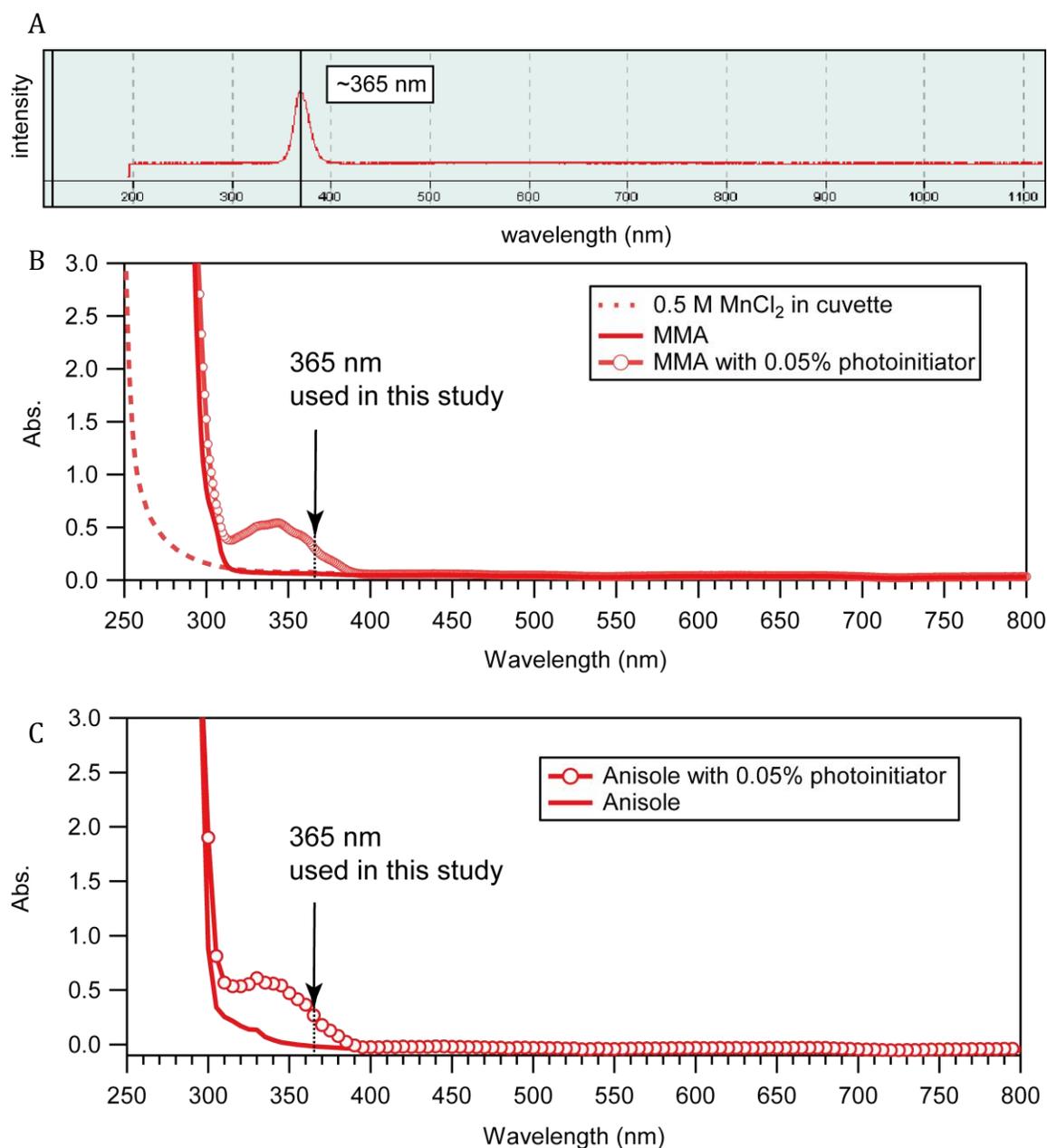


Figure S5: Theoretical model to derive the average rate of polymerization of a drop (A)
The geometry used to derive the average rate of photopolymerization for a block. (B) The
geometry used to derive the average rate of polymerization for a spherical drop.

