

Supporting Information

Magnetic rotational spectroscopy with nanorods to probe time-dependent rheology of microdroplets

Alexander Tokarev , Igor Luzinov , Jeffery R. Owens , Konstantin G. Kornev

S1

Polymerization of 2-hydroxyethyl-methacrylate(HEMA) with diethylene glycol dimethacrylate (DEGDMA)

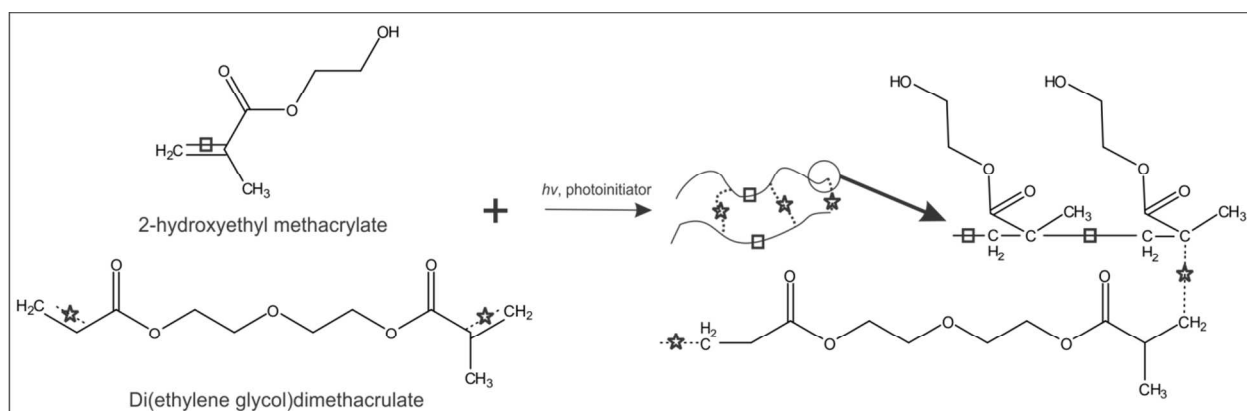


Figure S1. Polymerization of HEMA with DEGDMA.

HEMA polymerizes linearly through the carbon-carbon double bond in 2-hydroxyethyl-methacrylate marked with squares in the schematic S1, and crosslinks through the two carbon-carbon double bonds in diethylene glycol dimethacrylate shown as the dashed line marked with stars in Figure S1. Weight fractions of linearly polymerized and crosslinked parts were determined experimentally during different stages of the polymerization. Method is explained in S4 and results are presented in the Table 1.

Synthesis of the nanorods

Whatman Anodisc alumina membrane was used as a template. **The diameter of all nanorods was controlled by the diameter of pores in alumina membrane and it was equal to 200.6 ± 2.6 nm, Figure S2(c).** The membrane was covered with a conductive Gallium-Indium eutectic liquid. Covered membrane was placed on a copper plate, $76 \times 38 \times 4.2$ mm³, and sealed with water-proof tape. The 1 mm Ni wire was used as anode and was placed on the opposite side from the cathode in a beaker. The beaker was filled with the Watts solution (300 g/L NiSO₄·6H₂O, 45 g/L H₃BO₃, and 45 g/L NiCl₂·6H₂O). The DC regulated power supply (Gwinstek PSS-2005, Instek) was used to apply 1.5 V potential between anode and a cathode. The power supply was controlled with a LabView program (National Instruments Corporation). In order to control the electrodeposition process, the reference electrode was used to measure the current. After the Ni electrodeposition was completed, cathode was immersed in acetone to remove the water-proof tape. Cotton applicator was first soaked in a nitric acid and then was used to remove the Gallium-Indium layer. The alumina membrane was dissolved in a 10 mL of 6 M NaOH solution. Permanent neodymium magnet (K&J Magnetics®, DY81) was placed at the bottom of the beaker while nickel nanorods were rinsed several times with water. The length of nickel nanorods was measured by scanning electron microscope (SEM) Hitachi S4800. The SEM images were processed with ImageJ (NIH) and MatLab to get the rod length distributions (Figure S2(b))

