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Supporting Information

Near Infrared Light Induced Radical Polymerization in Water

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1 Additional Theoretical Considerations

The control of the photothermal conversion described in the main text requires an accurate understanding of the thermodynamic processes that occur when the gold nanorods (AuNR) are exposed to fs laser pulses. Here, further details are provided on the AuNR's calculated theoretical extinction cross section and temperature evolution. Each nanorod is characterized by a long and short axis that results in a longitudinal and transverse resonance, respectively. Thus, the extinction cross section depends on the orientation of the nanorod with respect to the incident light. Maximum temperatures were calculated by assuming rods were orientated such that the longitudinal resonance was excited. For an ensemble of randomly orientated AuNRs in solution the actual temperatures will in practice be lower.

Simulations of the thermal evolution of the AuNR and its surroundings were based on the widely accepted theoretical approach for nanospheres,[1] which was modified to cater for the asymmetric geometry of the AuNRs. As a result, the diffusion equation was solved in three dimensions using COMSOL Multiphysics rather than simply in one-dimension as required for nanospheres. The temperature distribution across an individual nanorod was assumed to be uniform due to the large thermal conductivity of gold in comparison to water[2, 3] and the high Kapitza resistance of the gold-water interface.

Thermal evolution of a AuNR illuminated by a pulsed laser can be described in three stages, (1) electronic absorption, (2) electron-phonon thermalization and (3) external heat diffusion.[5] The associated time scales are $\tau_e \approx 100$ fs for electronic absorption, $\tau_{e-ph} \approx$ 1.7 ps for electron-phonon thermalization in gold and hundreds of ps to a few ns depending on the particle size for external heat diffusion. For fs pulses, the pulse duration is significantly shorter than the electron-phonon thermalization time, implying the three stages occur successively. For a single 40 fs pulse with a wavelength of 800 nm, the initial temperature increase of the AuNR after electron-phonon thermalization was calculated.[4]

$$\delta T_{AuNR} = \frac{\sigma_{abs} F}{V \rho c}$$

Where σ_{abs} is the absorption cross section, F is the fluence of the laser pulse, V the volume, ρ the density and c the heat capacity of the AuNR. The repetition rate of the laser was 1 kHz, thus the pulse temporal spacing was significantly larger than the pulse duration and as a result cumulative thermal effects were unlikely.

2 Experimental Procedures

2.1 Laser System

A Ti:sapphire-based, regeneratively amplified femtosecond (fs) laser system (Coherent Astrella) served as light source. After optical compression, output pulses at a fundamental wavelength of 800 nm, a pulse duration of 35 fs, a repetition rate of 1 kHz and an energy of 7 mJ per pulse were obtained. To avoid non-linear effects in the optical setup, the fs pulses were split into several pulses using broadband beam splitters. One part of this laser beam was used in our experiments with an energy of 250 µJ and a beam diameter of about 5 mm, which results in a peak irradiance of 25 GW cm^{-2}.

2.2 Materials

N,*N*-dimethylacrylamide (99%, contains 500 ppm monomethyl ether hydroquinone (MEHQ) as inhibitor, Sigma-Aldrich), azoisobutyronitrile (AIBN, 98%, Sigma-Aldrich), 3-mercaptopropionic acid (99%, Sigma-Aldrich), gold nanorods AuNR (800 nm, OD=1, bare citrate, Biozol)

2.3 Characterization

2.3.1 Nuclear Magnetic Resonance Spectroscopy

The structures of the synthesized polymers were confirmed *via* ^{1}H-NMR spectroscopy using a Bruker AM 400 MHz spectrometer for hydrogen nuclei. Samples were dissolved in D_2O. The δ-scale was referenced with tetramethylsilane (δ = 0.00) as internal standard.

2.3.2 Gel Permeation Chromatography/Size Exclusion Chromatography

Gel Permeation Chromatography (GPC)/Size Exclusion Chromatography (SEC) measurements were performed on a SECurity^2-GPC-System 1260 Infinity II, comprising an autosampler, a GRAM Lux 5 µm (8x50 mm), one GRAM Lux 1000A 5 µm (8x300 mm), one GRAM Lux 100.000A 5 µm (8x300 mm) a UV-detector and a differential refractive index detector using DMAc as the eluent at 70°C with a flow rate of 1 mL min^{-1}. The SEC was calibrated with linear poly(methyl-methacrylate) standard ranging from 800-2.200.000 Da.

2.3.3 UV/Vis/NIR Spectroscopy

UV/Vis/NIR spectra were recorded in quartz cuvettes (optical path length 1 cm) on a Varian Cary 500 spectrophotometer at a spectral resolution of 1 nm.

2.3.4 Electrospray Ionization-Mass Spectrometry (ESI-MS)

Direct infusion ESI-MS measurements were performed in a THF/methanol (3:2 v/v) with 100 µM sodium trifluoroacetate (NaTFA). A polymer concentration of 0.03 mg ml^{-1} was applied. ESI-MS spectra were recorded on a LTQ mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA). The instrument was calibrated in the m/z range of 195-1822 using a mixture of SDS, sodium taurocholate and Ultramark 1621 in a acetonitrile-methanol- acetic acid solution. A constant spray voltage of 3.8 kV was used and nitrogen at a dimensionless sheath gas flow of 5 were applied. The capillary temperature was set to 320 °C.

