

Supporting Information

Liquid Metal Nanoparticles as Initiators for Radical Polymerization of Vinyl Monomers

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Experimental Section

Materials

Gallium and EGaIn were purchased from Indium Corporation. Acrylamide (AAm), N-isopropylacrylamide (NIPAAm), sodium acrylate (SA), 4-styrenesulfonic acid sodium salt hydrate (SSA), (2-dimethylaminoethyl) methacrylate (DMAEMA), 2-hydroxyethyl methacrylate (HEMA), styrene, toluene, dimethyl sulfoxide (DMSO), 4-vinyl pyridine (4VP), N,N'-methylenebisacrylamide (MBAA), glucono delta-lactone (GDL) were purchased from Sigma-Aldrich (St. Louis, MO). Isopropyl alcohol (IPA) was purchased from VWR International (Radnor, PA). 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was purchased from Enzo Life Sciences, Inc. (Farmingdale, NY). Unless otherwise specified, the chemicals used in the current work were used as received.

Characterization of liquid metal particles post-sonication

We determined the size distribution of the liquid metal nanoparticles by placing 0.2 g of liquid metal and 10 ml of water in a 20 ml vial. LMNPs were formed by sonicating the solution. Sonication was carried out as described below. A zeta-sizer (Zetasizer Nano ZS, Malvern Instrument, Malvern) measured the size distribution at room temperature. **Figure S1** plots the size distribution of the LMNPs.

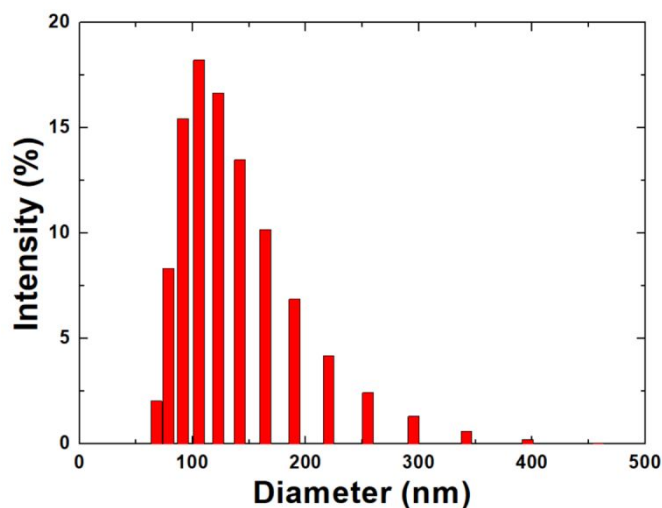


Figure S1. The typical size distribution of the LMNPs after 5 min of sonication. (0.2 g of EGaIn, 10 ml of water) as determined by dynamic light scattering.

Figure S2 depicts the structures of the monomers used in this study. All the monomers reported in **Figure S2** polymerized via sonication and formed a polymeric gel in the presence of LMNPs as the initiator except 4VP and styrene (shown in red). As monofunctional monomers cannot crosslink chemically; the formation of a hydrogel suggests that the monomer polymerized to high molecular weights and formed a physical gel (in some cases, gallium ions could also facilitate the gel formation). P4VP is relatively hydrophobic and did not form a gel in bulk, but it did polymerize. Styrene did not appear to polymerize at all; note, since it is insoluble in water, it was dissolved in toluene.

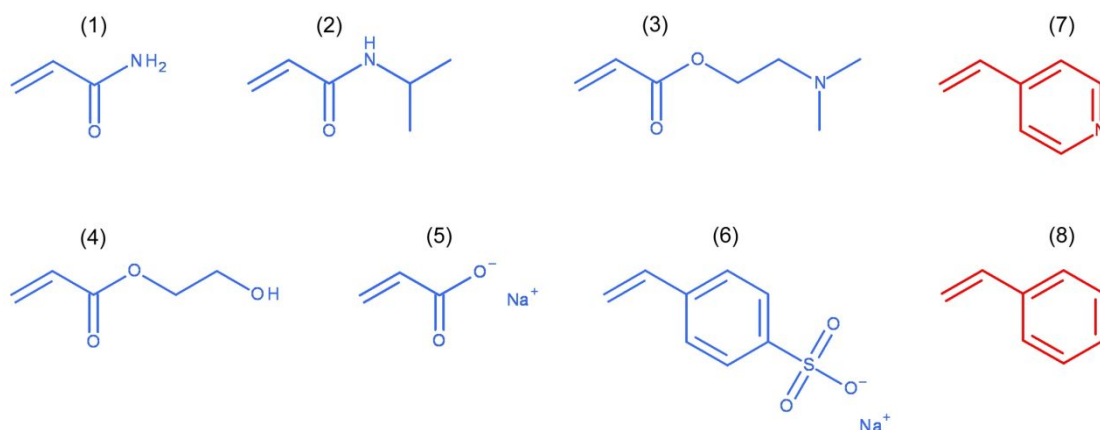


Figure S2. The chemical structures of hydrophilic (blue) and hydrophobic (red) vinyl monomers used in this study: (1) acrylamide, (2) N-isopropyl acrylamide, (3), 2-dimethylaminoethyl methacrylate, (4)

2-hydroxyethyl methacrylate, (5) sodium acrylate, (6) 4-styrenesulfonic acid sodium salt hydrate, (7) 4-vinyl pyridine, and (8) styrene.

