

SUPPORTING INFORMATION

Magnetic Iron Oxide Nanoparticles as Long Wavelength Photoinitiators for Free Radical Polymerization

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EXPERIMENTAL SECTION

Materials

Methyl methacrylate (MMA, 99%; Sigma-Aldrich) and methyl acrylate (MA, 99%; Sigma-Aldrich) monomers were purified by passing through a basic Al_2O_3 column to remove inhibitor. All other reagents were reagent grade and used as received without further purification. Oligo(ethylene glycol) monomethyl ether methacrylate (OEOMA, $M_n = 300 \text{ g mol}^{-1}$, Sigma-Aldrich), triethylene glycol dimethacrylate (TEGDMA; $M_n = 286.32 \text{ g mol}^{-1}$), iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), iron(II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), lauric acid (LA), and triethylamine (TEA) were purchased from Sigma-Aldrich. Ammonium hydroxide (NH_4OH , 26%), absolute ethanol, methanol, hexane, and toluene were purchased from Merck.

Instrumentation

UV-visible spectra were recorded with a Shimadzu UV-1601 spectrometer.

Fourier transform infrared (FTIR) spectra were recorded on PerkinElmer FTIR Spectrum One spectrometer with an ATR accessory (ZnSe, PikeMiracle accessory) and cadmium telluride (MCT) detector.

Molecular weights of polymers were measured with a gel permeation chromatography (GPC) (Agilent 1100) equipped with a refractive index detector. Polymer Labs PLgel $5\mu\text{m}$ Mixed-C column was used. THF was used as an eluent at flow rate of 1.0 mL/min at $30 \text{ }^\circ\text{C}$. All of the polymer solutions were filtered through $0.20 \mu\text{m}$ filters before injection to the column. Polystyrene standards with molecular weights ranging from 580 to $1.12 \times 10^6 \text{ Da}$ were used for calibration.

Photodifferential scanning calorimetry (photo-DSC) measurements were carried out by means of a modified Perkin-Elmer Diamond DSC equipped with a Polilight PL400 Forensic Plus light source between 320 and 500 nm. A uniform UV light intensity is delivered across the DSC cell to the sample and reference pans. The intensity of the light was measured as 40 mW cm⁻² by a UV radiometer covering broad UV range. The measurements were carried out in an isothermal mode at 25 °C with a nitrogen flow of 20 mL min⁻¹.

Synthesis of Nanoparticles

Lauric Acid-Coated Magnetic Iron Oxide (Fe₃O₄-LA) NPs. Iron salts FeCl₃·6H₂O (2.365 g, 8.75 mmol), and FeCl₂·4H₂O (0.870 g, 4.37 mmol) and 1.64 mL of LA were dissolved in 46 mL of deoxygenated water in a three-neck round-bottomed flask fitted with N₂ inlet/outlet and a reflux condenser. This solution was purged with nitrogen for at least 30 min and then heated to 85 °C in an oil bath. NH₄OH (12.06 mL, 26%) was injected rapidly to the hot solution under vigorous stirring which caused immediate formation of dark brown-black color indicating formation of Fe₃O₄. After 30 min reaction allowed for crystal growth, this solution was cooled to room temperature and placed on top of a magnet for one day. Any precipitate was removed with magnetic decantation. Magnetic NPs were washed with fresh DI water using the Amicon Ultra centrifugal filter (10kDa cutoff) with deionized water. These particles are coated with LA bilayer.

LA monolayer coated Fe₃O₄ NPs were prepared as follows: 10 mL of the aqueous colloidal solution of LA bilayer coated Fe₃O₄ NPs was shaken vigorously with 20 mL of toluene and 3 mL of isopropyl alcohol for 15 min, and was transferred into a separatory funnel. The organic phase,

containing the LA monolayer coated Fe₃O₄ was separated from the aqueous solution in a separatory funnel. This extraction procedure transfers all iron oxides into the organic phase.