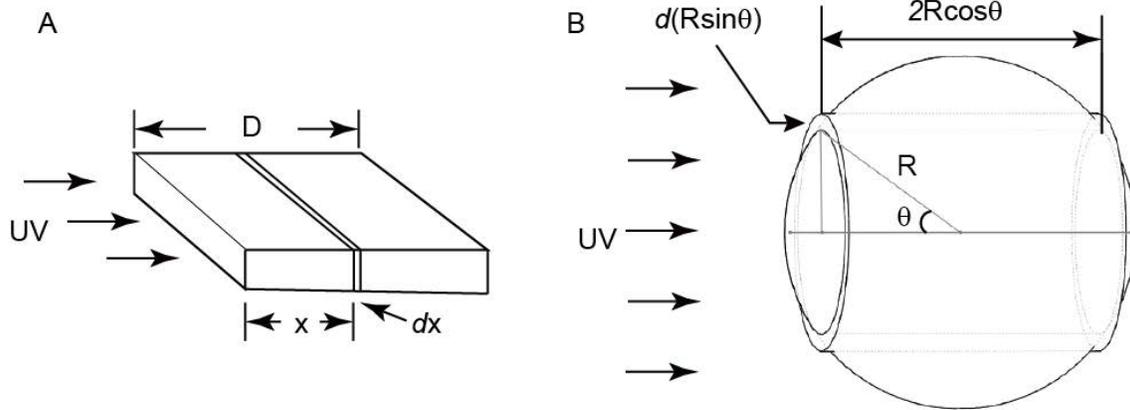


Figure S6 Dependence of the correction term (top panel) and the average rate of polymerization (bottom panel) on the concentration of the monomer and the radius of the drop. The exact equations used to generate the plots are given in eq S18 and eq S19. The absorption coefficient α for the photoinitiator, 2,2-dimethoxy-2-phenylacetophenone, was experimentally determined to be $1188 \text{ M}^{-1} \text{ cm}^{-1}$ in pure methyl methacrylate.

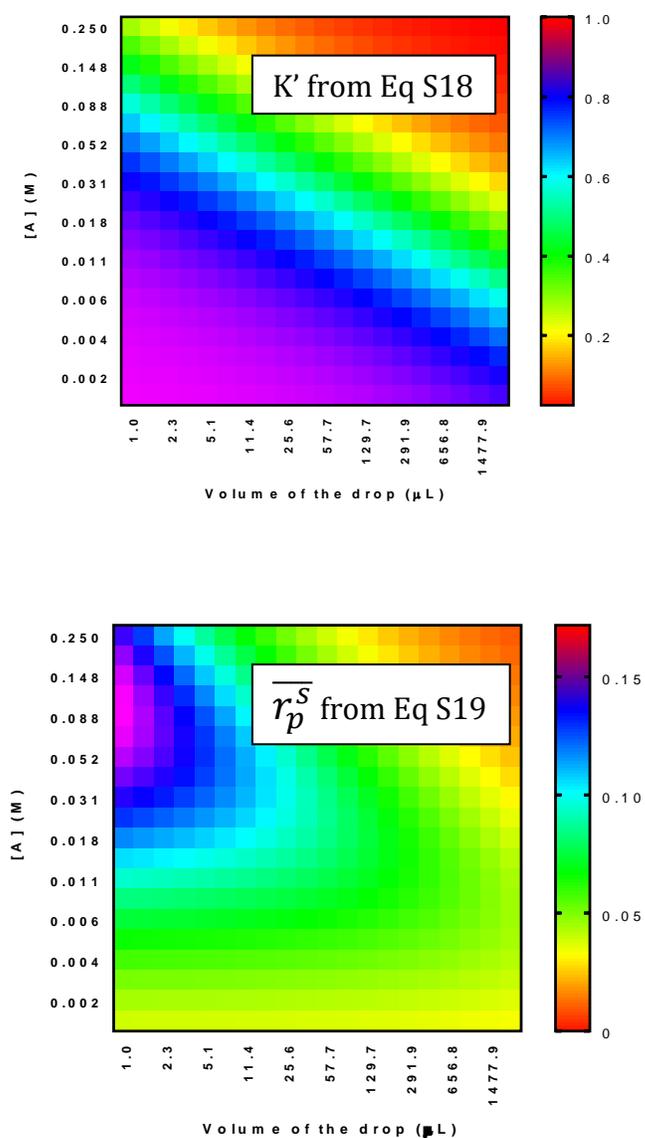


Figure S7 Comparison of fractional conversions of methyl methacrylate in photopolymerization using MagLev and ^1H NMR.