LMNPs-induced polymerization of alkene monomers

In a typical procedure (used throughout unless stated otherwise), 0.2 g of liquid metal was placed in 20 ml vial and 10 ml of an aqueous solution of monomer (0.5 - 4 M) was added to the vial. A probe sonicator (Q700, Qsonica LLC, Newtown, CT) sonicated the solution at an amplitude setting of 40%. The tip of the sonicator was placed ~5 mm above the bottom of the vial. To prevent the solution from heating during the sonication, and thus causing excessive oxidation of the liquid metal¹, the vial was placed in an ice bath, and the sonication was applied in a pulsed mode (2 s pulses with 2 s delay in between). To form a hydrogel, 2 M of AAm, 1 M of NIPAAm, 1 M of SA, 1 M of HEMA, 0.5 M of SSA, and 1 M of DMAEMA in water were sonicated with liquid metal.

Sonication of alkene monomers with liquid metal in non-aqueous solutions

0.2 g of liquid metal was placed in a 20 ml vial and 10 ml of a solution of monomer (*e.g.*, 1 M solution of acrylamide in DMSO, neat HEMA, or 1 M solution styrene in toluene) was added to the vial. We distilled DMSO under vacuum to remove moisture; the reflux ratio was 5:1. Sonication was carried out as described in the previous paragraph.

Preparation of hydrogels using LMNPs initiator

To create a highly stretchable PAAm hydrogel, 1.4 g (2 M) of AAm monomer, 38 mg (24.6 mM) of MBAA chemical crosslinker, 1.0 mg (1.2 mM) of LMNPs as an initiator, and 0.1 g (56.1 mM) of GDL as a slow etchant for LMNPs were mixed in 9 ml of deionized water. For a thermally responsive PNIPAAm hydrogel, 1 g (0.885 M) of NIPAAm, 26 mg (15.5 mM) of MBAA, 1.0 mg (1.2 mM) of

LMNPs, and 0.1 g (56.1 mM) of GDL were mixed in 9 ml of deionized water. After sonication, each solution was poured immediately into a mold made of poly(methyl methacrylate). The samples were removed from the mold the next day.

Free radical inhibitors quench polymerization.

Since the polymerization proceeds by a free-radical polymerization mechanism, it could be either slowed down or even completely terminated by adding radical inhibitors (*e.g.*, hydroquinone or diethylhydroxylamine). For example, **Figure S3a-b** shows photographs of vials with the reaction mixtures which did not form a gel due to the addition of hydroquinone, whereas a gel forms rapidly in the absence of hydroquinone (**Figure S3c-d**). Similar results were obtained using other radical inhibitors, such as diethylhydroxylamine (**Figure S3g**).

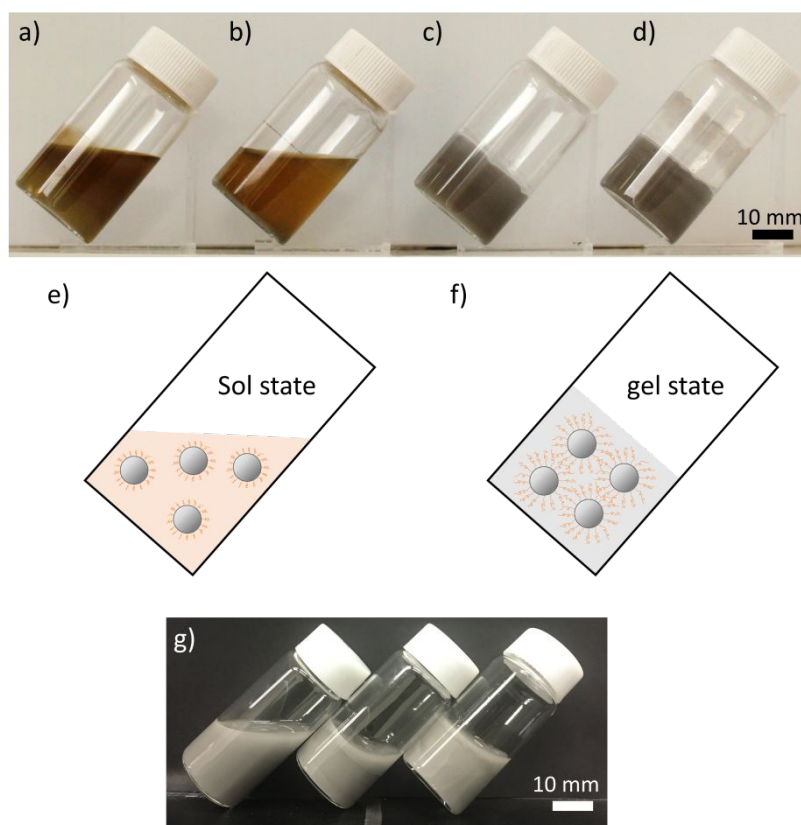


Figure S3. (a, b) Sonicating liquid metal (0.2 g), AAm (2 M for a, 4 M for b), and a radical inhibitor (hydroquinone) did not form a gel. The concentration of the hydroquinone was 0.5 M. (c, d) Sonication of liquid metal (0.2 g) and AAm (2 M for c, 4 M for d) formed a gel. Schematic diagram of the sol state (e) and gel state (f) of the LMNP-g-PAAm. (g) Sonication of liquid metal (0.2 g), AAm (2 M), and diethylhydroxylamine (another known radical inhibitor) affected the polymerization. The concentration of the diethylhydroxylamine was 50 mM (left), 10 mM (middle), and 1 mM (right).

