

PREPARATION OF AMPHIPHILIC BLOCK COPOLYMERS FOR THE STABILIZATION AND DELIVERY OF IRON NANOPARTICLES FOR REMEDIATION OF DNAPLS

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Introduction

Nanotechnology is one of the most rapidly developing fields in science. Nanoparticles are especially representative of a spectrum of novel materials with unique properties for chemical, electronic, magnetic, environmental and other industrial applications. These materials have utility not only in conventional applications such as enhancing mechanical, thermal, dimensional and gas-barrier properties but also in new ones including drug delivery, components for rechargeable energy devices and removal of environmental contaminants. The world market for nanoparticles is rising at an average annual rate of 12.8 % and is expected to reach \$900 million in 2005¹.

One of the most promising applications for novel nanoparticles is degradation of hazardous materials in the environment². DNAPLs (dense non aqueous phase liquids) are chemicals that have a higher density than water and exist as an immiscible phase when released to the environment. They include halogenated organic solvents such as trichloroethene (TCE) and 1,1,1-trichloroethane (TCA), substituted aromatics, phthalates, PCB mixtures and some pesticides. DNAPLs tend to migrate to considerable depths in an aquifer until reaching a low permeability zone that will retard further downward movement. Conventional purification methods, such as excavation, are rarely applicable. According to previous investigations, drinking water for 35~50 million people in the United States is potentially affected and 47 % of urban wells contain at least one kind of VOC³.

One previously devised method to remove DNAPLs from the environment involves encapsulating pollutants via reactions using nanoparticles consisting of an inorganic core and polymeric protective layers^{4,5}. Once nanoparticles are introduced into the contaminated site, they can react with the specific target materials and make them non-hazardous. Since the surface area of nanoparticles is extraordinarily high, their effectiveness will be proportionally high.

Iron is known as one of the most effective reducing dechlorinating agents. Therefore, removing halogen moieties in the groundwater using iron nanoparticles is clearly a potential solution to this environmental problem. But in order to be able to deliver iron nanoparticles to contaminated water supplies, it is essential to cover the iron particles with protective polymer layers because iron is liable to be corroded and the iron particles should be kept dry until they react with chlorinated contaminants. To improve the stability of iron nanoparticles in water media in contact with soil, the particles were protected with a functional triblock copolymer. Functional ABC block copolymers [poly(methacrylic acid)-poly(methyl methacrylate)-poly(styrene sulfonate)] and [poly(methacrylic acid)-poly(butyl methacrylate)-poly(styrene sulfonate)] amphiphilic triblock copolymers were synthesized by ATRP⁶⁻¹⁰ and designed to allow the reduction of chlorinated solvents by the functionalized iron nanoparticles at the water/DNAPL interface. The role of each block is illustrated in **Fig. 1**. Poly(methacrylic acid) (PMAA) is the anchoring block, directly interacting with the iron nanoparticles. Poly(methyl methacrylate) (PMMA) or poly(butyl methacrylate) (PBMA) is used as a hydrophobic block to improve the solubility of the nanoparticles in DNAPL and to protect the iron nanoparticle from oxidation during transportation through the soil. The poly(styrene sulfonate) (PStS) block was envisioned to be the charged hydrophilic segment that allows solubilization of the iron nanoparticles in water and decreases particles aggregation via electrostatic repulsion.

Experimental

Synthesis of poly(tert-BMA). 204 mg of tosyl chloride and 0.11 ml of PMDETA were dissolved in a mixture of 1 ml of deoxygenated acetone, 1 ml of deoxygenated toluene and 13 ml of deoxygenated t-butyl methacrylate. 53.1 mg of CuCl was then added under nitrogen flow, and the reaction was allowed to proceed for 6 h at 60 °C. The reaction mixture was diluted with THF and passed through a column packed with neutral alumina. The solvent

and monomer was removed by evaporation and the polymer was dried to constant weight. The polymer was analyzed by GPC ($M_n = 6,820$, polydispersity = 1.26). Other reactions under similar conditions provided poly(tert-BMA) having various degrees of polymerization ($M_n = 6,000$, 2,170, 6,100 and PDI = 1.27, 1.16, 1.29; respectively).