2.4 UV/Vis/NIR Stationary Absorption Spectrum AuNR

The absorption properties of AuNR are dependent on their size and geometry. Since we intended to perform experiments at 800 nm, we purchased AuNR with a size of 55 x 15 nm, which have an absorption maximum at 800 nm (Figure S1). The AuNR solution (bare citrate in water) has an OD of 1.

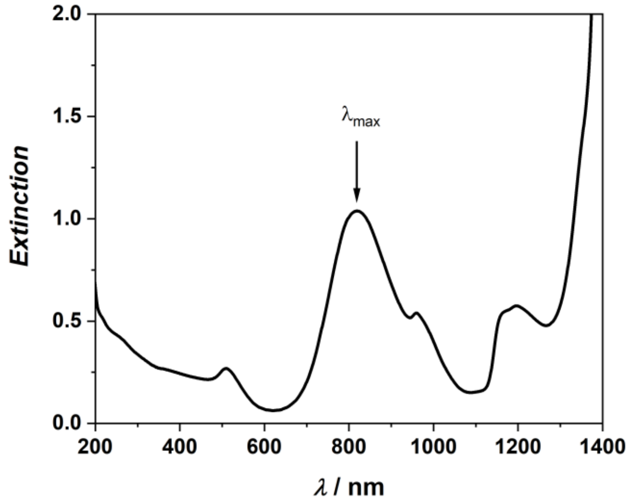


Figure S1: Extinction of the purchased solution of AuNR in water (55x15 nm, bare citrate, OD 1) in the range of 200 – 1400 nm. The stationary absorption spectrum was measured in a 1 cm cuvette. The AuNR solution shows an absorption maximum at 800 nm with an extinction of 1.

2.5 Synthesis

The monomer dimethyl acrylamide (DMA) was purchased with MEHQ as inhibitor. Thus, the inhibitor had to be removed to enable initialization of the polymerization reaction. DMA was freed from inhibitor by means of a syringe filled with basic aluminium oxide to remove the inhibitor. As an initial experiment, *N*,*N*-dimethylacrylamide (4.04 mol L^{-1}), AuNR (150 uL) and azoisobutyronitrile (9 mmol L^{-1}) were irradiated in a 1 mm cuvette with fs laser pulses at 800 nm for 30 min. The formed polymer precipitated (Figure S2).

Figure S2: Picture of 1 mm cuvette with precipitated polymer after irradiation of a solution of 6.73 mol L^{-1} DMA, 9 mmol L^{-1} AIBN and 50 µL AuNR.

To avoid precipitation of the polymer in all subsequent experiments, 3-mercaptopropionic acid (10^{-2} mol L^{-1}) was added as transfer agent to control the polymer chain length. For the systematic parameter variation experiments, individual bulk solutions were prepared. In each bulk solution one parameter was variable and all the other parameters kept constant (refer to Table S1). A defined amount of the bulk solution was placed into a 1 mm cuvette and filled with the variable parameter or water to set the desired parameter concentration. All concentrations were calculated for a cuvette volume of 350 µL and subsequently scaled on the number of samples for the variation experiment. The product was either filled in an aluminium pan to evaporate the monomer for SEC or transferred to an NMR tube and extended with 250 µL D_2O for NMR spectroscopy to determine the monomer to polymer conversion.

2.5.1 Monomer Variation

Bulk solution	**0.69 mol L^{-1} DMA**	**1.34 mol L^{-1} DMA**	**2.38 mol L^{-1} DMA**	**4.04 mol L^{-1} DMA**	**5.38 mol L^{-1} DMA**	**6.73 mol L^{-1} DMA**
350 µL AuNR in water, *350 µL DMA,* *3.5 mg AIBN*	*100 µL bulk* *+ 250 µL water*	*100 µL bulk* *+ 50 µL DMA* *+ 200 µL water*	*100 µL bulk* *+ 100 µL DMA* *+ 150 µL water*	*100 µL bulk* *+ 150 µL DMA* *+ 100 µL water*	*100 µL bulk* *+ 200 µL DMA* *+ 50 µL water*	*100 µL bulk* *+ 250 µL DMA*

2.5.2 AuNR Variation

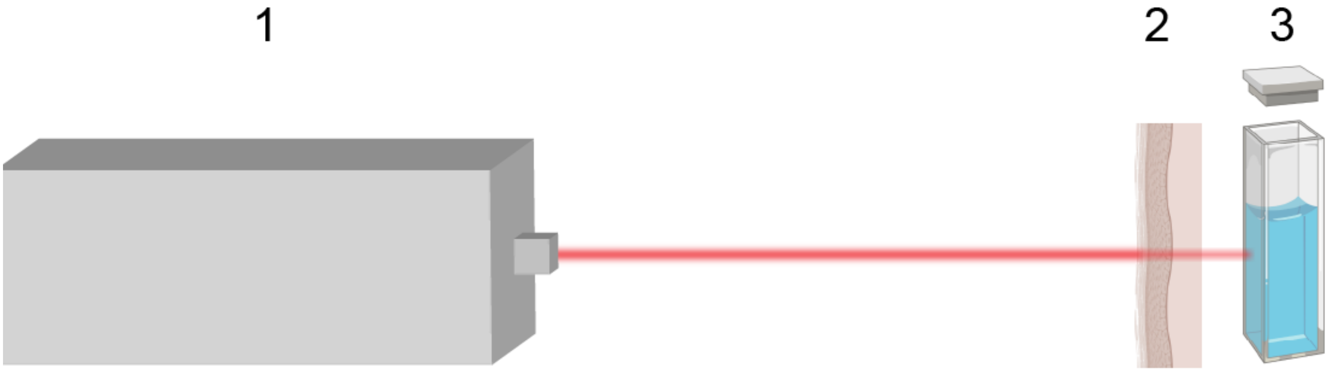
Bulk solution	**50 µL AuNR**	**100 µL AuNR**	**150 µL AuNR**	**200 µL AuNR**	**250 µL AuNR**	**300 µL AuNR**
350 µL AuNR in water, *350 µL DMA,* *3.5 mg AIBN*	*100 µL bulk* *+ 250 µL water*	*100 µL bulk* *+ 50 µL AuNR* *+ 200 µL water*	*100 µL bulk* *+ 100 µL AuNR* *+ 150 µL water*	*100 µL bulk* *+ 150 µL AuNR* *+ 100 µL water*	*100 µL bulk* *+ 200 µL AuNR* *+ 50 µL water*	*100 µL bulk* *+ 250 µL AuNR*