Electron Paramagnetic Resonance (EPR) measurements

EPR measurements were carried out to detect radical species immediately after sonication. X-band (9.86 GHz) continuous wave EPR spectra were measured with a Bruker ELEXSYS E500 spectrometer (Bruker Biospin, Billerica, MA). Immediately after the sonication, aqueous dispersions or solutions were drawn into a polytetrafluoroethylene tube (PTFE, 0.81 mm \times 1.12 mm, Jaguar Industries, Stony Point, NY). The tube was folded four times and inserted into a standard X-band 3 mm \times 4 mm (*i.e.*, inner diameter \times outer diameter) quartz EPR tube (Norell, Marion, NC). All the EPR measurements were performed at room temperature. The following spectrometer settings were used: microwave power

= 2 mW, modulation frequency = 100 kHz, modulation amplitude = 1 G, sweep width = 100 G, sweep time = 30.39 s, time constant = 20.48 ms, and conversion time = 29.68 ms.

EPR spin-trapping experiment

A 10 ml aqueous suspension containing LMNPs (0.2 g) and acrylamide (0.5 M) were probe-sonicated in a vial surrounded by ice with the following power settings on the sonicator: 40 % intensity, 2 s pulse length, 2 s delay over 5 min total. Within 1 min of completing sonication, 90 μ l of the reaction mixture was transferred to an Eppendorf tube, and 10 μ l of 1 M aqueous solution of DMPO was added to reach the final DMPO concentration of 100 mM. The resulting mixture was mixed by a vortexer and drawn into the PTFE tube for EPR measurements.

Polymer characterization

To characterize the polymers formed via sonication with liquid metal, the polymers were detached from the LMNP surfaces using 1 M HCl or NaOH solutions. As gallium based liquid metal was used, which easily reacts with a strong acid or base and thereby produces water-soluble salts, the interface between the polymer and metal was etched using HCl or NaOH solutions (**Figure S4**). Once detached, the solutions were centrifuged to separate the particles from the polymer. The polymer was purified and examined via FT-IR and an SEC, as described in the manuscript and in **Figure S7** and **Figure S12** in this document.

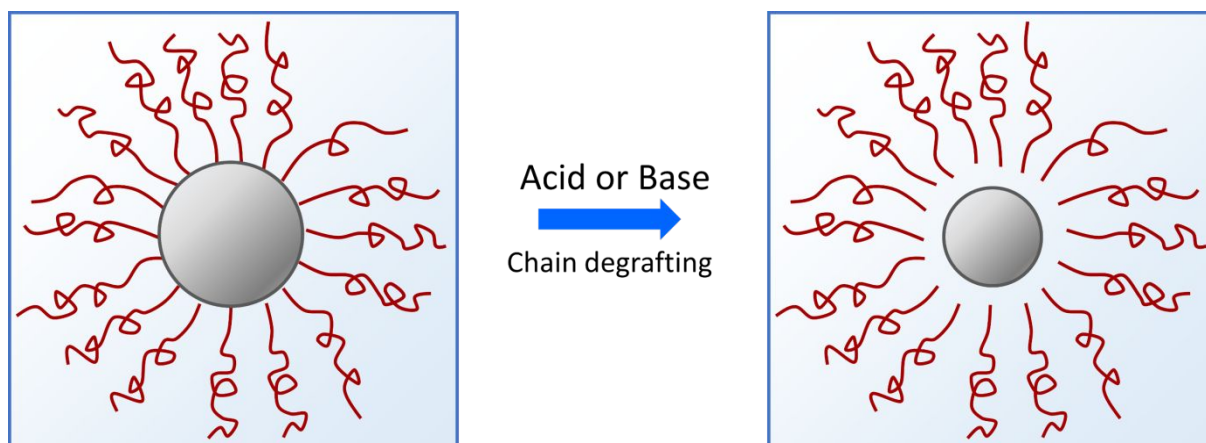


Figure S4. A cartoon illustrating the degrafting of the polymer from the LMNPs by etching the surface with a strong acid or base.

Size Exclusion Chromatography (SEC) measurements

To estimate the molecular weight of the polymers, size exclusion chromatography (SEC) was carried out using a Waters 2695 separations module and a differential refractive index (DRI) detector (Optilab Rex, Wyatt Technology Co., Santa Barbara, CA). The setup had 2 columns in series (designed to detect number average molecular weights, M_n , with ranges: 2–1000 and 1–80 kDa), and the mobile phase was 0.1 M NaNO_3 in water with a flow rate of 0.25 ml/min. The columns and detectors were maintained at 25 °C. Conventional calibration was generated using five monodisperse poly(ethylene oxide) standards (Agilent Technologies, Santa Clara, CA), ranging from 20.26 to 498.7 kDa.

