

Surface Modification of Iron Oxide (Fe₃O₄) Micro- and Nano-particles with Stimuli Responsive Polymers

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ABSTRACT

The synthesis of stimuli responsive polymer brushes was carried out using surface-initiated atom transfer radical polymerization (ATRP) on iron oxide (Fe₃O₄) micro- and nano-particles. Commercially available SAM-modified Fe₃O₄ micro- and nano-particles (1 micron and 200 nm nom. d(H)) were obtained, and a bromine-based initiator was attached onto the particle surface. After addition of the initiator, either poly(methacrylic acid) (PMAA), poly(N-isopropylacrylamide) (PNIPAM), or PMAA-*b*-PNIPAM was grown from the surface of the micro- and nano-particles. DRIFTS results confirmed the presence of PMAA with peaks for CH₂ and CH₃ (2900-3000 cm⁻¹) and a broad O-H stretch (3300 cm⁻¹) observed as the ATRP reaction was carried out. TEM measurements demonstrated nanomaterials with the magnetic nanoparticle core and silicate shell surrounded by amorphous material. DLS measurements on 200 nm Fe₃O₄ grafted with PMAA-*b*-PNIPAM revealed a decrease in the radius of gyration of the nanoparticles as temperature was increased. Therefore, DLS results demonstrate the thermo-responsive size change of these metal-polymer composite nanoparticles.

Keywords: ATRP, magnetic nanoparticles, thermo-responsive, pH-responsive

1 - INTRODUCTION

Nanoparticles are materials that are well known to have a high surface area to volume ratio and are considered as an emerging tool for biomedical applications, electronics, environmental treatments and many other areas of study [1-3]. Recently, magnetic nanoparticles (MNPs) have gained more interest due to their inherent magnetic properties which allow manipulation and hyperthermic applications of these particles under the presence of a magnetic field. The ease of manipulation of magnetic nanoparticles is widely studied in electronically devices, sensors, catalysts and drug delivery applications [4].

Stimuli-responsive polymers (SRP) are materials used for a wide range of applications and are recognized as "smart materials" [5]. Stimuli for SRPs can be pH, temperature, ionic strength, UV-radiation and many other conditions [6]. One of the most widely SRP polymers

studied to-date is poly (N-isopropylacrylamide) (PNIPAM). PNIPAM is well known to have a lower critical solution temperature (LCST) at 32 °C [7]. Weak polyacids are often studied as pH-responsive polymer brushes. Poly(methacrylic acid) (PMAA) has been previously studied and is known to be a pH-sensitive polymer. A hybrid inorganic-organic composite system can then be produced using magnetic nanoparticles and stimuli-responsive polymers. This hybrid composite system will combine the capabilities of easy nanoparticle manipulation and responsive behavior in a single material.

Stimuli responsive polymer-magnetic nanoparticle (SRP-MNP) hybrid materials have been previously synthesized using different techniques such as ultraviolet heat treatments, living radical polymerizations, and emulsion processes [8-9]. In this study, a living radical polymerization is undertaken as this process allows for controlled growth of the polymer layer attached to a surface. Atom transfer radical polymerization (ATRP) is used as a "grafting from" approach to produce a polymer brush from the surface of the magnetic nanoparticles [10]. Homo- and co-polymers of PNIPAM/MAA grafted to MNPs have been obtained using this living radical polymerization technique.

In this work, the synthesis of PNIPAM-Fe₃O₄, PMAA-Fe₃O₄ and PMAA-PNIPAM-*b*-Fe₃O₄ copolymer structures is reported. First, a self-assembled monolayer (SAM) is deposited on the surface of the nanoparticles. Then, a bromine-functional initiator is reacted to finally proceed with the polymerization on the surface of the nanoparticles. Morphology and characterization of the MNPs was analyzed using TEM, DLS, and FTIR techniques as the polymerization was carried out.

2 - EXPERIMENTAL

2.1 Materials

Fe₃O₄ nanoparticles (MTI), Fe₃O₄-NH₂ (Chemicell), copper (I) chloride (Aldrich, 97%), triethylamine (Aldrich, 99.5%), Me₆TREN (Aldrich, 96%), methacrylic acid (Aldrich, 99%), N-(isopropylacrylamide) (NIPAM; TCI, 98%), ethanol (Fisher Sci., 99.9%), water (Aldrich, HPLC grade), 2-bromoisobutryl bromide (Aldrich, 98%), toluene (Acros, 99.8%), tetrahydrofuran (THF; Fisher Sci., 99.9%),

propanol (Aldrich, 99.7%), uranyl acetate (EMS, 98%), and copper (I) bromide (Aldrich, 98%).