2.5.3 AIBN Variation

Bulk solution	**0.69 mol L^{-1} AIBN**	**0.35 mol L^{-1} AIBN**	**0.17 mol L^{-1} AIBN**	**0.08 mol L^{-1} AIBN**
0.014 mg AIBN, *350 µL DMA,*	*100 µL bulk* *+ 50 µL AuNR* *+ 200 µL water*	*50 µL bulk* *+ 50 µL DMA* *+ 50 µL AuNR* *+ 200 µL water*	*25 µL bulk* *+ 75 µL DMA* *+ 50 µL AuNR* *+ 200 µL water*	*12.5 µL bulk* *+ 87.5 µL DMA* *+ 50 µL AuNR* *+ 200 µL water*

2.5.4 Irradiation Through Biological Tissue

To demonstrate the ability of initiating the reaction after the laser beam propagates trough tissue, we placed a 1 mm slice of bacon directly in front of the cuvette (**3**, Figure S1). Due to light scattering due to the natural structure of bacon tissue (**2**), the bacon was directly adhered to the sample holder to minimize the distance between bacon and cuvette. However, Scheme S1 shows the bacon slightly distanced from the cuvette to demonstrate the weakening of the laser intensity after penetrating the tissue.



Scheme S1: Schematic picture of the through tissue irradiation set-up; the incident 800 nm laser beam (40 fs, 1 kHz, 25 GW cm^{-2}) propagates through a 1 mm thick slice of bacon, which decreases the laser intensity to 10 GW cm^{-2}). Subsequently the laser beam penetrates a 1 mm cuvette. The bacon closely adhered to the sample holder. The distance between the bacon and the cuvette in the picture only portrays the weaker laser beam after tissue penetration.

3 Additional Experimental Data

3.1 Mass Spectrometry

ESI-MS records isotopic patterns of polymers with different end groups depending on radical fragment initiation and termination. The isotopic pattern serves as fingerprint of the analyzed polymer because the natural distribution of isotopes makes every chemical structures unique in its peak pattern and height. An orbitrap mass analyzer features a resolution of more than 60000. Thus, it is possible to gain almost Gaussian-shaped peaks. In our experiment we mainly obtained polymers with a molecular weight of 1000 – 3000 g mol^{-1}, which is well-suited for the analysis *via* ESI-MS. We recorded ESI-MS spectra in the range of 1000 – 2000 m/z. A solution of 350 µL (5.34 mol L^{-1} DMA, 100 µL AuNR, 9 mmol L^{-1} AIBN, 10^{-2} mol L^{-1} CTA) was prepared and irradiated in a 1 mm cuvette with an intensity of 25 GW cm^{-2} for 30 min. Subsequently, 10 µL of this solution were filled in a vial and 2 mL of a THF/methanol (3:2) solution with 100 µM NaTFA added. The program Xcalibur (Thermo Fisher) was used to simulate isotopic patterns of a polymer distribution with specific end group fragments. The agreement of simulated species with the experimental isotopic pattern is a measure of quality of the structural assignment and aids in postulating the end group distribution. By means of the simulated pattern, we identified four main species that can be assigned to the experimental mass spectrum. In Figure S4, the mass spectrum is exemplary shown in the *m/z* range of 1110 – 1210. The polymer species P1, P2, P3 and P4 feature the same end groups, constituted of a hydrogen added to the α-terminus and thiol-containing function at the ω-end. However, the assigned species differ in their counter ions and charge. The largest peak at close to 1119 *m/z* can be assigned to a polymer product with a sodium counter ion (P1). Further, we identify a double charged product (P2) with two sodium counter ions close to 1116 and 1166 *m*/z. A triple charged species with three sodium counter ions can be found at approximately 1115, 1148 and 1181 *m/z* (P3). At 1196 *m/z*, we assign a polymer product with a hydrogen counter ion (P4). We also identify a polymer species with a hydrogen and a thiol end group plus an additional water molecule at 1142 *m/z* (P5). Further, we can assign the peak at 1135 *m/z* to a product that is similar to P1, yet with an oxidized sulphur atom (P6).