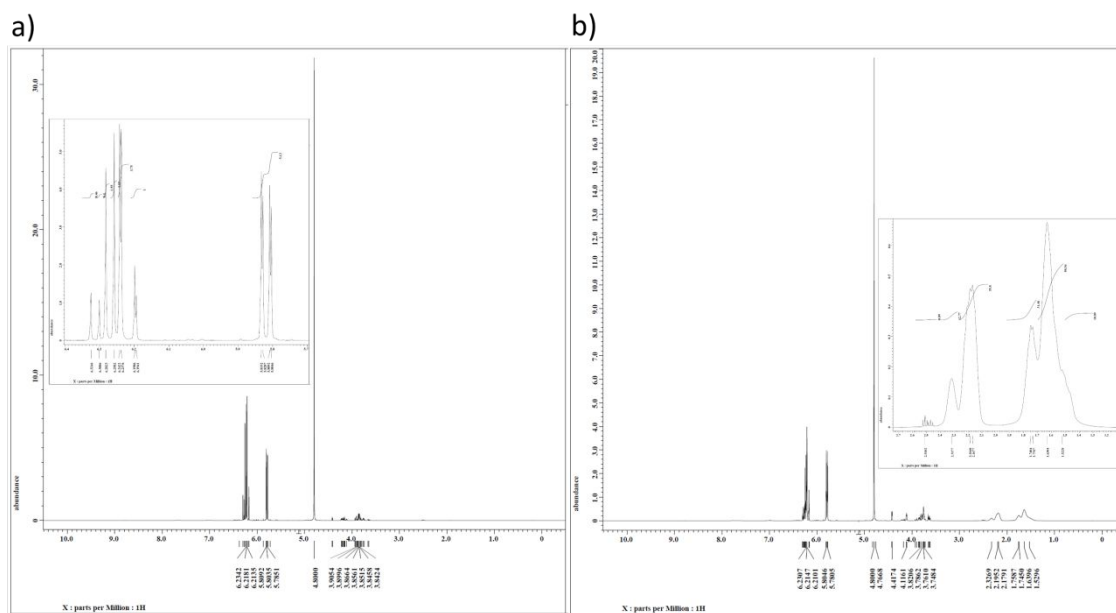


Figure S5. ^1H -NMR spectra of the polymer formed by first sonicating liquid metal and then adding the particles to AAm and GDL in D_2O (a) ^1H -NMR spectrum of LMNPs, AAm, and GDL right after mixing (b) ^1H -NMR spectrum of LMNPs, AAm, and GDL mixture after 24 h from mixing.

Nuclear Magnetic Resonance Spectroscopy (NMR) experiments

To study the exact composition of the polymer, ^1H -NMR spectra were recorded with mixtures of LMNPs, AAm, and GDL. ^1H -NMR spectra were acquired at 298 K using a 400 MHz NMR spectrometer (JNM-LA400 with Liquid Field Gradient, Jeol, Akishima). All chemical shifts (δ) in D_2O were reported in parts per million (ppm) relative to D_2O (4.8 ppm) as the internal standard.

For the NMR samples, EGaIn was sonicated in D_2O , and a small amount of the solution was mixed with a solution consisting of AAm, GDL, and D_2O . GDL etched the oxide skin (GDL was used instead of NaOH, because NaOH removes the oxide so rapidly that the particles merge). Removing the oxide should produce radical sites for polymerization. No polymer was detected by NMR at time equals zero (*i.e.*, immediately after the AAm solution was added to the sonicated EGaIn, **Figure S5a**), but PAAm was detected 24 h after the exposure of EGaIn to the aforementioned mixture (**Figure S5b**). As the radical reaction progressed, the NMR peaks corresponding to PAAm (1.48 ppm or 2.04 ppm) appeared after 24 h of the exposure to the aforementioned mixture and matched those previously

reported for PAAm.² There was no signal for LMNPs in the NMR spectrum (**Figure S6a**). The signals in the NMR spectrum correspond only to monomer, polymer, and the etchant. The signal of the etchant (~ 4 ppm) is distinct from the monomer or polymer (**Figure S6b**).