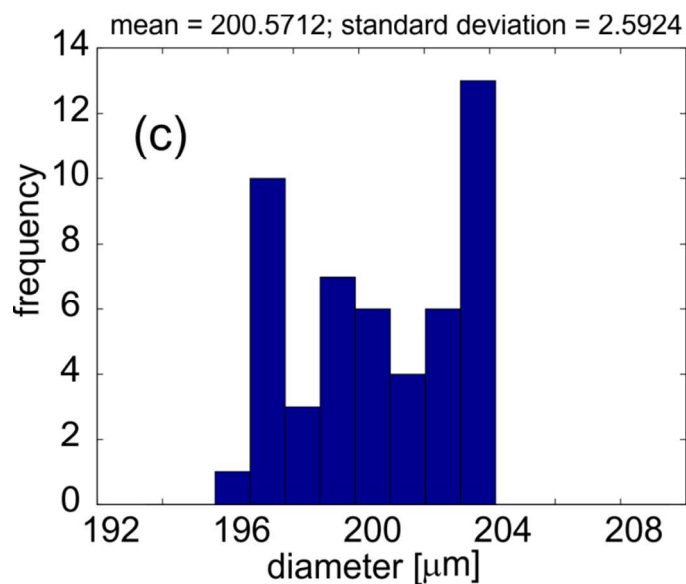
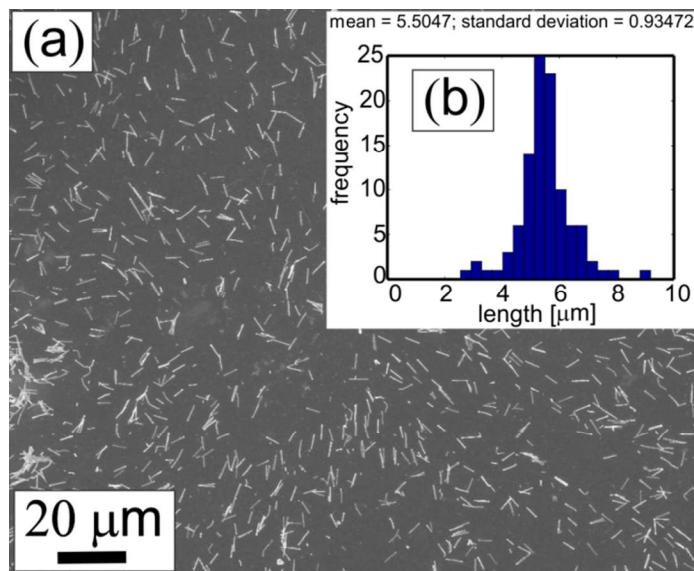


Figure S2. (a) SEM micrograph of nickel nanorods, (b) the length distribution of nickel nanorods after processing. (c) The pore size distribution for the alumina membrane which was used in the nanorods synthesis.

S3

We carried out experiments with nanorods of different length suspended in ethylene glycol with known viscosity $\eta = 16 \text{ mPa}\cdot\text{s}$. The critical frequency f_{cr} corresponding to the frequency at which nanorod stops rotating synchronously with magnetic field was obtained for nanorods with different

aspect ratios. The results are shown in Figure S2. Magnetic moment of Ni nanorods was approximated as $m = VB\chi / \mu_0$. Then the formula for critical frequency was rewritten as

$$f_c = \frac{\chi B^2}{8\pi\eta\mu_0} \left(\frac{l}{d}\right)^{-2} \left(3\ln\left(\frac{l}{d}\right) - 2.4\right) \quad (\text{S3})$$

Least square fitting was used to fit eq (S3) to the experimental data by using χ as an adjustable parameter.

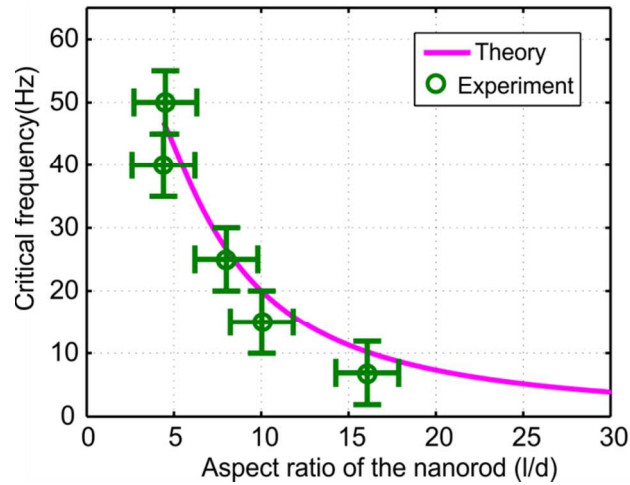


Figure S3. The critical frequency of Ni nanorods rotating in ethylene glycol as a function of nanorod aspect ratio, $B=0.0015\text{T}$.