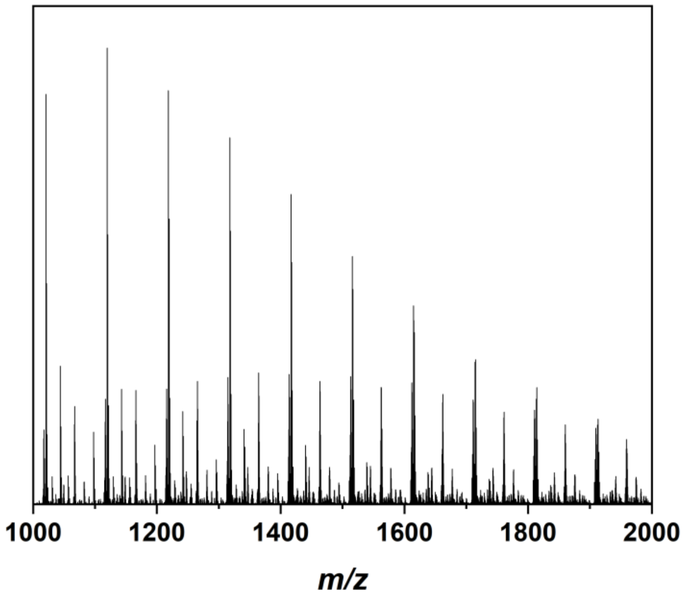


Figure S3: Full ESI-MS spectrum of a polymerization resulting from irradiating a mixture of 4.04 mol L^{-1} DMA with 100 µL AuNR, 9 mmol L^{-1} AIBN and 10^{-2} mol L^{-1} CTA after 30 min irradiation with 25 GW cm^{-2} laser pulses at 800 nm. 10 µL of the irradiated solution were dissolved in 2 mL THF/methanol (3:2) solution with 100 µM NaTFA.

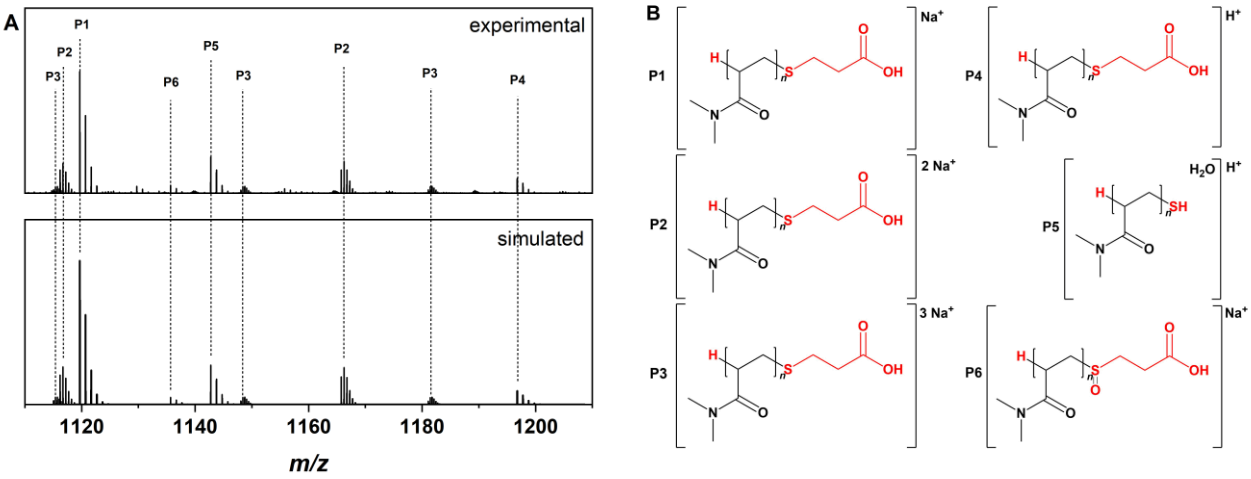


Figure S4: (A) Comparison of experimental ESI-MS spectrum (zoom into one repeat unit) of PDMA in THF/methanol (3:2) (top) with simulated isotopic pattern (bottom) in the *m/z* range of 1110 – 1210. The experimental mass spectrum was obtained after 30 min irradiation of 4.04 mol L^{-1} DMA with 100 µL AuNR, 9 mmol L^{-1} AIBN and 10^{-2} mol L^{-1} CTA with 25 GW cm^{-2} laser pulses at 800 nm. 10 µL of the irradiated solution were dissolved in 2 mL of a THF/methanol (3:2) solution with 100 µM NaTFA. (B) main species that can be assigned to the isotopic pattern of the conducted mass spectrum.

Table S1: Overview of the exact mass and resolution of the assigned species in the recorded and simulated spectrum.

Species	*Exact Mass* / Da (experimental)	*Resolution* (experimental)	*Exact Mass* / Da (simulated)	*Resolution* (simulated)
P1	1119.681	62115	1119.682	59947
P2	1116.712	62115	1116.713	59653
	1166.247	62395	1166.248	59668
P3	1115.724	63574	1115.724	59558
	1148.746	62245	1148.747	59598
	1181.769	61441	1181.769	59608
P4	1196.768	62221	1196.769	59947
P5	1142.757	64417	1142.758	59947
P6	1135.677	65373	1135.677	59947