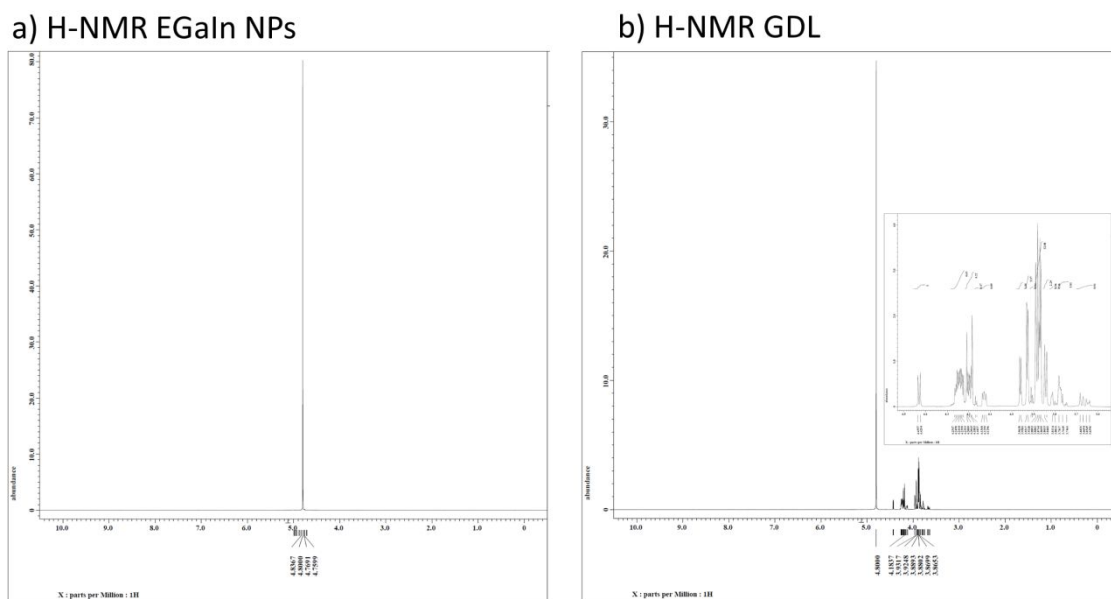


Figure S6. (a) ¹H-NMR spectra of LMNPs in D₂O. (b) ¹H-NMR spectra of GDL in D₂O.

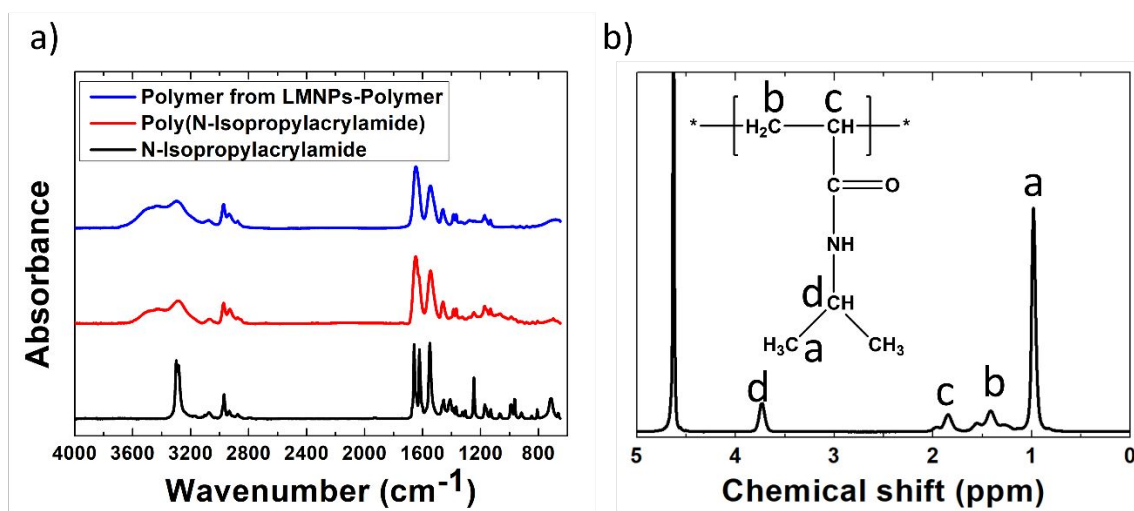


Figure S7. Chemical characterization of the PNIPAAm detached from LMNPs-g-poly(NIPAAm) (a) FT-IR spectra of PNIPAAm detached from LMNPs-g-PNIPAAm (blue), PNIPAAm which was initiated by the thermal initiator ammonium persulfate (red), NIPAAm monomer (black) (b) ¹H-NMR

spectra of the PNIPAAm detached from LMNPs-g-PNIPAAm.

FT-IR measurements

After polymerization (thermally initiated or using LMNPs as initiator), PAAm was precipitated in IPA (PNIPAAm was precipitated by heating the solution above 50 °C) and dried in the vacuum oven for one day. For the LMNPs-g-PAAm and LMNPs-g-PNIPAAm, polymers were detached (*cf.* **Figure S4**). Once detached, the solutions were placed in a centrifuge to separate the particles from the polymer. The polymer was precipitated and dried, as described above. The dried powder was pressed to form a self-standing sheet. FT-IR spectra in the 600-4000 cm⁻¹ frequency range and a step of 4 cm⁻¹ were recorded using a Nicolet iS 9 FT-IR spectrometer (Thermo Scientific, Waltham, MA) operating in the attenuated total reflection (ATR) mode.

