



POLYMER MODIFIED IRON NANOPARTICLES FOR ENVIRONMENTAL REMEDIATION

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Introduction

Nanoparticles are attractive for remediation of various contaminants because of their unique physiochemical properties¹⁻². Various chlorinated aliphatic hydrocarbons³, toxic metals⁴⁻⁵, and explosives⁶⁻⁹ have been remediated using metal nanoparticles such as zero valent iron (Fe⁰) nanoparticles (nZVI).

The effectiveness nZVI for groundwater remediation depends upon the effective delivery of the nanoparticles to the water/contaminant interface without flocculation and severe oxidation. To accomplish effective delivery of nZVI, a delivery system that provides for dispersability and colloidal stability of individual nanoparticles in water is required. In addition, the delivery system should protect the nZVI from severe oxidation by dissolved oxygen and water and provide an affinity for the water/contaminant interface.

Colloidal stability of nZVI has been accomplished using surfactants¹⁰. The hydrophobic “tails” of the surfactants physically absorb on the nZVI surface while the hydrophilic “heads” inhibit flocculation and allow for suspension in the aqueous medium. While surfactants enable colloidal stability in water, the highly reversible nature of surfactant absorption limits its application as a delivery system for ground water decontamination since desorption will be favored when the nanoparticles are transported through surfactant-free ground water. In contrast, high molecular weight, amphiphilic polymers show essentially irreversible absorption and, thus, are more suitable as a delivery system for ground water remediation¹¹⁻¹².

Saleh, et al.¹³ have shown that amphiphilic triblock copolymers with an A-B-C triblock microstructure are effective delivery systems for nZVI. The triblock copolymers were produced using atom transfer radical polymerization (ATRP) in conjunction with a post-polymerization ester-hydrolysis step and a post-polymerization sulfonation step. The results of the research demonstrated enhanced colloidal stability and an increased affinity for a water/organic interface provided by the amphiphilic triblock copolymer. The amphiphilic triblock copolymers synthesized and evaluated by Saleh, et al.¹³ showed promising results with respect to enhanced colloidal stability of nZVI and the creation of a thermodynamic affinity of the nanoparticles for the water/contaminant interface. However, kinetic studies showed a decrease in the rate of contaminant degradation by the polymer-modified nZVI as compared to unmodified nZVI¹⁴. The reduction in contaminant degradation rate was attributed to low permeability of the contaminant through the film absorbed onto the nZVI. In addition to issues associated with contaminant degradation rate, the synthesis method required to produce the triblock copolymer structure is quite sensitive to impurities and oxygen and quite slow. Further, catalyst residues can be difficult to remove. As a result, there exists a need to prepare tailored, multifunctional polymeric materials using a cost-effective, synthetic route that can serve as a highly effective delivery system for nZVI.

Considering the requirements of an effective delivery system for nZVI, functionalized amphiphilic polysiloxanes are an ideal class of polymers for the application. **Figure 1** provides a schematic representation of amphiphilic polysiloxane graft copolymers (APGCs) that could be easily synthesized and evaluated.

The hydrophobicity of the polysiloxane polymer backbone will protect the nZVI from excessive oxidation by creating a barrier to water while also creating an affinity of the coated nanoparticles for the water/contaminant interface as illustrated schematically in **Figure 2**. Since polysiloxanes have a very low glass transition temperature (-120°C) and are highly soluble in most

hydrocarbons, they will readily allow permeation of organic contaminants such as trichloroethene to the Fe⁰ nanoparticle surface providing fast, efficient contaminant remediation. Additionally, the versatility of the hydrosilylation reaction enables tailoring of the polysiloxane polymer backbone chemical structure to enhance contaminant specificity.

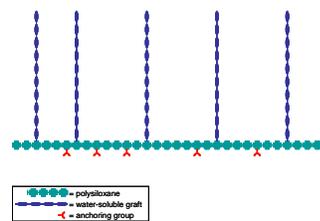


Figure 1. A schematic representation of amphiphilic polysiloxane graft copolymers (APGCs)

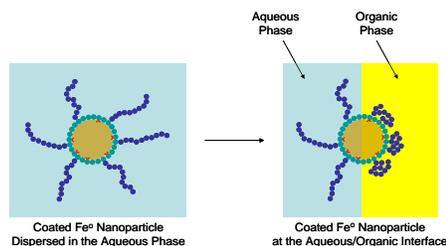


Figure 2. A schematic representation of the polymer coated nanoparticles both in water and at the water/contaminant interface.

In addition to possessing the ideal characteristics for a nZVI delivery system, this class of polymers can be easily synthesized from a wide variety of commercially available starting materials. For example, Gelest® Inc. sells a variety of poly(dimethylsiloxane-co-methylhydrosiloxanes) copolymers with varying methylhydrosiloxane content and molecular weights as well as poly(methylhydrosiloxane) homopolymers of varying molecular weight. With regard to precursors for the generation of hydrophilic polymer grafts, Clariant® sells an array of monovinyl-terminated PEGs of varying molecular weight. Thus, with this class of graft copolymers, extensive structure-property relationships can be developed by varying polysiloxane backbone molecular weight, hydrophilic polymer graft content and molecular weight, and anchoring group content.