Photopolymerization

To a dispersion of Fe₃O₄-LA NPs (23 mg) in toluene (1 mL) was added monomer (9.4 mmol) and TEA (30 μL, 0.2 mmol). Then this solution was transferred to a Pyrex tube and degassed with high purity nitrogen for 20 min. It was then irradiated under UV light ($\lambda > 350$ nm) at the light intensity of 22 mW cm⁻². After irradiation, polymers were precipitated and dried in vacuum. NPs were separated from the polymers before GPC analysis as follows: polymers were added to a mixture of 20% aqueous HF and THF and stirred for 24 h. Polymers free from NPs were precipitated into a large excess of water, and dried under vacuum at 25 °C.

Kinetics Studies by PhotoDSC

To a solution of TEGDMA (0.5 ml, 2 mmol) in a few drops of toluene was added TEA (15 μL, 0.1 mmol) and Fe₃O₄-LA NPs (11.5 mg). Approximately 10 mg of this solution was transferred to a photo-DSC pan. The sample was kept under nitrogen flow for at least 5 min to exclude oxygen from the solution. Before irradiation, it was stabilized by keeping the sample in the dark for 1 min, after which irradiation was started in an isothermal mode at 25 °C. The obtained heat is relative to the number of reacted double bonds and the rate of polymerization (R_p) can be calculated according to:

$$R_p = Q_t / (n \times E_{db}) \quad (1)$$

where Q_t ($\text{J mol}^{-1} \text{s}^{-1}$) is the rate of heat released at time t , n the number of (meth)acrylate double bond, and E_{db} (J mol^{-1}) is the energy of double bond ($\sim 54400 \text{ J mol}^{-1}$).¹ By integrating eq 1, double bond conversion was calculated. Calculations were made after baseline corrections.

Characterization of Fe_3O_4 -LA NPs:

Transmission Electron Microscopy (TEM)