LMNPs-g-PNIPAAm were formed using sonication of liquid metal in the presence of 0.5 M of NIPAAm. Sonication was carried out as described above. Isolating the polymer from LMNPs-g-PNIPAAm, shows the following characteristics. Vibrations corresponding to the C=C peaks in FT-IR at 1610 cm⁻¹ disappeared as the polymerization took place, and the IR spectrum of the polymer was nearly identical to that of PNIPAAm prepared using a conventional bulk thermal free radical polymerization using ammonium persulfate as the initiator (70 °C, 24 h) (**Figure S7a**). The FT-IR spectrum of the polymer detached from the LMNPs-g-polymer confirms that the polymer formed is PNIPAAm. The ¹H-NMR peaks at 1.10, 1.54, 1.97, 3.85 ppm match well with those previously reported for PNIPAAm.³ (**Figure S7b**)

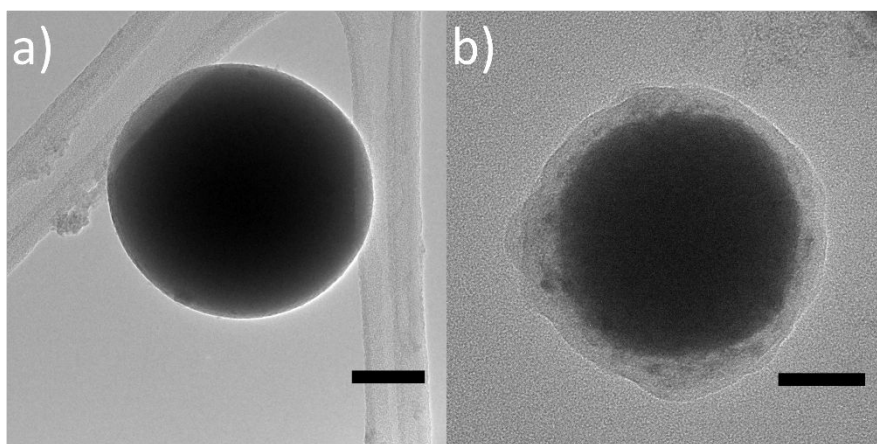


Figure S8. Representative TEM images of (a) LMNPs (b) LMNPs-g-PAAm. Scale bar corresponds to 50 nm. The halo surrounding the particle suggests a grafted layer of polymer from the particle surface.

Transmission electron microscopy (TEM) imaging of particles

TEM was employed to visualize the LMNPs and LMNPs-g-PAAm. Gallium (0.1 g) or gallium in the presence of AAm monomer (1 M) was sonicated as described in the main text to form LMNPs and LMNPs-g-PAAm, respectively. After sonication, 0.1 ml of the suspension (for LMNPs) or 0.1 g of the hydrogel (for LMNPs-g-PAAm) was added to 10 ml of water. The hydrogel dissolved in water completely, which indicated that the physical gel formed due to hydrogen bonding or/and entanglements among the PAAm chains. Then, the diluted solutions were drop-cast on holey carbon-coated TEM grids. The TEM grids were stored in a desiccator for 1 day to remove water. The images were collected using a high-resolution TEM (F20, FEI, Hillsboro, OR) at an acceleration voltage of 200 kV.

If gallium directly initiates FRP, the growing polymer chains should be attached to the metal substrate. In general, visualization of the polymer layer on top of EGaIn particles is challenging; EGaIn possesses a relatively thick oxide when sonicated in water, and the contrast between the oxide and the polymer is not sufficiently high. In some instances, however, polymer layers on top of EGaIn particles can be detected; e.g., EGaIn nanoparticles sonicated with alginate show a Ga-alginate halo by TEM⁴.

We used gallium (instead of EGaIn) particles for TEM imaging because gallium nanoparticles feature only a few nm thick oxide layer at the particle surface (Figure S8a). Also, PAAm carries no charge or cross-linkable ligands when polymerized; thus, it is reasonable to assume that any polymer on the surface of the particle is grafted. Figure S8b shows an image of a PAAm halo surrounding Ga-based LMNPs. The thickness of the dry PAAm layer is ~ 20 nm.

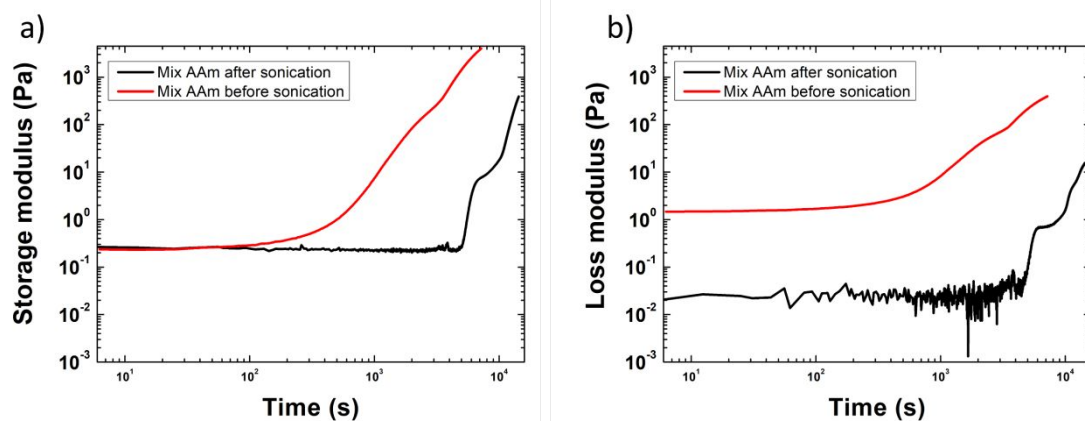


Figure S9. Rheology provides a proxy for the kinetics of polymerization. Adding monomer before or after sonication has an impact on the reaction kinetics. (a) Storage modulus (G') versus time for acrylamide and LMNP solution. (b) Loss modulus (G'') versus time for acrylamide and LMNP solution.