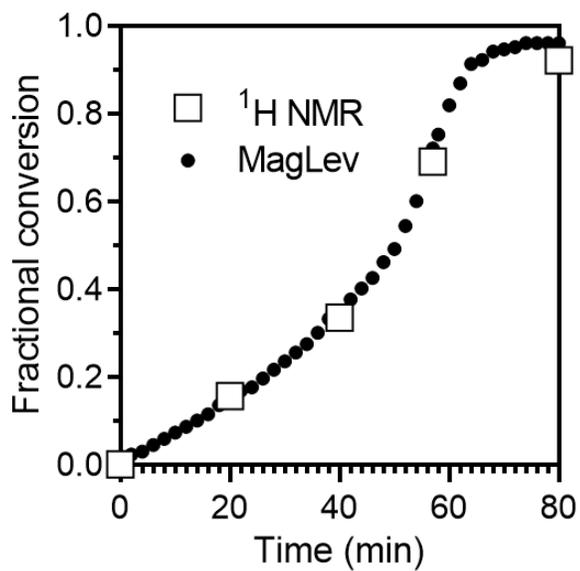
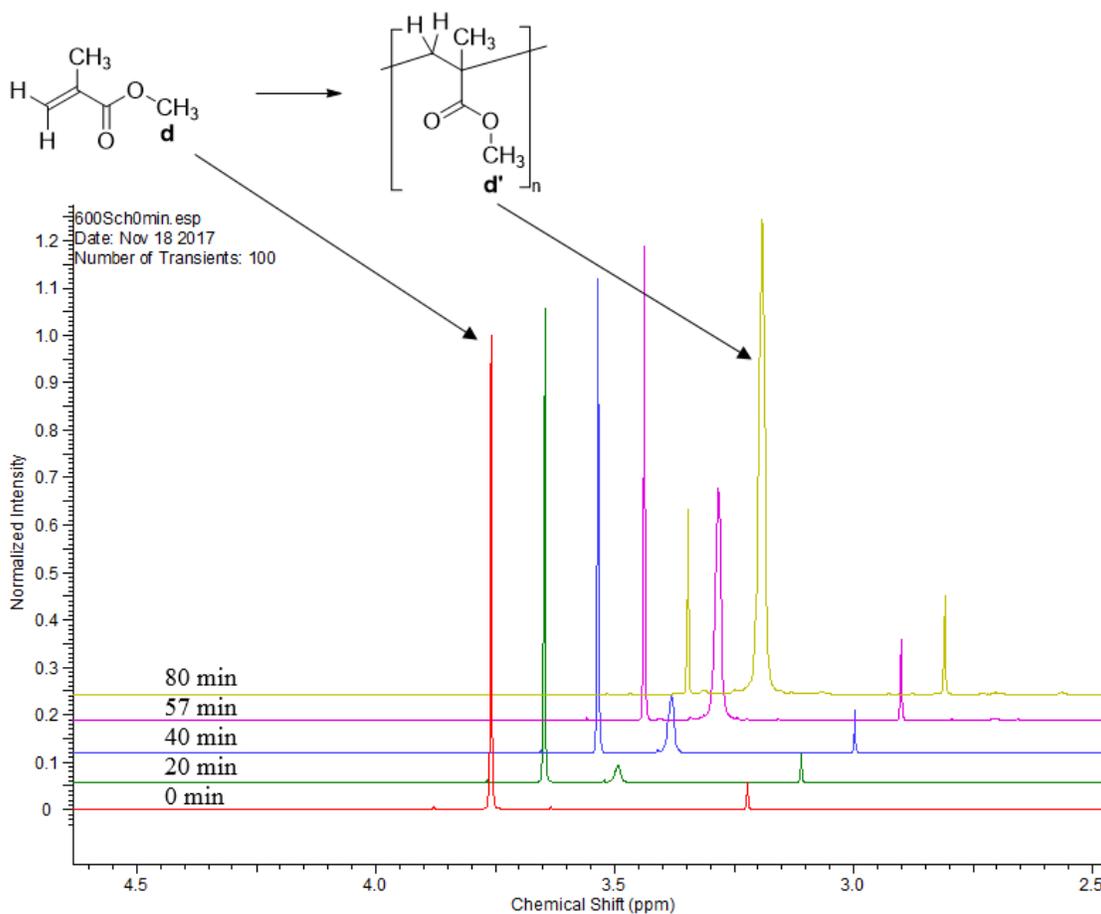
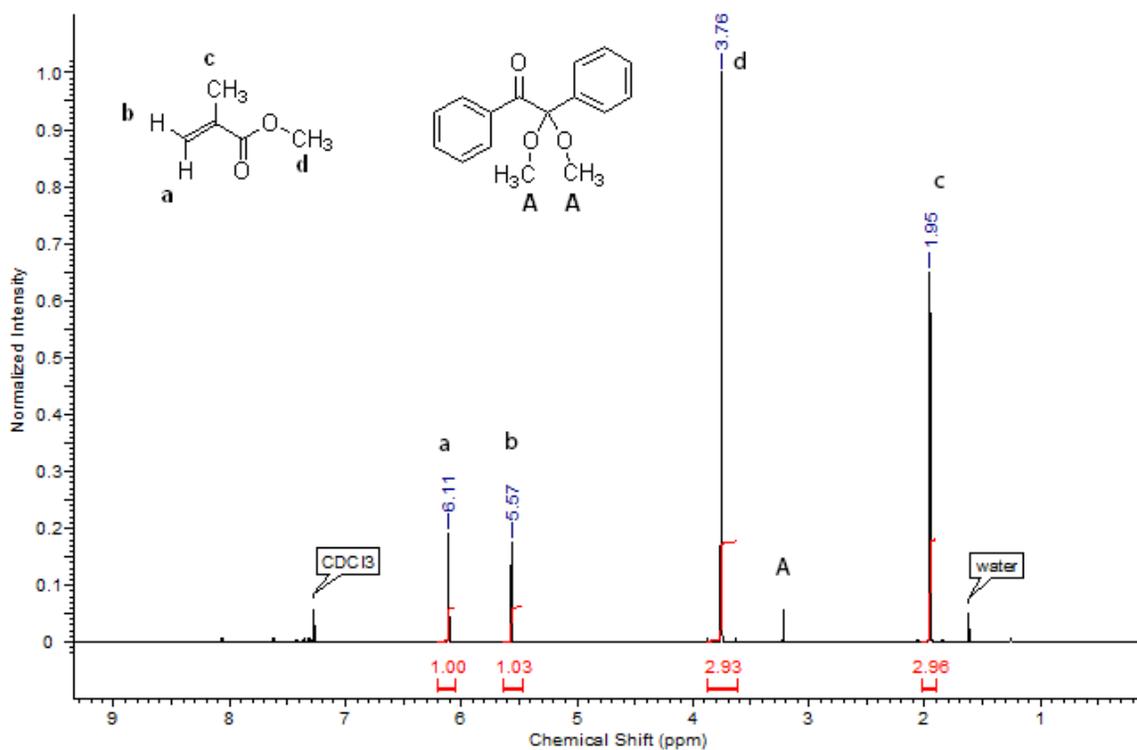