After magnetic parameters of nanorods were obtained, we tested this method to measure viscosity of glycerol (Fisher Scientific Inc.) and its mixture with water. First, we measured bulk viscosity with DV-III Ultra Rheometer(Brookfield Eng.), then conducted the MRS experiments and calculated the viscosity from the eq S1. The results of these measurements are presented in Table S3:

Table S3:

| Sample (22.5°C) | Bulk measurements with a rheometer (mPa*s) | MRS measurements (mPa*s) | Literature (22.5°C) |
|------------------------|---|--------------------------|-------------------------|
| 98% Glycerin +2% water | 778 | 790±45 | 784 ¹ |
| 89 %Glycerin+11%water | 175 | 191±14 | 169 ¹ |
| Ethylene glycol | We were not able to measure it using DV-III Ultra Rheometer | 18±2 | 17.4(25°C) ² |

S4 Calculating carbon-carbon double bond conversion from the FTIR measurements.

Figure S4 shows the 1638 cm⁻¹ absorption peaks at time 0s (a) and after 60 second of polymerization (b) and 1720cm⁻¹ peak at time 0(c) and time 60s (d):

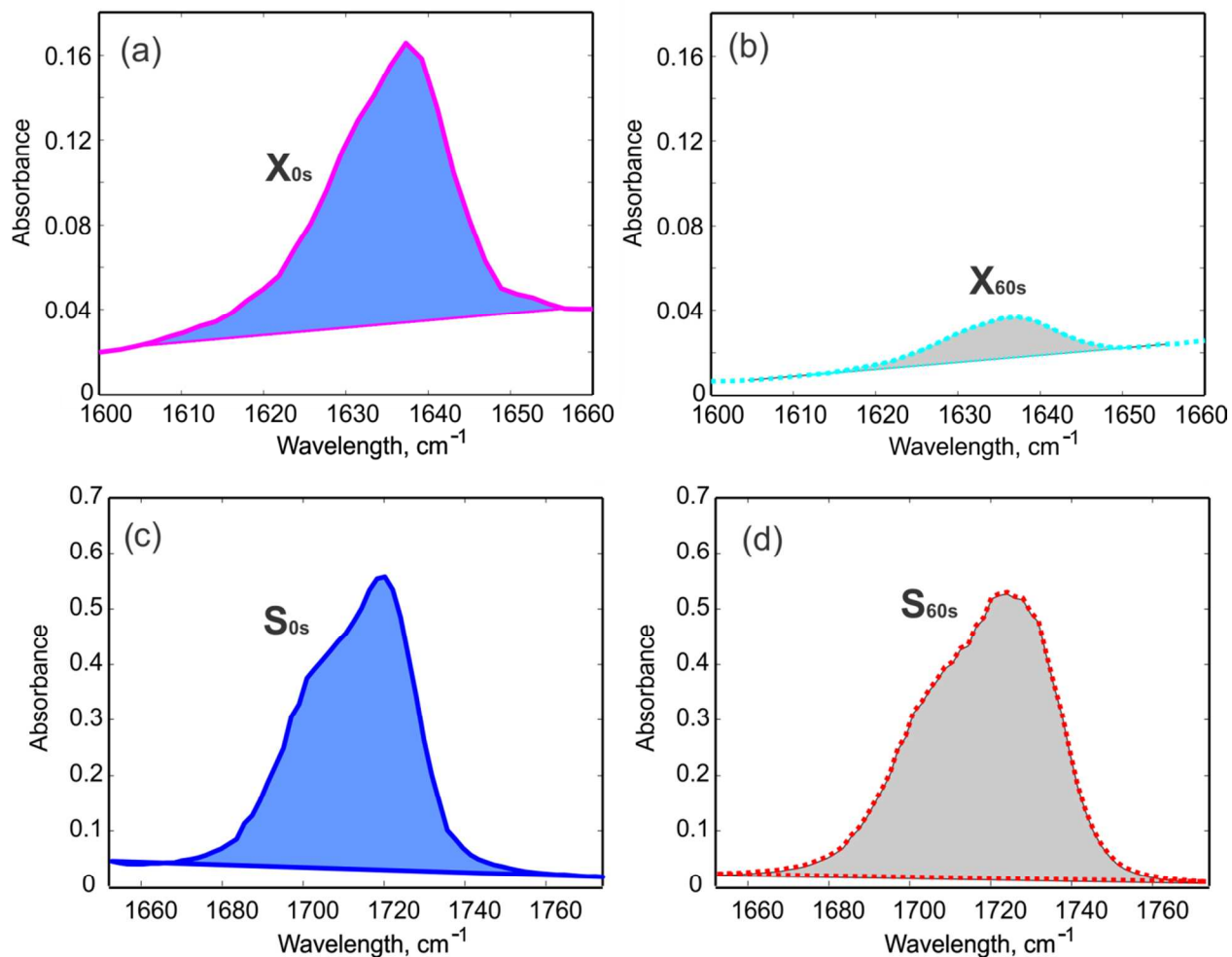


Figure S4. 1638 cm⁻¹ peak at time 0s (a) and after 60 second of polymerization, (b) 1720cm⁻¹ peak at time 0(c) and time 60s(d)