Rheological characterization of the LMNPs-g-PAAm

Sonicated liquid metal in AAm solution initiates that free radical polymerization proceeds rapidly. In contrast, “aged” metal particles, which possess an oxide layer, polymerize the AAm more slowly. To compare the rates of these two routes, we recorded the rheological behavior of a solution prepared by sonication AAm in the presence of liquid metal (red line in Figure S9), as well as LMNPs added to AAm (black line in Figure S9). The viscoelastic responses of LMNPs-g-PAAm were determined by employing a rheometer DHR-2 (TA Instruments, New Castle, DE). 0.2 g (247 mM) of EGaIn and 1.4 g (2 M) of AAm were mixed in 10 ml of water before or after 3 h from sonication. Fixed oscillation tests at 0.1% strain with 0.1 of strain rate were carried out for 2 h.

As the polymerization progresses, a physical hydrogel forms as inferred from the increase of the storage modulus (G') and the loss modulus (G''). As shown in **Figure S9**, the time in which G' and G'' increase differs depends on when the monomer was exposed to the LMNPs. Their values differ by more than an order of magnitude with respect to time, thus showing that “aged” nanoparticles (*i.e.*, those added to monomer after sonication) polymerize at a slower rate and with a delay compared to when the particles were formed in the presence of the monomer.

Time-of-Flight Secondary Ion Mass Spectroscopy (TOF-SIMS) measurements

To detect the nature of the bonding at the metal-polymer interface, time-of-flight secondary ion mass spectrometry (TOF-SIMS) measurements were performed. LMNPs-g-PAAm films were spin-coated on a silicon substrate at 2000 rpm, 30 s, and dried for 1 day in a vacuum oven. The TOF-SIMS spectra were recorded in the range of 0-1000 m/e. A pulsed Bi^{3+} primary ion beam at 25 keV impact energy with less than 1 ns pulse was used. The total accumulated primary ion dose for data acquisition was less than 10^{13} ions/cm².

We recorded the TOF-SIMS spectra from the LMNPs-g-PAAm samples to confirm that PAAm was attached to the gallium substrate. The spectra showed peaks at $m=139.9621$ AMU and $m=227.9811$ AMU corresponding to one- and two AAm sub-units attached to ^{69}Ga atom (see **Table S1**). One or two AAm units attached to gallium were detected, as shown in **Table S1**.

Table S1. Mass and mass deviation of secondary ions in ToF-SIMS measurement.

	Secondary ion mass (AMU)	Peak area (a.u.)	Mass deviation (ppm)
Ga-69-acrylamide (N)	139.9621	83947	-8.0173
Ga-71-acrylamide (N)	141.9614	54854	-6.8358

Ga-69-diacrylamide (N)	227.9811	420059	-96.4033
Ga-71-diacrylamide (N)	229.9765	289600	-111.6963
Ga-69-acrylamide (P)	140.9643	139063	-40.3232
Ga-71-acrylamide (P)	142.9662	91977	30.7164

N=negatively charged ions, P=positively charged ions

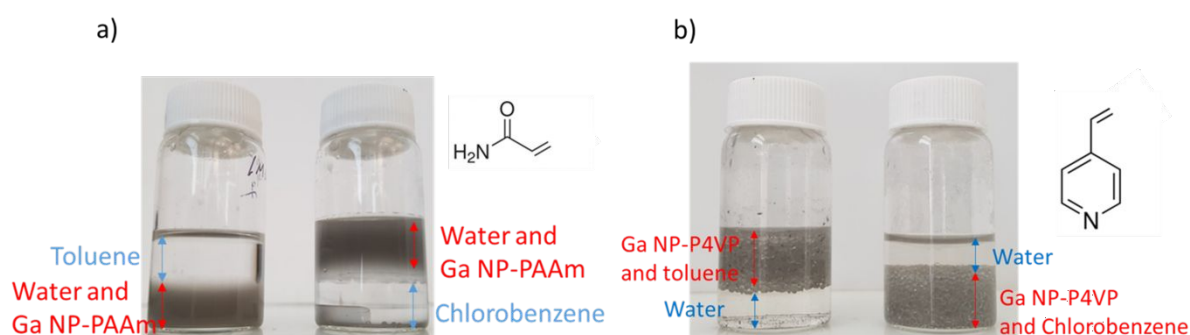


Figure S10. Interactions between nanoparticles and a solvent and the hydrophobicity of polymers grafted on the LMNP's surface dictate system behavior. AAm or 4VP [0.3 M] and 0.05 g of gallium were sonicated in 10 ml of the solutions. (a) Gallium nanoparticles-g-PAAm were dispersed in the water phase. (b) Gallium nanoparticles-g-P4VP were dispersed in the toluene or chlorobenzene phase.