2.2 Synthesis of Fe₃O₄-initiator

Modified Fe₃O₄-NH₂ nanoparticles were placed in 5 mL of 0.12 M triethylamine/THF solution for 10 seconds at ~ 0 °C. Then, a 0.1 M 2-bromopropionyl bromide/THF solution was added to the reaction tube. This initiation reaction was allowed to proceed overnight and was performed under an inert atmosphere (nitrogen). A flow of nitrogen was used to sparge the solution. Additionally, an ultrasonication water bath was utilized to ensure proper mixing. After completion, the reaction was quenched by opening the solution to ambient conditions. The solvent was then removed from the particles by vacuum. After solvent removal, the particles were washed thoroughly with water three times obtaining the magnetic particles with surface-confined bromine initiator as shown in Figure 1.

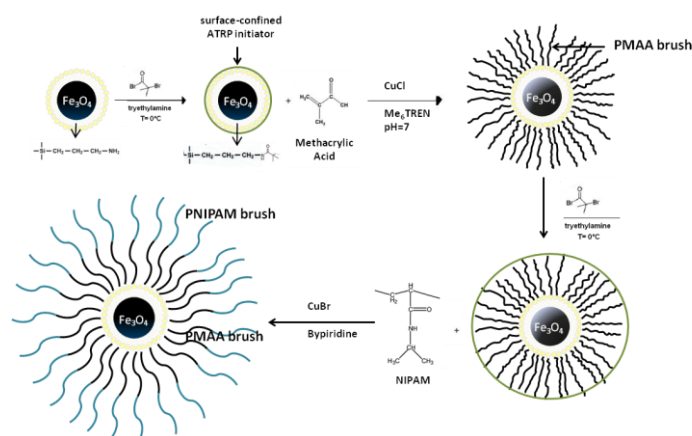


Figure 1. ATRP synthetic route for PMAA and PMAA-b-PNIPAM surface grafted to magnetic nanoparticles.

2.3 Synthesis of Fe₃O₄-PMAA/Fe₃O₄-PNIPAM

After attachment of the bromine initiator to the surface of the MNPs, the ATRP reaction was started using either NIPAM or MAA monomer. NIPAM ATRP was performed using a 26.6 mM concentration in propanol/water (70/30 %v/v) mixed solvent. This mixture was purged with nitrogen for one hour. Then, 2,2-bipyridine (bpy) and Cu(I)Br were added to the solution to start the reaction. The resultant molar ratio was 9.5/2/1 (monomer/ligand/catalyst). NIPAM polymerization was allowed to react for 12 hours under an inert atmosphere at room temperature. ATRP of MAA, either as a homopolymer or the second block, was conducted at a neutral pH. A 2 M solution of MAA/HPLC water was prepared and then NaOH (1 M) was used to neutralize the solution. At a pH of 7, the solution was placed under a stream of nitrogen for about an hour. After that, a 0.1 mM

solution of Me₆TREN and Cu(I)Cl was added to the monomer solution to start the polymerization.

2.4 Synthesis of Fe₃O₄-PNIPAM-*b*-PMAA

Block copolymers systems, Fe₃O₄-PNIPAM-*b*-PMAA, were obtained by reinitializing the terminal group from the “first” ATRP polymerization. For this purpose, bromine initiation was carried out again as previously described. Then, ATRP of the second monomer was performed under the reactions conditions appropriate for the characteristics of the second monomer.

2.5 Characterization

Fourier Transform Infrared (FTIR) Spectroscopy. FTIR spectra were obtained using diffuse reflectance infrared spectroscopy (DRIFTS). A Nicolet 6700 FT-IR with a mercury cadmium telluride (MCT) detector and dry gas purging was used to collect the DRIFT spectra. Thermo Scientific Ommic 8.1.10 software was used for data acquisition and analysis. Surface-modified Fe₃O₄ nanoparticles were mixed with KBr powder for sampling and pure KBr was used as a background. Scans were collected from 400 cm⁻¹ to 4000 cm⁻¹ with a total of 256 scans collected at a 4 cm⁻¹ resolution.

