SUPPORTING INFORMATION

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

Sajjad Dadashi-Silab, a Yasemin Yar, b Havva Yagci Acar, b and Yusuf Yagci a, c*

a Department of Chemistry, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey.

b Graduate School of Sciences and Engineering, Koc University, 34450 Sariyer, Istanbul, Turkey.

c Center of Excellence for Advanced Materials Research (CEAMR) and Department of Chemistry, Faculty of Science, King Abdulaziz University, Jeddah, 21589, Saudi Arabia.

Correspondence to: yusuf@itu.edu.tr (Y.Y.)
EXPERIMENTAL SECTION

Materials

Methyl methacrylate (MMA, 99%; Sigma-Aldrich) and methyl acrylate (MA, 99%; Sigma-Aldrich) monomers were purified by passing through a basic Al₂O₃ column to remove inhibitor. All other reagents were reagent grade and used as received without further purification. Oligo(ethylene glycol) monomethyl ether methacrylate (OEOMA, $M_n = 300$ g mol$^{-1}$, Sigma-Aldrich), triethylene glycol dimethacrylate (TEGDMA; $M_n = 286.32$ g mol$^{-1}$), iron(III) chloride hexahydrate ($\text{FeCl}_3\cdot6\text{H}_2\text{O}$), iron(II) chloride tetrahydrate ($\text{FeCl}_2\cdot4\text{H}_2\text{O}$), lauric acid (LA), and triethylamine (TEA) were purchased from Sigma-Aldrich. Ammonium hydroxide ($\text{NH}_4\text{OH}$, 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 5µm Mixed-C column was used. THF was used as an eluent at flow rate of 1.0 mL/min at 30 °C. All of the polymer solutions were filtered through 0.20 µm filters before injection to the column. Polystyrene standards with molecular weights ranging from 580 to $1.12\times10^6$ 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 (Fe\(_3\)O\(_4\)-LA) NPs.* Iron salts FeCl\(_3\)\(\cdot\)6H\(_2\)O (2.365 g, 8.75 mmol), and FeCl\(_2\)\(\cdot\)4H\(_2\)O (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 N\(_2\) 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. NH\(_4\)OH (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 Fe\(_3\)O\(_4\). 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 Fe\(_3\)O\(_4\) NPs were prepared as follows: 10 mL of the aqueous colloidal solution of LA bilayer coated Fe\(_3\)O\(_4\) 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 (λ > 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:

\[
R_p = \frac{Q_t}{(n \times E_{db})} \quad (1)
\]
where $Q_t$ (J mol\(^{-1}\) 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 (~54400 J mol\(^{-1}\)).\(^1\) By integrating eq 1, double bond conversion was calculated. Calculations were made after baseline corrections.

**Characterization of Fe\(_3\)O\(_4\)-LA NPs:**

Transmission Electron Microscopy (TEM)

![TEM images of LA-Fe\(_3\)O\(_4\) NPs. Scale bar = 10nm](image)

**Figure S1.** TEM images of LA-Fe\(_3\)O\(_4\) NPs. Scale bar = 10nm
Figure S2. XRD pattern of Fe₃O₄-LA NPs.

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

References