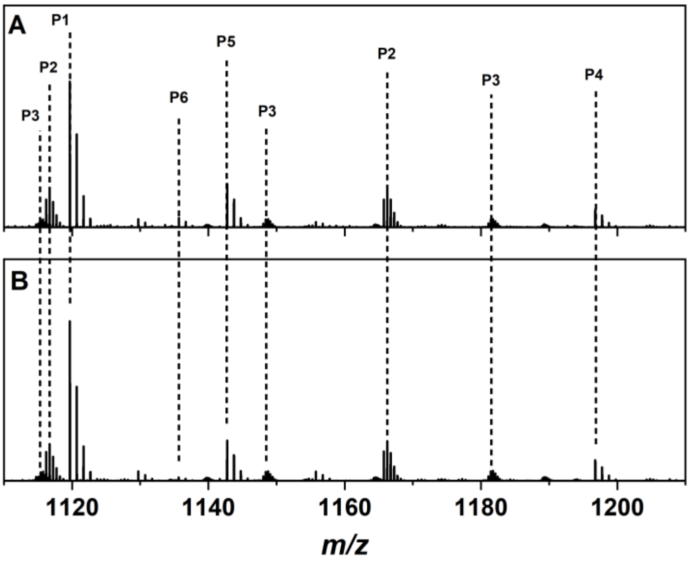


Figure S5: ESI-MS spectrum of PDMA with end group assignment. (A) The ESI-MS spectrum was obtained after 30 min irradiation of 4.04 mol L^{-1} DMA with 100 µL AuNR, 9 mmol L^{-1} AIBN and 10^{-2} mol L^{-1} CTA with 25 GW cm^{-2} laser pulses at 800 nm. 10 µL of the irradiated solution were dissolved in 2 mL of a THF/methanol (3:2) solution with 100 µM NaTFA, (B) The ESI-MS spectrum was obtained after an identical experiment as in (A) but without AIBN.

3.2 NMR Spectroscopy

3.2.1 Determination of Monomer to Polymer Conversion

Figure S2 displays the ^{1}H NMR spectrum of a sample of 4.04 mol L^{-1} DMA with 9 mmol L^{-1} AIBN, 100 µL AuNR solution and 10^{-2} mol L^{-1} CTA dissolved in 250 µL D_2O prior to irradiation (A) and after 30 min irradiation with 25 GW cm^{-2} at 800 nm (B).

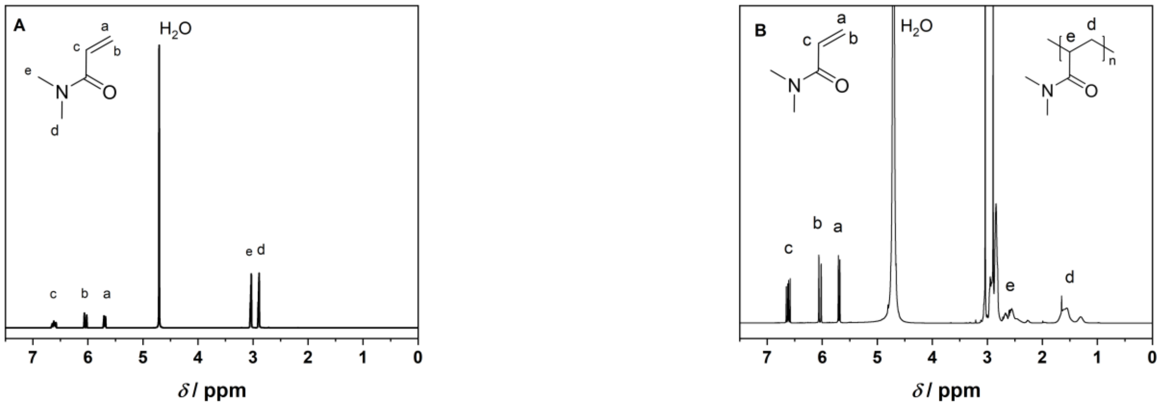


Figure S6: (A) ^{1}H NMR spectrum of pure DMA dissolved in D_20 without irradiation. The resonances are assigned to the protons of DMA; (B) ^{1}H NMR spectrum of a solution of DMA, AIBN, AuNR and CTA dissolved in D_2O after irradiation of 30 min. The resonances are assigned to the protons associated with the DMA monomer and the generated polymer.

Since the sample was not irradiated and thus there was no polymer formation, all resonances are assigned to protons of the monomer in (a). In (b) there are additional peaks, that refer to the polymer. The monomer conversion can be determined by the ratio of the integral that are assigned to the polymer resonances and the sum of the integrals of both the polymer and the monomer resonances.

$$\text{Conversion:}\,\frac{\int(\mathrm{d})}{\int(\mathrm{a})+\int(\mathrm{b})+\int(\mathrm{d})}*100\%$$

The polymer resonances close to 2.5 – 3 ppm ((B), e) are not suitable for the calculation of conversion as they are overlapping with the monomer associated resonances at 3 ppm. The polymer associated resonances between 1 and 2 ppm (d), however, are well separated from the monomer signals, allowing their use as reference signals for the calculation of the monomer to polymer conversion. Considering that the monomer resonances a and b are the analogue protons to the protons d in the polymer, the monomer conversion can be readily calculated by rationing the polymer resonances d and the sum of d and the monomer resonances a and b.