Dynamic Light Scattering (DLS) Measurements. A Dynapro Nanostar manufactured by Wyatt was used for DLS measurements. Dynamics 7.0.0 software (Wyatt) was used to fit the data. A cumulant method was used for the autocorrelation function. A stabilization time of 5 minutes was allowed prior to data collection. Data was collected at 25 °C and studies were also performed over the temperature range from 20 °C to 50 °C.

Transmission Electron Microscopy (TEM). A JEOL JEM-2000 FE II TEM instrument at 100 kV was used for collecting the TEM images. Prior to imaging, particles were deposited on 300 mesh copper grids and allowed to dry at ambient conditions.

3- RESULTS AND DISCUSSION

FTIR spectroscopy was performed on PMAA-Fe₃O₄ and the spectra (Figure 2) showed expected changes in the chemical functional groups as the polymerization was carried out. In particular, Figure 3 shows absorption peaks in the wavenumber region from 2900-3000 cm⁻¹, which corresponds to -CH₂ and -CH₃ vibrations, and a broader -O-H stretch (3300 cm⁻¹) as a result of the acid alcohol group present in the PMAA structure[11].

Another functional group easily identified from Figure 2 is the -Si-O-Si- bond, which presents as a sharp double peak 1080 cm⁻¹ [12]. Additionally, the carbonyl (C=O) of the carboxylate anion (C(=O)-O⁻) and acid (C(=O)OH) are observed at approximately 1414 cm⁻¹ and 1700 cm⁻¹, respectively [13]. Our results indicate the presence of the

carboxylate anion peak at the described region. Therefore, the presence of the CH_3/CH_2 and the acid/anion carbonyl groups supports the presence of methacrylic acid on the surface of the nanoparticles.

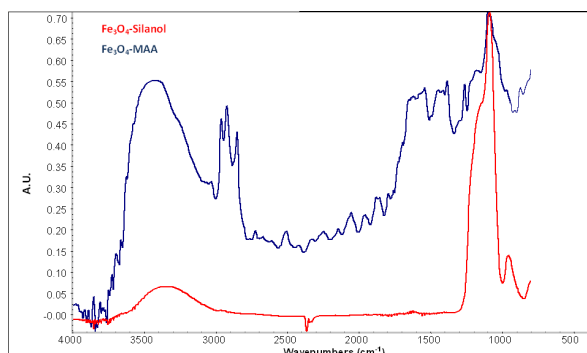


Figure 2. DRIFTS FTIR spectra of Fe_3O_4 with a) silanol and b) PMAA grafted to the surface.

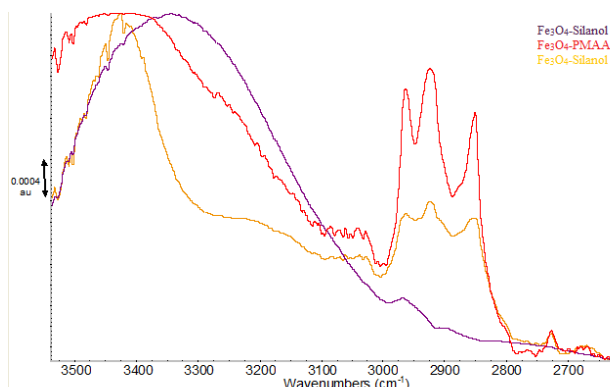


Figure 3. Select portion of the DRIFT FTIR spectra of PMAA- Fe_3O_4 just after polymerization.

The morphology of the particles was obtained using TEM. First, homo-polymerized magnetic nanoparticles were characterized as shown in Figure 4 and an organic layer surrounding an inorganic core can be observed. These TEM images confirm the attachment of polymer to the surface of the nanoparticles. Since the particles were washed thoroughly prior to characterization, the PMAA is expected to be chemisorbed to the NP surface, not merely physisorbed.

After adding the first polymer brush to the surface of the magnetic nanoparticles, a second polymer block was then grown from the first polymer that was attached already to the magnetic nanoparticle. Figure 5 illustrates the block copolymer structure PMAA-PNIPAM- b - Fe_3O_4 after completion of both polymerizations. For these TEM images, surface-modified MNPs were placed on a copper grid and allowed to dry. Once the particles were dry, uranyl acetate stagnant was placed on top of the copper grid and

the modified MNPs. The stagnant was left to dry under ambient conditions. After drying, the sample was put under vacuum in the TEM instrument. As observed in Figure 5, uranyl acetate colored the PNIPAM structure and a second polymer can be observed outside of the first core layer.