Experimental

Synthesis and characterization of APGCs. APGCs were synthesized by hydrosilylation using PtO₂ as a catalyst. The synthesis between commercially available hydride-functional polysiloxanes and commercially available monofunctional vinyl compounds is shown in **Figure 3**.

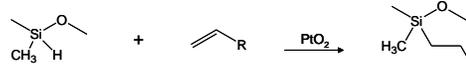


Figure 3. Hydrosilylation between hydride-functional polysiloxanes and monofunctional vinyl compounds.

The following is a representative procedure used to produce a PDMS-g-PEG graft copolymer containing pendant carboxylic acid groups: 20.4 mmol hydride of a poly(methylhydrosiloxane-dimethylsiloxane) copolymer (PDMS), 10.2 mmol of monoallyl-functional polyethyleneglycol (PEG), and 10.2 mmol of *tert*-butylacrylate (tBA) were dissolved in toluene. A catalytic amount of PtO₂ was added, and the mixture was heated at 90°C overnight. Upon completion of the reaction, the reaction mixture was cooled to room temperature, platinum oxide removed by vacuum filtration, and the polymer isolated by vacuum stripping the toluene.

To generate the carboxylic acid anchoring groups, the *tert*-butyl ester groups of the graft copolymer were hydrolyzed as follows: Two grams of PDMS/PEG/tBA (EW 1348.7g) was dissolved in 5mls of dichloromethane. Trifluoroacetic acid (TFA) was added to the solution (0.55mL, 5 molar

equivalent), and the mixture was stirred at room temperature overnight. The carboxylic acid-functional graft copolymer was isolated by vacuum stripping dichloromethane, TFA, and *tert*-butanol. Each synthesis step was monitored using ¹H-NMR, ¹³C-NMR, and FTIR.

Sedimentation rate measurements. An aqueous slurry of Fe⁰ nanoparticles was combined with a 10 g/L APGC polymer solution. The mixture was sonicated for 30 min followed by gentle end-over-end rotation for 72 h to disperse the nanoparticles and allow the polymer to adsorb on the surface of the nanoparticles. The APGC coated nZVI were then filtered and washed multiple times to remove any excess non-adsorbed APGCs.

The colloidal stability of the APGC coated nZVI was then evaluated by measuring sedimentation rates of nanoparticle suspensions using a UV-spectrometer. The optical density at a wavelength of 508 nm was monitored over several hours to determine sedimentation rate.

Results and Discussion

Carboxylic acid-functional APGCs containing polyethylene glycol grafts (PDMS/PEG/AA) were successfully synthesized using the synthetic process shown in **Figure 4**. The proton absorption peaks at δ 0.4-0.5 ppm and δ 1.4-1.6 ppm in the proton NMR spectrum shown in **Figure 5** correspond to methylene protons created as a result of successful hydrosilylation of the vinyl functional precursors to the hydride functional polysiloxane copolymer.

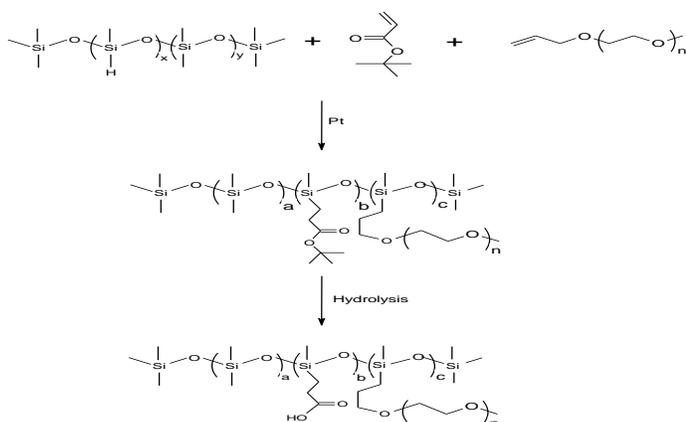


Figure 4. A schematic of the synthetic process used to produce a series of carboxylic acid-functional APGCs containing polyethylene glycol grafts.

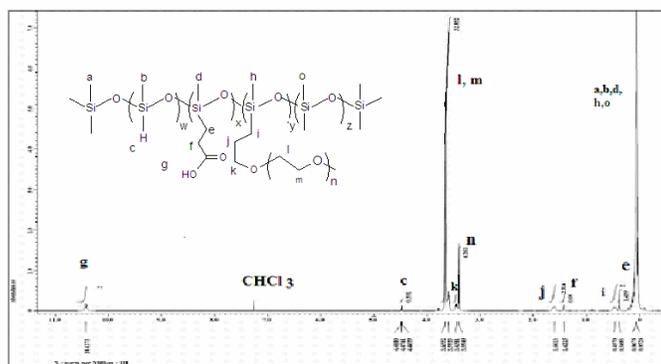


Figure 5. A proton NMR spectrum of a representative carboxylic acid-functional APGC containing polyethylene glycol grafts.