3.2.2 NMR Spectra of Variation Experiments

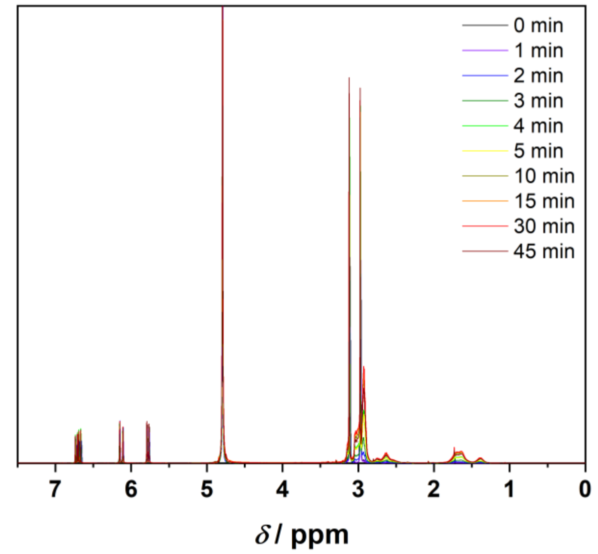


Figure S7: Superimposed ^{1}H-NMR spectra of solutions with 4.04 mol L^{-1} DMA, 9 mmol L^{-1} AIBN, 50 µL AuNR and 10^{-2} mol L^{-1} CTA, dissolved in D_2O, irradiated with 25 GW cm^{-2} at 800 nm for various times: (black) without irradiation – 0 min, (violet) 1 min, (blue) 2 min, (dark green) 3 min, (pale green) 4 min, (yellow) 5 min, (pale orange) 10 min, (orange) 15 min, (red) 30 min, (dark red) 45 min.

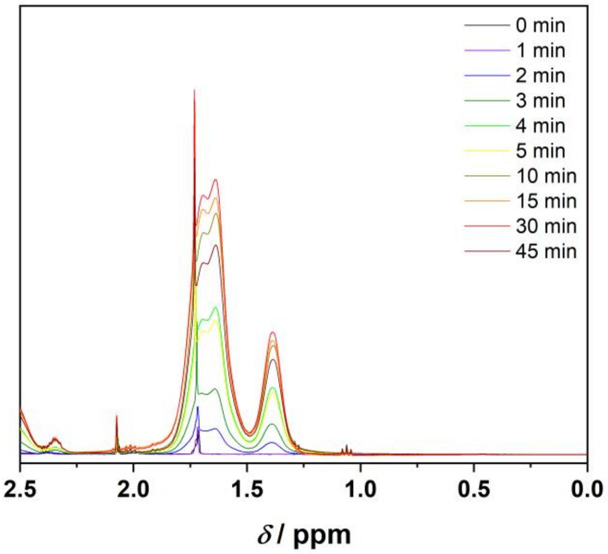


Figure S8: Superimposed ^{1}H NMR spectra of solutions with 4.04 mmol L^{-1} DMA, 9 mmol L^{-1} AIBN, 50 µL AuNR and 10^{-2} mol L^{-1} CTA, dissolved in D_2O, irradiated with 25 GW cm^{-2} at 800 nm for various times, zoomed into the regions of resonance associated with the polymer between 1 – 2 ppm: (black) without irradiation – 0 min, (violet) 1 min, (blue) 2 min, (dark green) 3 min, (pale green) 4 min, (yellow) 5 min, (pale orange) 10 min, (orange) 15 min, (red) 30 min, (dark red) 45 min.

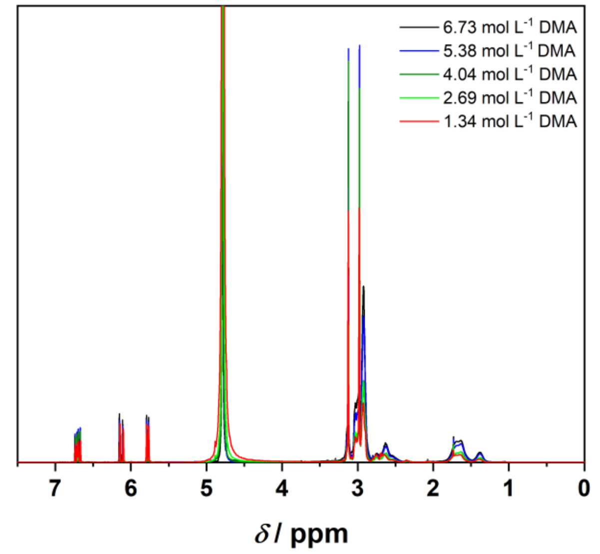


Figure S9: Superimposed ^{1}H-NMR spectra of solutions with 50 µL AuNR, 9 mmol L^{-1} AIBN, 10^{-2} mol L^{-1} CTA and various monomer concentrations, irradiated with 25 GW cm^{-2} at 800 nm for 30 min, dissolved in D2O: (black) 6.73 mol L^{-1} DMA, (blue) 5.38 mol L^{-1} DMA, (green) 4.04 mol L^{-1} DMA, (yellow) 2.69 mol L^{-1} DMA, (red) 1.34 mol L^{-1} DMA.