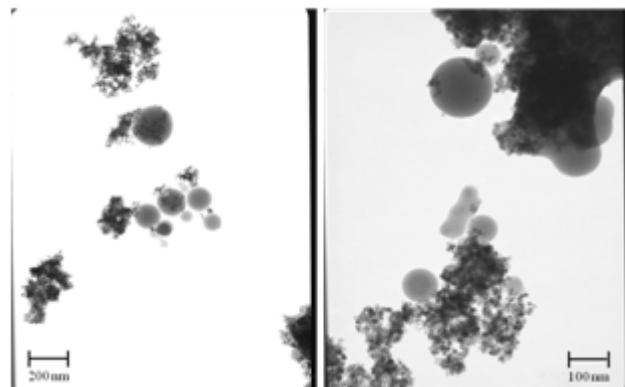


Figure 4. TEM images of PMAA-MNP after polymerization.

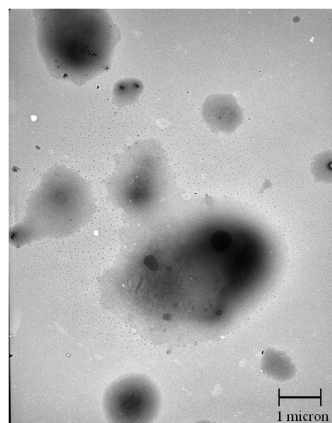


Figure 5. TEM image of PMAA-PNIPAM- b - Fe_3O_4 block copolymer structure with PNIPAM stained.

The thermal response of these SRP surface-modified nanoparticles was also studied using DLS characterization. First, Br-initiator modified magnetic nanoparticles (Br-MNPs) were tested in a temperature range (25°C to 50°C) to observe any change in size due the initiator attachment and to ensure no size change was observed in the base MNP sample. In the temperature range studied, particle hydrodynamic radius remained at about 100 nm (Figure 6) with data collected at 5°C steps. Figure 6 also shows that the size of the PMAA-PNIPAM- b - Fe_3O_4 particles decreased as the temperature was increased. This behavior can be explained as PNIPAM is well known to be a thermoresponsive polymer that undergoes a low-critical solution temperature at $\sim 32^\circ\text{C}$. Above this temperature, PNIPAM brushes tend to become hydrophobic and

insoluble in water resulting in a contracted state as the temperature is increased. Our results show this expected behavior as the temperature was increased. Therefore, thermo-responsiveness of PMAA-PNIPAM-*b*-Fe₃O₄ is indeed an effect of the polymer brush coating the magnetic nanoparticle substrate.

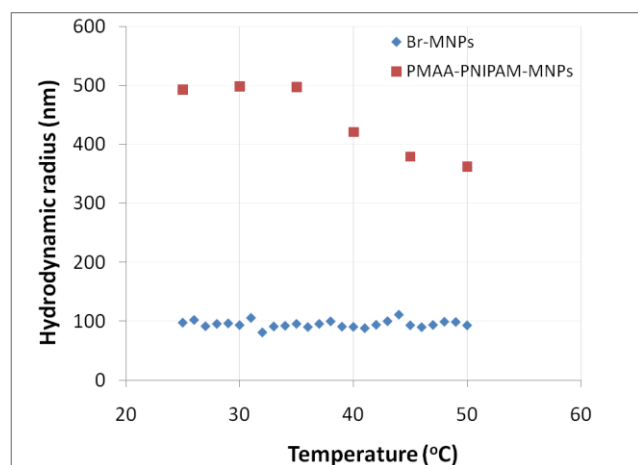


Figure 6. DLS measurements of modified PMAA-PNIPAM-Fe₃O₄ and Br-MNPs.

4- CONCLUSIONS

PMAA and PNIPAM have been grown from the surface of magnetic nanoparticles using surface-initiated ATRP polymerization. DRIFTS confirmed changes in the particle surface chemical functionality as the polymerization proceeded. Moreover, the morphology and size of the particles was obtained by TEM and DLS. Copolymer structures were clearly observed by TEM as two different phases using a stain for PNIPAM. Lastly, the thermo-responsive behavior of these hybrid SRP-MNP systems was demonstrated by temperature-dependent DLS measurements.

5- ACKNOWLEDGMENTS

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