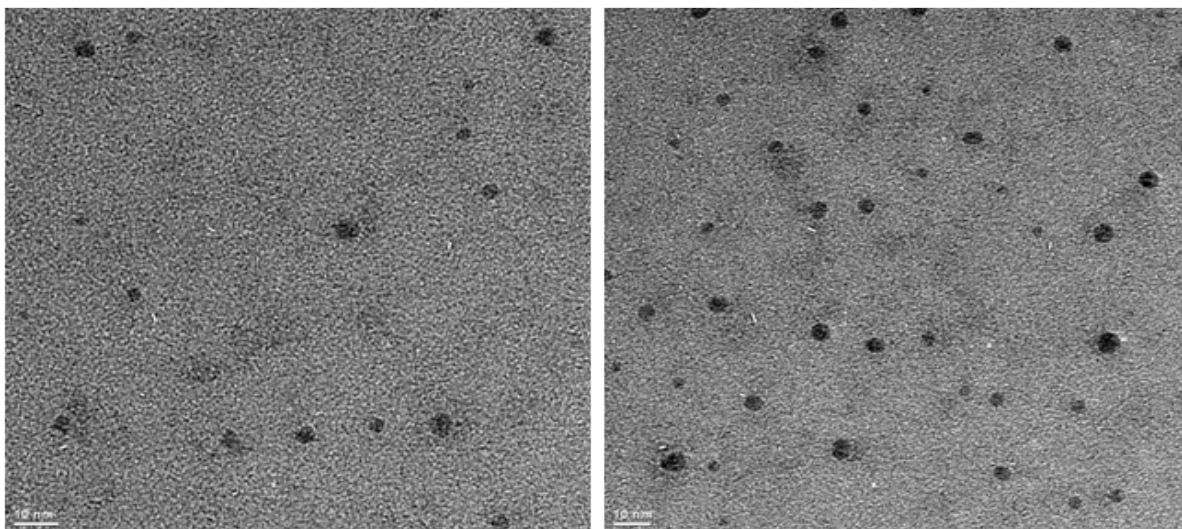


Figure S1. TEM images of LA- Fe_3O_4 NPs. Scale bar = 10nm

XRD pattern

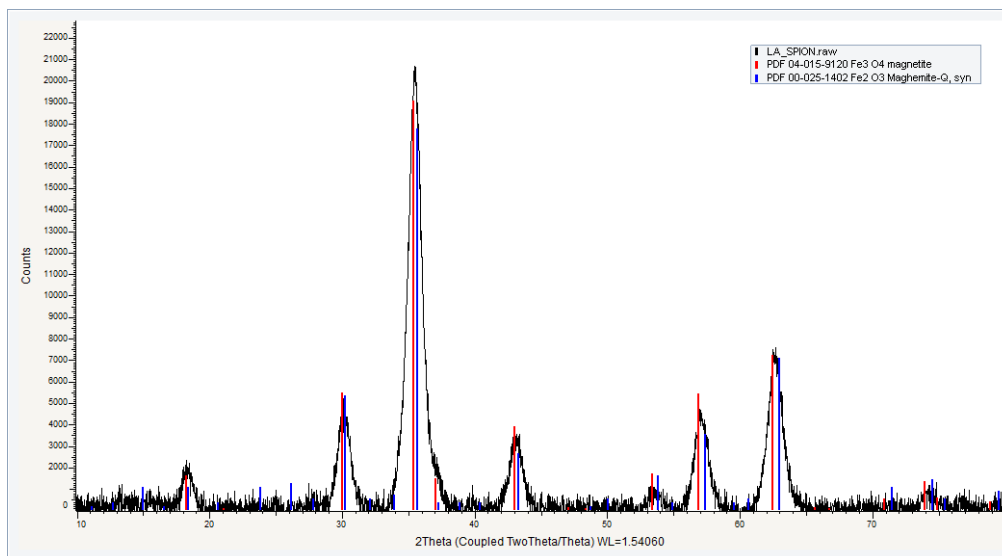
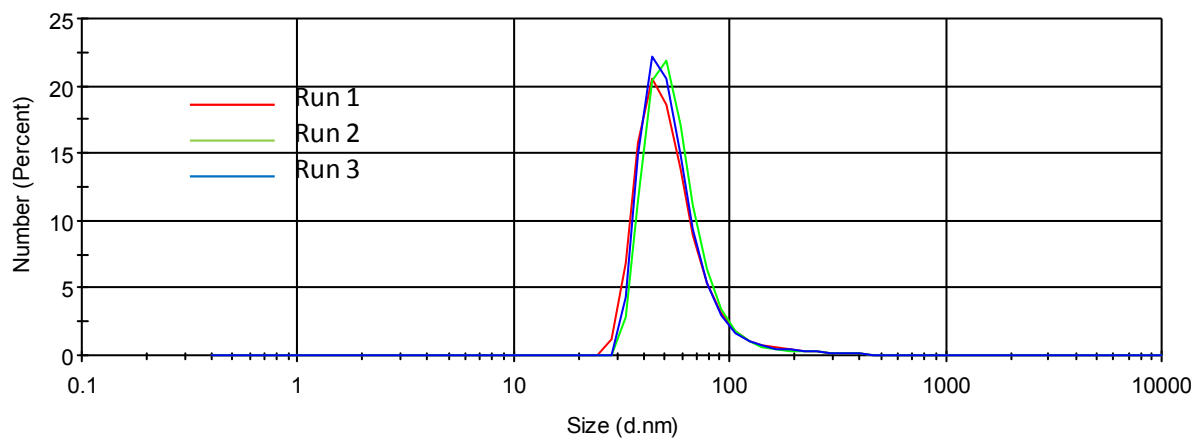


Figure S2. XRD pattern of Fe₃O₄-LA NPs.

Hydrodynamic Size Distribution



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Figure S3. Hydrodynamic size distribution of Fe₃O₄-LA NPs in toluene measured by dynamic light scattering and reported as the number average.

References

1. L. K. J. Tong and W. O. Kenyon, *J. Am. Chem. Soc.*, 1945, **67**, 1278–1281.