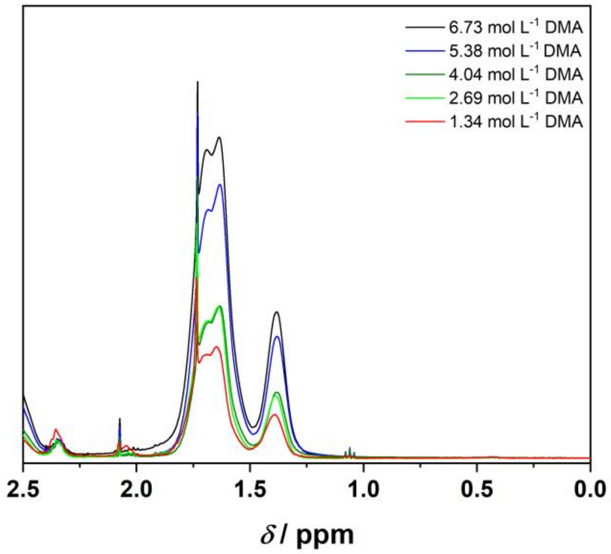


Figure S10*:* Superimposed ^{1}H-NMR spectra of solutions with 50 µL AuNR, 9 mmol L^{-1} AIBN, 10^{-2} mol L^{-1} CTA and various monomer concentrations, irradiated with 25 GW cm^{-2} at 800 nm for 30 min, dissolved in D_2O, zoomed into polymer peak between 1 – 2 ppm: (black) 6.73 mol L^{-1} DMA, (blue) 5.38 mol L^{-1} DMA, (green) 4.04 mol L^{-1} DMA, (yellow) 2.69 mol L^{-1} DMA, (red) 1.34 mol L^{-1} DMA.

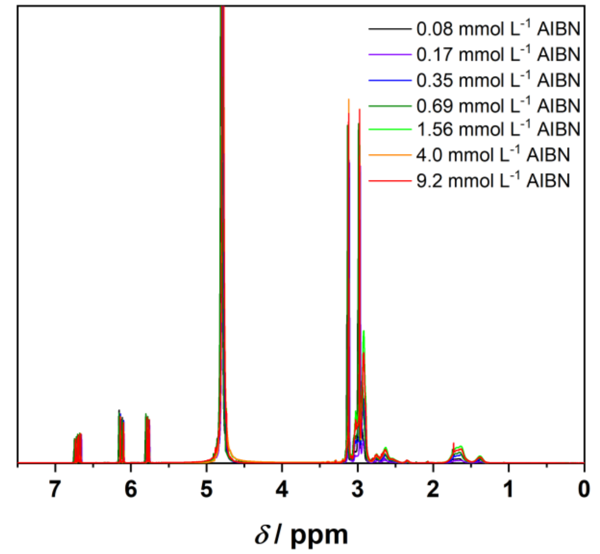


Figure S11: Superimposed ^{1}H-NMR spectra of solutions with 50 µL AuNR, 6.73 mol L^{-1} DMA, 10^{-2} mol L^{-1} CTA and various AIBN concentrations, irradiated with 25 GW cm^{-2} at 800 nm for 30 min, dissolved in D$_2$O: (black) 0.08 mol L^{-1} AIBN, (violet) 0.17 mol L^{-1} AIBN, (blue) 0.35 mol L^{-1} AIBN, (dark green) 0.69 mol L^{-1} AIBN, (yellow) 1.56 mol L^{-1} AIBN, (orange) 4 mol L^{-1} AIBN, (red) 9.2 mol L^{-1} AIBN.

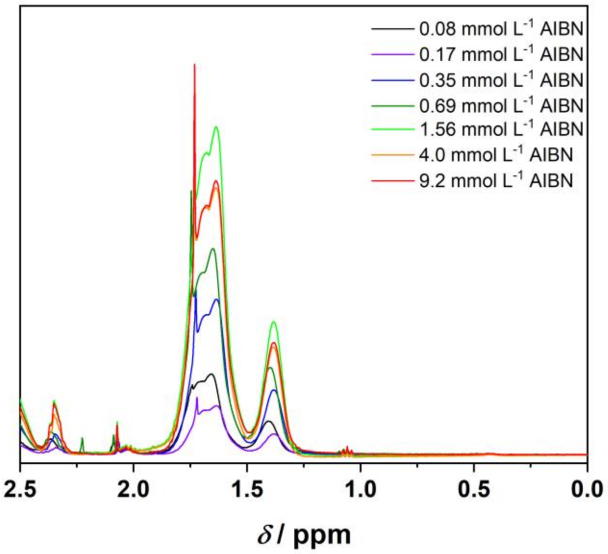


Figure S12: Superimposed ^{1}H-NMR spectra of solutions with 50 µL AuNR, 6.73 mol L^{-1} DMA, 10^{-2} mol L^{-1} CTA and various AIBN concentrations, irradiated with 25 GW cm^{-2} at 800 nm for 30 min dissolved in D$_2$O, zoomed into polymer peak between 1 – 2 ppm: (black) 0.08 mol L^{-1} AIBN, (violet) 0.17 mol L^{-1} AIBN, (blue) 0.35 mol L^{-1} AIBN, (dark green) 0.69 mol L^{-1} AIBN, (yellow) 1.56 mol L^{-1} AIBN, (orange) 4 mol L^{-1} AIBN, (red) 9.2 mol L^{-1} AIBN.