Figure S8. Overlaid ^1H NMR spectra of sample drops (dissolved in deuterated chloroform) removed from the aqueous suspending media placed in the MagLev device at specified time points. Each spectrum is successively offset by 0.1 ppm. See appended spectra at 0 min and 80 min for assignments of peaks to protons in the monomer and in the polymer.

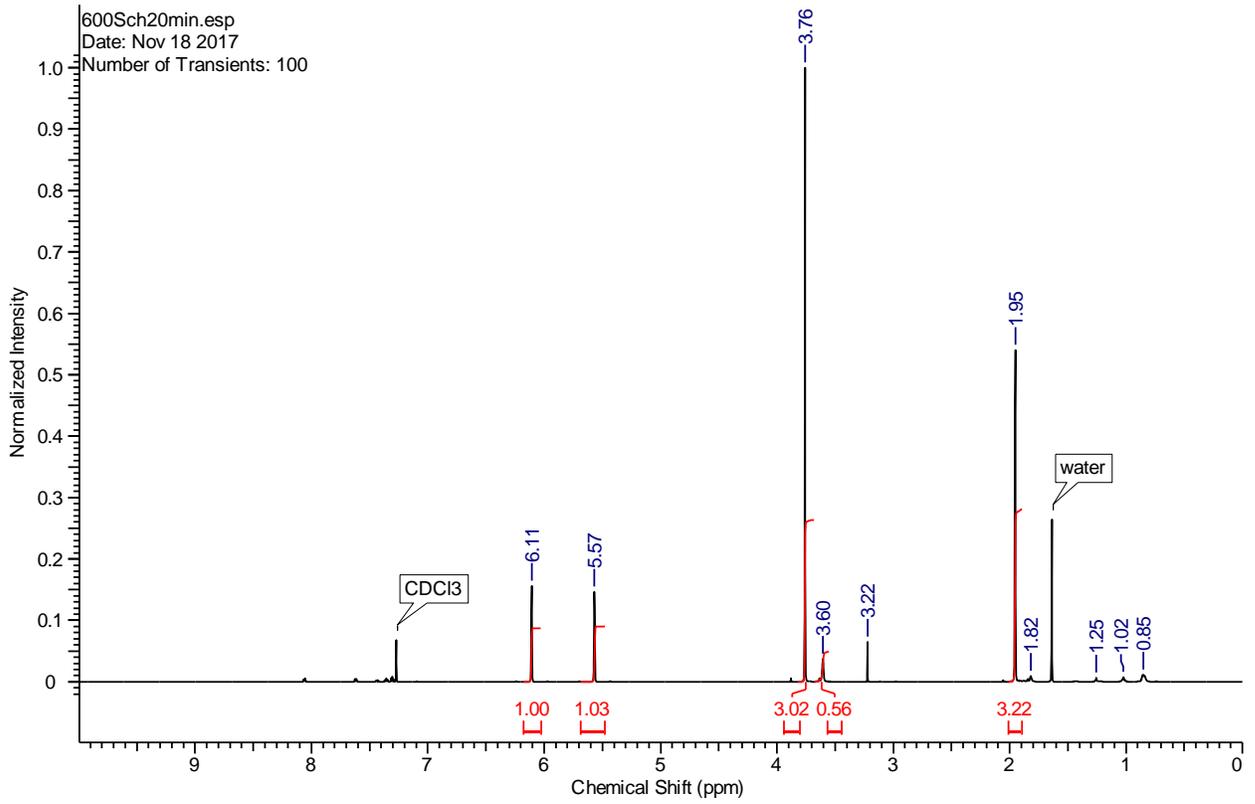


^1H NMR Spectra of polymerizing drops containing the monomer, methyl methacrylate, and the photoinitiator, 2,2-dimethoxy-2-phenylacetophenone. See spectra at 0 min and 80 min for assignments of peaks.