The grafted polymer can dictate the hydrophobicity of the particles.

The chemical nature of polymers attached to LMNPs governs the solubility of the particles in various solvents (*cf.* **Figure S10**). PAAm-coated LMNPs only disperse in the water phase because PAAm is hydrophilic. LMNPs coated with a hydrophobic P4VP formed Pickering emulsions (*i.e.*, particles of water suspended in toluene due to the presence of particles at the interface) in the nonpolar solvent phase, such as toluene or chlorobenzene, as shown in **Figure 2f** and **Figure S10**.

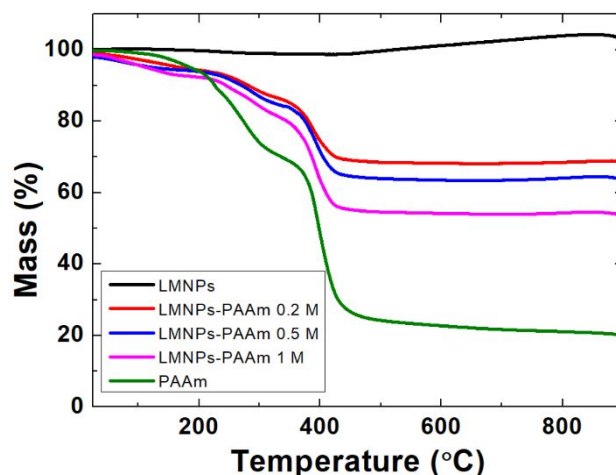


Figure S11. TGA curves of the LMNPs (black), LMNPs-g-PAAm (red, blue, magenta), and PAAm (green). The number in the legend indicates the concentration of the monomer in the solution. Thus, the greater the amount of monomer, the greater the weight loss, and thus, presumably the higher the molecular weight.

Thermal Gravimetric Analysis (TGA)

A thermogravimetric analyzer (SDT 650 series, TA Instruments, New Castle, DE) was used to conduct thermal gravimetric analyses. After the fabrication of LMNPs-g-PAAm (using the general procedure described earlier), the solutions were directly precipitated in IPA and dried in the vacuum oven for 1 day. Then, 5 mg of LMNPs-g-PAAm powder was placed in an open alumina pan (Note: use of the standard aluminum pans was avoided due to the possible interactions with gallium) and heated using standard ramping at a heating rate of 10 °C/min from 25 to 900 °C under 10 ml/min of dry nitrogen.

The degree of polymerization should increase with increased monomer concentration. Thus, TGA was performed for the resulting gels (*cf.* **Figure S11**). There is a slight increase in mass for pure LMNPs with respect to temperature. This may be due to the formation of nitride compounds at ~500°C. For pure PAAm, ~20 % of the mass remained after the temperature sweep, which agrees with previous reports.⁵ If the polymerization is initiated only by the LMNPs, the mass of the polymer lost in the TGA should correspond to the mass of the polymer attached to the LMNPs. As shown in **Figure S11**, the weight of the polymer increased with increasing the monomer concentration. This result shows that the

mass of the polymer attached to the particle increased with increasing the monomer concentration.

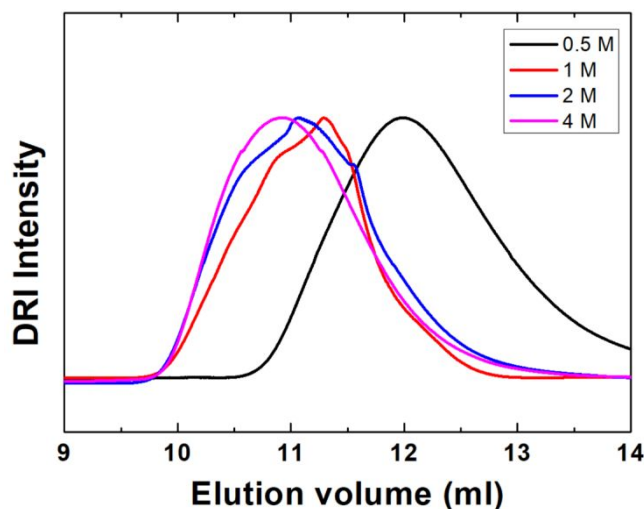


Figure S12. Size-exclusion chromatography spectrum of the polyacrylamides detached from LMNPs-g-PAAm with the various monomer concentrations.

Size Exclusion Chromatography

To measure the molecular weight of the grafted PAAm, PAAm was detached from the LMNPs by etching the oxide skin with NaOH (1 M), then centrifuged the solution (10,000 rpm, 10 mins) to remove the LMNPs. **Figure S12** shows the DRI intensity in SEC versus elution time. The molecular weight of the PAAm was larger than the limit (~ 1 MDa) of the SEC. Thus although the exact molecular weight of the polymer is unknown, the molecular weight appears to be very high.

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