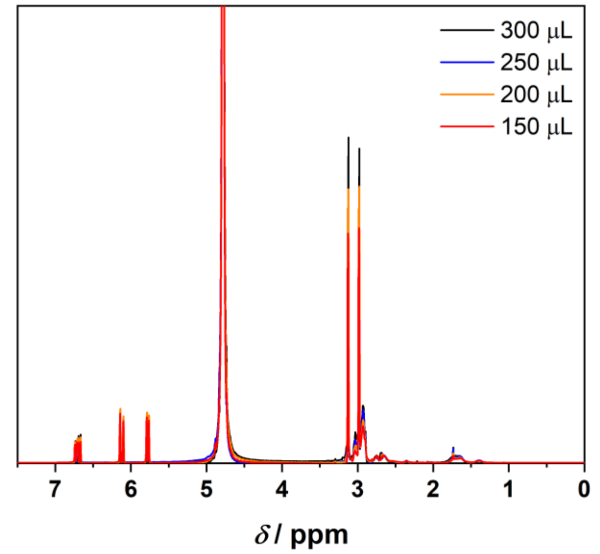


Figure S13: Superimposed ^{1}H-NMR spectra of solutions with 0.69 mol L^{-1} DMA, 9 mmol L^{-1} AIBN 10^{-2} mol L^{-1} CTA and various AuNR concentrations, irradiated with 25 GW cm^{-2} at 800 nm for 30 min, dissolved in D_2O: (black) 300 µL AuNR, (blue) 250 µL AuNR, (yellow) 200 µL AuNR, (red) 150 µL AuNR.

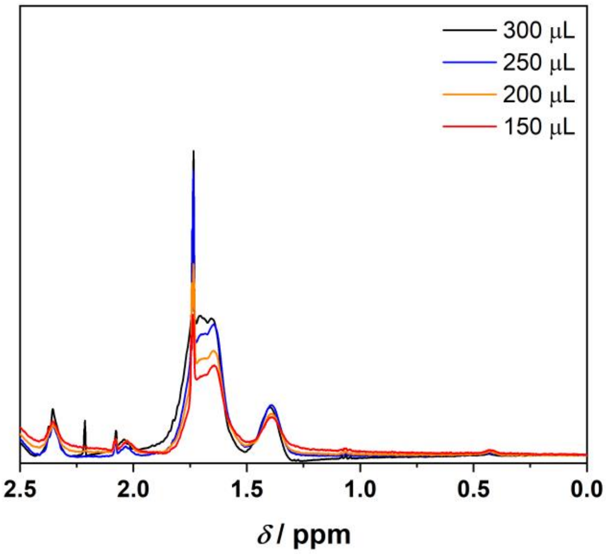


Figure S14: Superimposed ^{1}H-NMR spectra of solutions with 0.69 mol L^{-1} DMA, 9 mmol L^{-1} AIBN 10^{-2} mol L^{-1} CTA and various AuNR concentrations, irradiated with 25 GW cm^{-2} at 800 nm for 30 min, dissolved in D_2O, zoomed into polymer peak between 1 – 2 ppm: (black) 300 µL AuNR, (blue) 250 µL AuNR, (yellow) 200 µL AuNR, (red) 150 µL AuNR.

3.3 Overview of GPC and NMR Results

Table S2: Overview of the conversions obtained in three independent experiments and the average conversions with errors of the monomer variation experiment. For each run, identical bulk solutions were prepared so that each sample contained 50 µL AuNR, 9 mmol L^{-1} AIBN, 10^{-2} mol L-1 CTA and various monomer concentrations, 30 min irradiation time for each sample.

c (DMA) / mol L^{-1}	*Conversion* (1) / %	*Conversion* (2) / %	*Conversion* (3) / %	*Conversion* / %
0.69	42.5	17.7	22.6	27.6 ± 7.0
1.34	58.4	39.2	47.8	45.8 ± 9.8
2.69	61.7	45.5	56.6	62.7 ± 9.7
4.04	68.2	52.3	61.4	63.8 ± 8.2
5.38	71.7	63.7	68.5	70.2 ± 4.3
6.73	76.9	72.2	75.9	75.0 ± 1.3

Table S3: Overview of the M_n values, dispersity,after the irradiation of a solution with various monomer concentrations and 50 µL AuNR, 9 mmol L^{-1} AIBN and 10^{2} mol L^{-1} CTA; 30 min irradiation time.

c (DMA) / mol L^{-1}	M_n / g mol^{-1}	*Dispersity*
0.69	1500	1.7
1.34	2500	2.0
2.69	3300	2.0
4.04	4200	1.9
5.38	4700	1.7
6.73	5000	1.6

Table S4*:* Overview of the M_n values, dispersities, and monomer conversion after the irradiation of a solution with various AIBN concentrations and 50 µL AuNR, 6.73 mol L^{-1} DMA and 10^{-2} mol L^{-1} CTA; 30 min irradiation time.

c (AIBN) / mmol L^{-1}	M_n / g mol^{-1}	*Dispersity*	*Conversion* / %
0.08	-	-	27.1
0.17	2500	1.7	22.4
0.35	-	-	45.2
0.69	2300	1.7	51.9
1.56	2200	1.6	71.2
4	1900	1.7	67.8
9.2	1100	2.4	67.8

Table S5*:* Overview of the M_n values, dispersities and monomer conversion after the irradiation of a solution with various AuNR concentrations and 9 mmol L^{-1} AIBN, 6.73 mol L^{-1} DMA and 10^{-2} mol L^{-1} CTA; 30 min irradiation time.

V (AuNR) / µL	M_n / g mol^{-1}	*Dispersity*	*Conversion* / %
100	2000	1.4	-
150	1600	1.5	32.5
200	1400	1.4	33.1
250	1300	1.4	43.1
300	1048	1.4	51.4

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