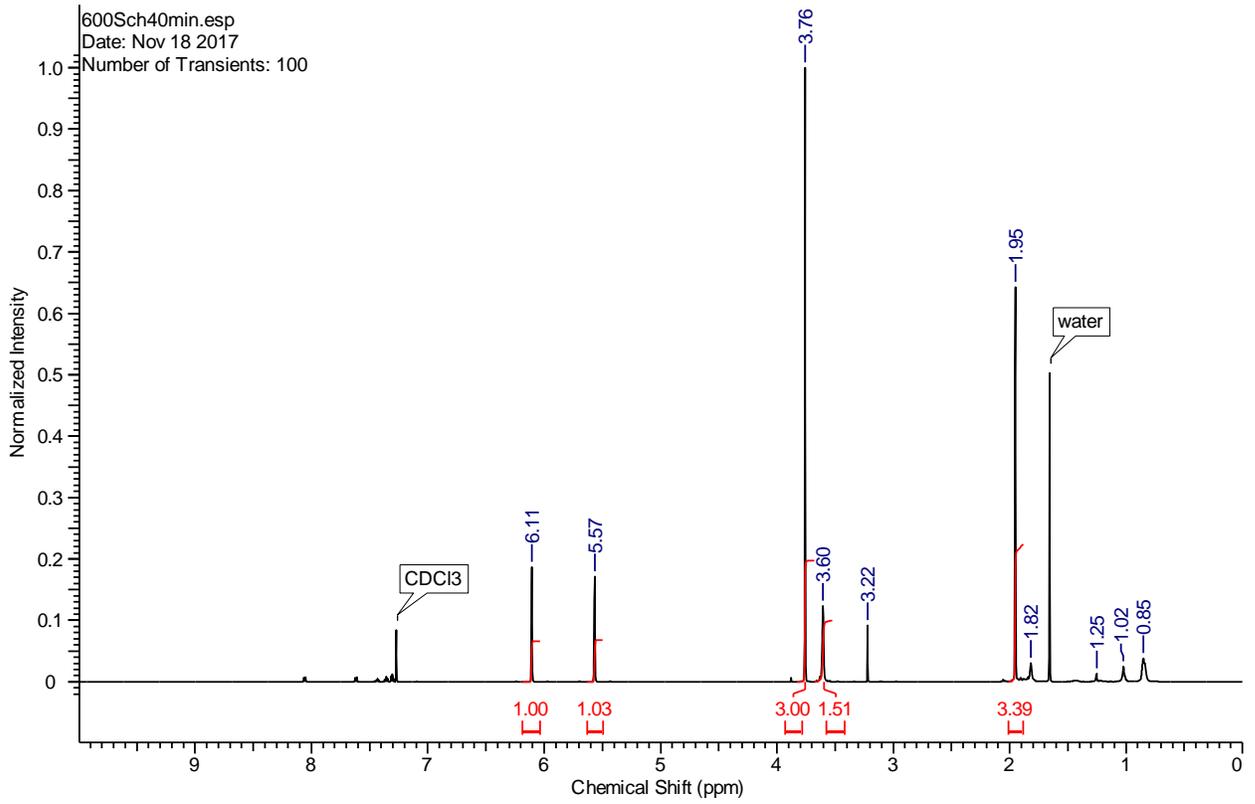
Time $t = 0$ min



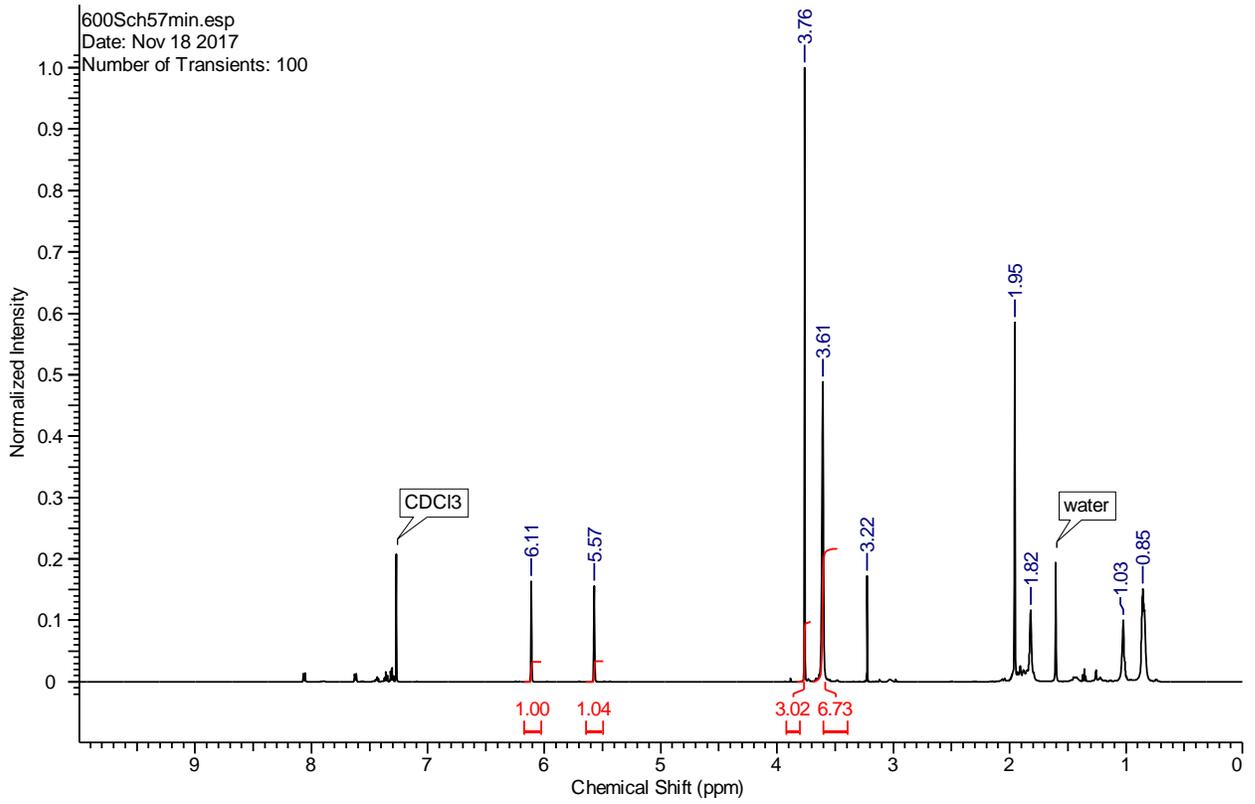
Time t = 20 min



Time t = 40 min



Time t = 57 min



Time t = 80 min

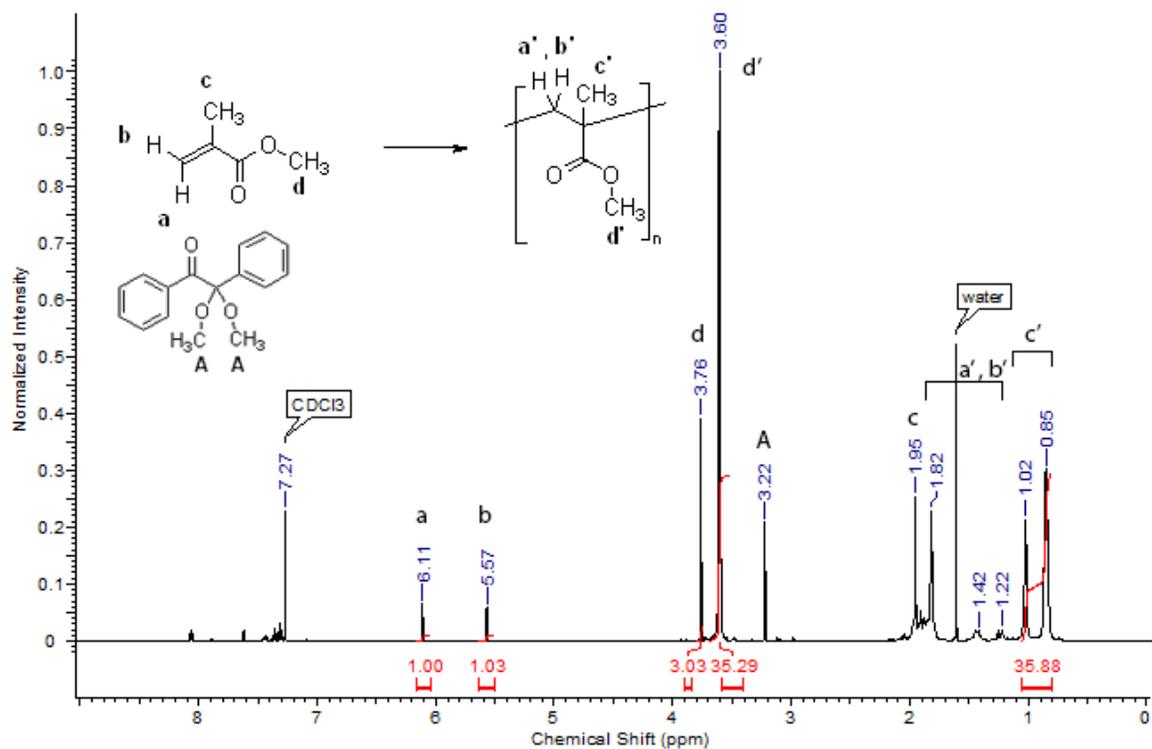


Figure S9 Changes in shape of the polymerizing drops (A) A drop (43.3 μL) of methyl methacrylate with dissolved photoinitiator levitated in an aqueous solution of 0.5 M MnCl_2 . (B-E) Changes in the ratio of width to height over time for polymerizing drops having different volumes.