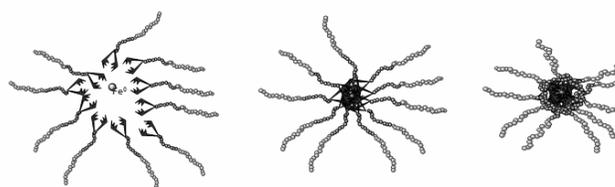
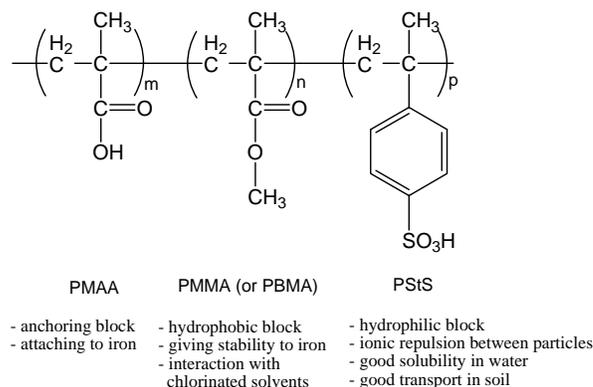


Fig. 1. Structure of a triblock copolymer and diagram describing the interaction with, and encapsulation of, the iron particle

Synthesis of poly((tert-BMA)-b-(MMA)). 1 g of poly(t-butyl methacrylate) ($M_n = 6,820$), 1.6 mg of CuBr₂, 31.3 μ l of PMDETA were dissolved in 0.77 ml of deoxygenated methyl methacrylate and 2 ml of deoxygenated toluene. 20.8 mg of CuBr was then added under nitrogen flow. The reaction was carried out at 30 °C for 40 minutes. The reaction mixture was diluted with THF and passed through a neutral alumina-packed column to remove the catalyst complex and the solvent was evaporated and the isolated polymer was dried under vacuum. The polymer was analyzed by GPC (M_n , poly(MMA) = 1,700, polydispersity = 1.23). Similarly, three other polymers were prepared; poly(tert-BMA)₄₂-(MMA)₂₆ (M_n , poly(MMA) = 2,600, PDI = 1.27), poly(tert-BMA)₁₅-(BMA)₆₄ (M_n , poly(BMA) = 9,030, PDI = 1.25) and poly(tert-BMA)₄₃-(MMA)₂₆ (M_n , poly(MMA) = 2,600, PDI = 1.32).

Synthesis of poly((tert-BMA)-b-(MMA)-b-(St)). 1 g of poly((t-butyl methacrylate)-block-(methyl methacrylate)) and 46 μ l of PMDETA were dissolved in 10.2 ml of deoxygenated styrene and 1 ml of deoxygenated toluene. 31.6 mg of CuBr was then added under nitrogen flow. The reaction was carried out at 80 °C for 3 days. The reaction mixture was diluted with THF and then passed through neutral alumina. The solvent was removed by evaporation and the polymer was dried under vacuum. The polymer was analyzed by GPC indicating the preparation of an ABC block copolymer with (tert-BMA)₄₈(MMA)₁₇(St)₆₅₀ (M_n , poly(St) = 67,730) and polydispersity = 1.62. Three similar ABC block copolymers were prepared; poly(tert-BMA)₄₂(MMA)₂₆(St)₄₆₆ (M_n , poly(St) = 48,600, PDI = 1.14), poly(tert-BMA)₁₅(BMA)₆₄(St)₂₁₃ (M_n , poly(St) = 22,170, PDI = 1.52) and poly(tert-BMA)₄₃(MMA)₂₆(St)₅₉₇ (M_n , poly(St) = 62,200, PDI = 1.12).

Preparation of acetyl sulfate. 40 ml of chloroform and 28 ml of acetic anhydride were mixed and cooled to 0 °C. 10.4 ml of sulfuric acid were then added slowly. The reaction was allowed to stir for 10 minutes.

Preparation of poly((MAA)-b-(MMA)-b-(PStS)). 5 g of poly((tert-BMA)-b-(MMA)-b-(St)) were dissolved in 200 ml of CHCl₃. 78 ml of acetyl sulfate were then added and the reaction mixture was stirred overnight at 60 °C. 50 ml of methanol was added to terminate the reaction and the appropriate amount of NaHCO₃ was introduced until the pH was neutral. The polymer was purified by dialysis versus distilled water and recovered using a rotary evaporator.