It was hypothesized that the carboxylic acid anchoring groups in conjunction with the polysiloxane polymer backbone would allow for efficient absorption of polymer molecules on to the surface of the nZVI while the water-soluble grafts (PEG) would allow for dispersability and colloidal stability in an aqueous medium.

The polymers produced varied with respect to the relative molar concentration of carboxylic acid groups to PEG grafts. **Figure 6** displays representative data illustrating the effect of APGC composition on colloidal stability of nZVI. Colloidal stability was determined by measuring the

sedimentation rate of aqueous nZVI suspensions. From the figure, it can be seen that modification of the APGC-coated nZVI have decreased sedimentation rate and the magnitude of the decrease was a function of APGC composition. The APGC with the highest concentration of carboxylic acid anchoring groups provided the highest colloidal stability. These results confirm that the proposed approach for enhancing Fe⁰ nanoparticle colloidal stability is valid as is the synthetic process for creating novel carboxylic acid-functionalized APGCs.

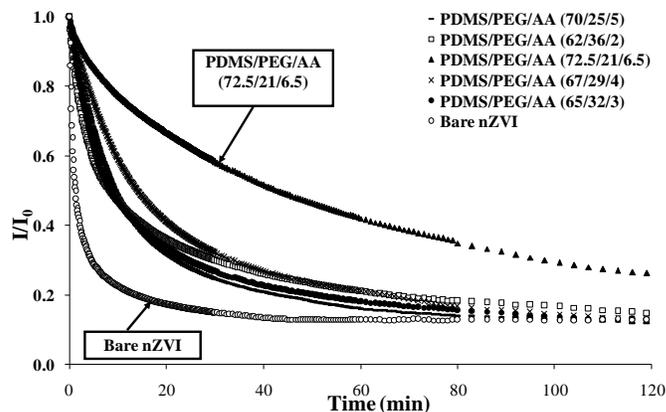


Figure 6. Results of Fe⁰ sedimentation studies. PEG = polyethylene glycol and AA = acrylic acid. Ratio represents weight percent of each component.

Conclusions

A series of APGCs were successfully synthesized using a process that consisted of hydrosilylation of *tert*-butylacrylate and monoallyl-functional PEG to a polysiloxane copolymer containing hydride groups and subsequent hydrolysis of the *tert*-butylester groups. Treatment of nZVI with APGCs was found to enhance nanoparticle colloidal stability in water and the magnitude of the enhancement was a function of APGC chemical composition. The APGC possessing the highest concentration of carboxylic acid anchoring groups provided the highest colloidal stability.

Acknowledgements

Grants from USGS/NDWRRI (ID:2007ND150B) and North Dakota State University Development Foundation are thankfully acknowledged. Help from Eric Jarabek, and David Christianson of the Center for Nanoscale Science and Engineering is highly appreciated.

References

- Zhang, W.-X. *Environ. Sci. Technol. A*, **2005**, 39, 94A.
- Zhang, W.-X. *J. Nanoparticle Res.*, **2003**, 5, 323.
- Gillham, R.W.; O'Hannesin, S.F. *Groundwater*, **1994**, 32, 958.
- Blowes, D.W.; Ptacek, C.J.; Jambor, J.L. *Environ. Sci. Technol.*, **1997**, 31, 3348.
- Fiedor, J.N.; Bostick, W.D.; Jarabek, R.J.; Farrell, J. *Environ. Sci. Technol.*, **1998**, 32, 1466.
- Hundal, L.S.; Singh, J.; Bier, E.L.; Shea, P.J.; Comfort, S.D.; Power, W.L. *Environmental Pollution*, 1997, 97, 55.
- Oh, B.-T.; Just, C.L.; Alvarez, P.J.J. *Environ. Sci. Technol.*, **2001**, 35, 4341.
- Oh, S.-Y.; Chiu, P.C.; Kim, B.J.; Cha, D.K. *Wat. Res.*, **2005**, 39, 5027.
- Singh, J.; Comfort, S.D.; P.J. Shea. *J. Environ. Qual.*, **1998**, 27, 1240.
- Rosen, M.J. *Surfactants and Interfacial Phenomena*, 3rd. ed., **2002**, New York, Wiley Interscience.
- Braem, A.D.; Biggs, S.; Prieve, D.C.; Tilton, R.D. *Langmuir*, **2003**, 19, 2736.
- Velegol, S.B.; R.D. Tilton. *Langmuir*, **2001**, 17, 219.
- Saleh, N.; Phenrat, T.; Sirk, K.; Dufour, B.; Ok, J.; Sarbu, T.; Matyjaszewski, K.; Tilton, R.D.; Lowry, G.V. *Nano Lett.*, 2005, 5, 2489.
- Saleh, N.; Sirk, K.; Liu, Y.; Phenrat, T.; Dufour, B.; Matyjaszewski, K.; Tilton, R.D.; Lowry, G. V. *Environ. Eng. Sci.*, **2007**, 24, 45.