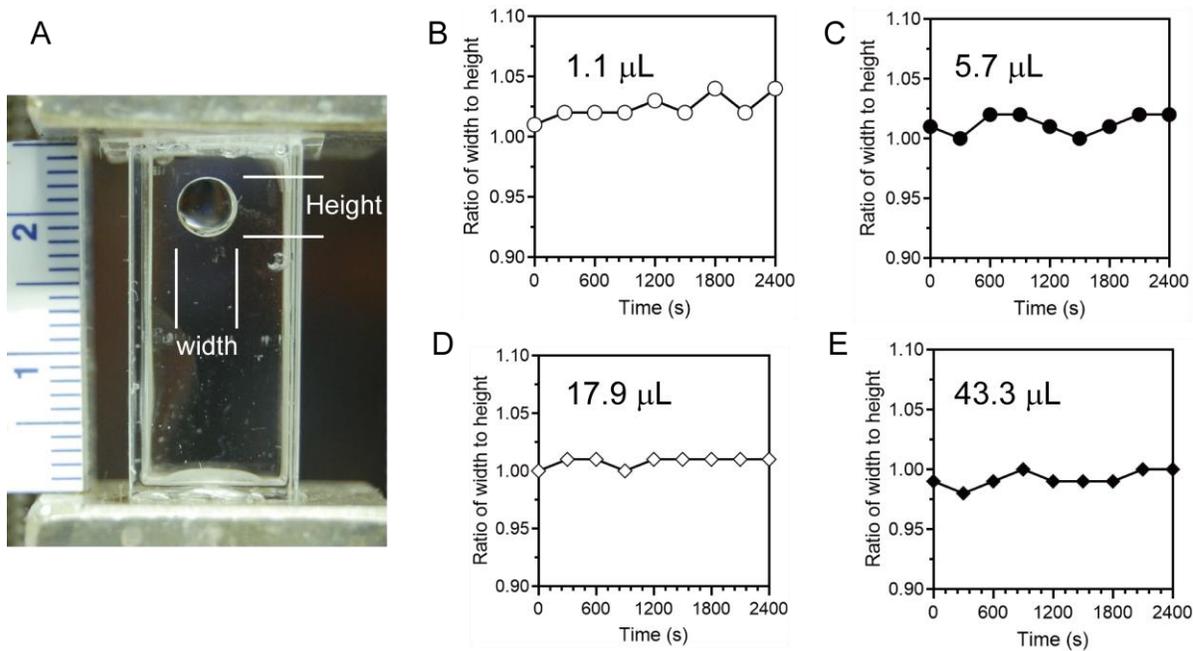


Figure S10 Changes in temperature of a polymerizing drop in a MagLev device monitored with a thermocouple. (A) A small drop (drop 2, $\sim 3.7 \mu\text{L}$) of methyl methacrylate containing photoinitiator (5%, wt%) was placed on the tip of a thermocouple, and a second drop (drop 1, $\sim 1.3 \mu\text{L}$) levitated in the suspending medium (0.5 M MnCl_2). The levitation heights of drop 1 were marked by the white arrows, and the adherent drop 2 was marked by the black arrowhead. The UV lamp sat to the right side of the cuvette. (B) Side view of the adherent drop supported on the tip of a thermocouple. Drop 1 was not shown. (C) Fractional conversion of methyl methacrylate in drop 1 (filled circles) indicates the progress of polymerization in drop 2. The temperature of the polymerizing drop 2 (open circles) was plotted on y-axis on the right.