In order to find the peak areas, we used the Omnic software (Nicolet Corp.). Integration intervals were set manually, then the corrected baseline was set by the Omnic software and the peak areas were calculated. X_0 and X_t (shaded regions) are the areas under the 1638 cm⁻¹ peak at time 0s and time 60s respectively (integration interval is 1604 - 1656 cm⁻¹), S_0 and S_t are the areas under the reference 1720cm⁻¹ peak at time 0 and time 60s respectively (integration interval is 1652 - 1774 cm⁻¹). By using the formula $\phi = 100 \times (1 - X_t S_0 / X_0 S_t)$, we obtained the 91.4% conversion of carbon-carbon bonds after 60 seconds of polymerization. Same method was used to calculate the conversion at t=30 and 50s (Figure 5, the dashed line).

S5

We followed the same polymerization as described in the Article. After 45, 50 and 55 seconds of the UV-exposure of the 4.5wt% solution, the resulted gel was collected with a blade from the glass slide. The sample was cured for time t as specified in Table 1, weighted and washed in water to remove unreacted water soluble monomer (HEMA) then centrifuged and washed again with a hexane (VWR International, LLC) to remove hexane soluble unreacted cross-linker (DEGDMA) and photoinitiator. Then the sample was dried in the oven under the vacuum at 75°C for 2 hours. The sample was weighted again and the gel fraction was calculated by dividing the weight of the washed and dried sample by the weight of the initial sample. Experiment was repeated 3 times for each stage of polymerization.

S6

Movie S6.avi shows the nanorod rotation in a Newtonian ethylene glycol with constant viscosity in magnetic field rotating at 0.5 Hz frequency

S7

Movie S7.avi - shows the nanorod rotation during HEMA photopolymerization in magnetic field rotating at 0.5 Hz frequency

S8

Movie S8.avi shows the behavior of a nanorod subject to the Brownian fluctuations during the HEMA photo polymerization in the absence of magnetic field. Mostly in-plane fluctuations were observed and the nanorod was persistently stayed in focus while the film was recorded.

S9

In order to exclude the interactions between the nanorods, we always double checked that the chosen nanorod was far away from its neighbors. The distance to the closest nanorod was at least

7 times greater than the nanorod length (Figure S9).

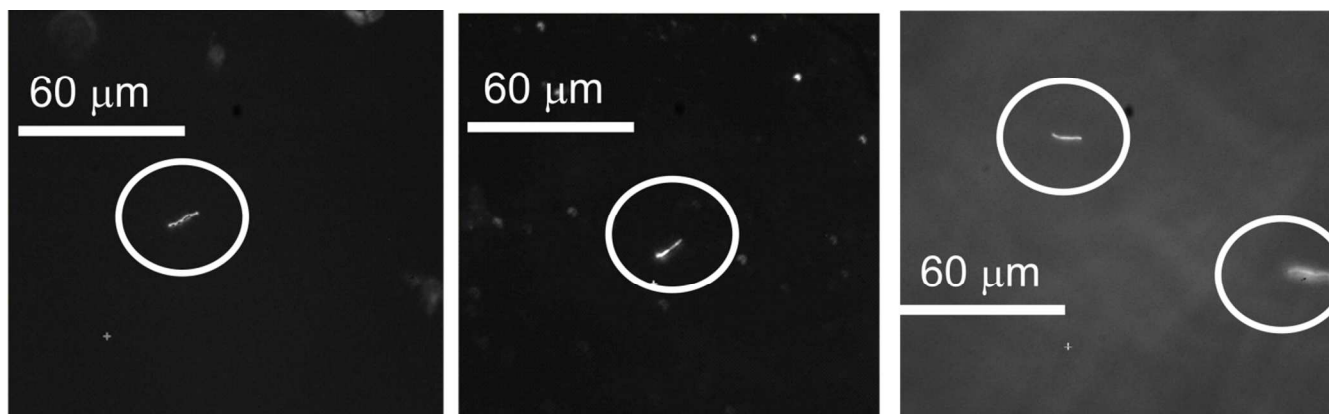


Figure S9. The circled nanorod was used in the MRS analysis. These pictures were taken from 3 different experiments to show that the closest neighbor is situated far away from the chosen nanorod. The width of the screen is 160 μm.

- (1) Sheely, M. L. Glycerol Viscosity Tables. *Industrial & Engineering Chemistry* **1932**, 24 (9), 1060-1064.
- (2) Flick, E. W., *Industrial solvents handbook*. 5th ed.; Noyes Data Corp.: Westwood, N.J., 1998.