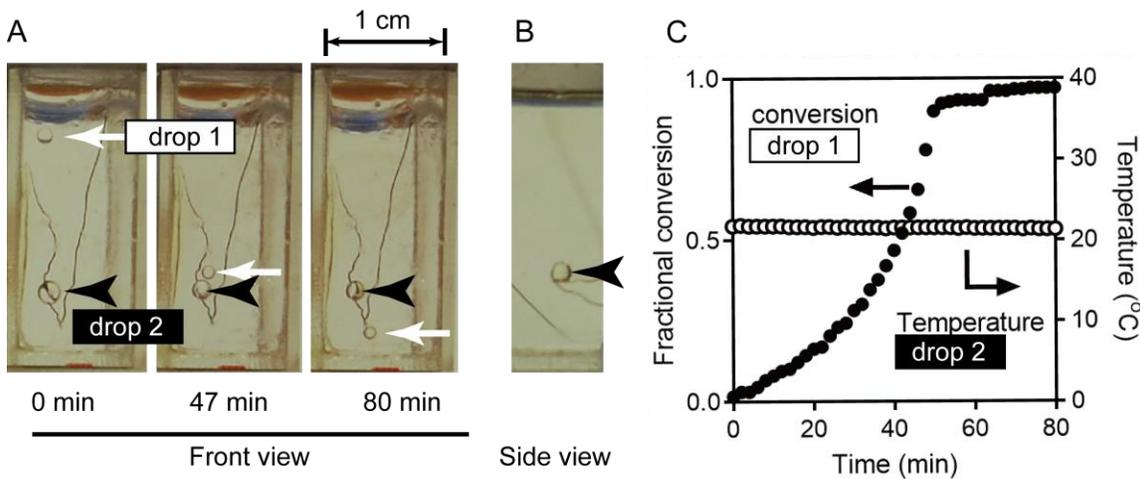
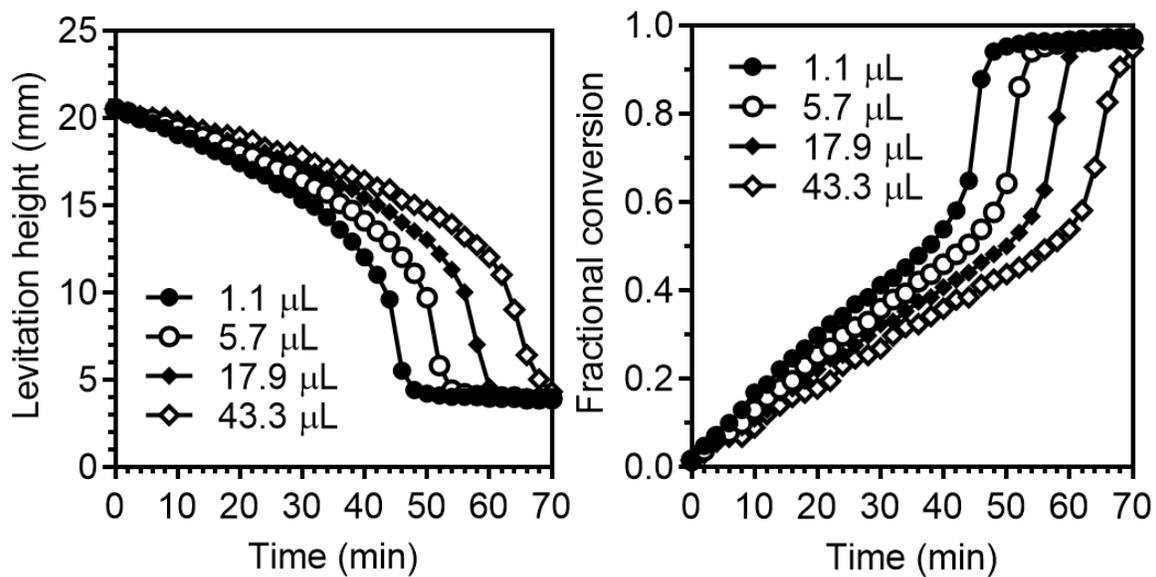


Figure S11 Levitation heights of polymerizing drops (left) and fractional conversions of monomer in polymerizing drops having different volumes (right).



References

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