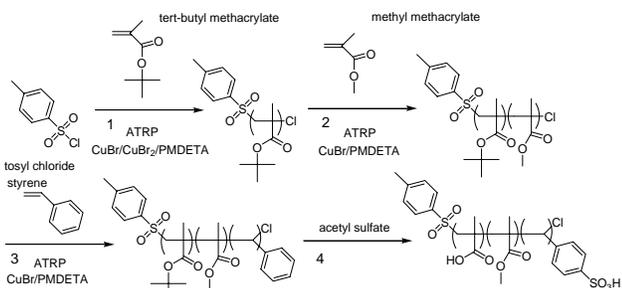
Preparation of iron/polymer nanoparticles. The prepared ABC block copolymer was dissolved in a sufficient amount of water and iron nanoparticles. The iron nanoparticles were manufactured by Toda Kogyo as a

form of aqueous slurry. Average particle size of the particles was 70 nm and specific surface area was 30 m²/g. The slurry was added slowly with vigorous mechanical stirring. During the attachment step the average size of the formed nanoparticles were measured using dynamic light scattering (DLS) to compare with original diameters.

Analysis. Conversion of monomers was measured using a Shimadzu GC14-A gas chromatograph with a FID detector equipped with a J&W scientific 30m DB WAX Megabore column. Molecular weights were measured on a GPC system consisting of a Waters 510 HPLC pump, three Waters Ultrastaygel columns (10⁵ and 10³ Å) and a Waters DRI detector, with a THF flow rate of 1.0 ml/min. Polystyrene was used as standard. The efficiency of the sulfonation was determined by elemental analysis (Midwest Microlab Inc.). Tapping mode AFM measurement was performed using a Multimode Nanoscope III system (Digital Instruments, Santa Barbara, CA). The measurements were carried out under ambient conditions using commercial Si cantilevers with 40N/m of nominal spring constant and 300 kHz of resonance frequency.

Results and Discussion

The pathway and individual steps for the synthesis of the poly((MAA)₄₆-(MMA)₁₇-(PSSt)₆₅₀) triblock copolymer are shown in **Scheme 1**. Most experiments were performed under standard ATRP conditions.



Scheme 1. Schematic sequence of the preparation of poly((MAA)₄₆-(MMA)₁₇-(PSSt)₆₅₀) triblock copolymer by ATRP.

In the first step, a mixture of CuBr and CuBr₂ was adopted as the catalyst in order to provide controlled polymerization of tert-BMA. The synthesized poly(tert-BMA)-Br was used as a macroinitiator in the second step and neither an unstable nor an abnormal situation was observed. In case of the third step, chain extending the AB block copolymer with polystyrene took a relatively long time. Sulfonation and hydrolysis reactions were simultaneously undertaken in a fourth step using acetyl sulfate. Finally the iron nanoparticles were attached or encapsulated with the interactive block copolymer.

The triblock copolymer showed progressive change in elution volumes from GPC measurements (**Fig. 2**). In the last step for polymerization of styrene there was a huge decrease of elution volume, i.e. an enormous rising in molecular weight. In contrast, change in elution volume occurred in second polymerization step for poly(MMA) was not great because of relatively small growth in molecular weight.

As noted, the nanoparticles were prepared using the 'grafting onto' method. Polymers with functional groups having high affinity to metals were synthesized in advance and then assembled through combination between organic and inorganic parts.

AFM image of poly(tert-BMA)₁₅-(BMA)₆₄ attached to iron particles shows particles of different dimensions (**Fig. 3**). The enlarged size of particles after combining with triblock copolymers was observed from AFM image. The average size of small particles was 70–120 nm while that of sparse big ones was 140–200 nm. The dark area surrounding bright spheres might indicate relatively softer copolymer segments and the image shows that the particles are distributed evenly.

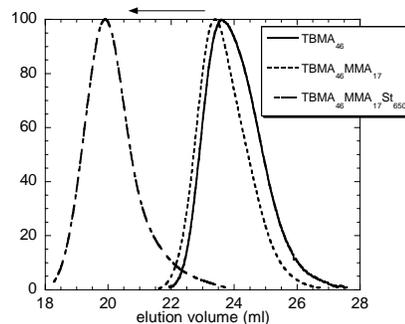


Fig. 2. Progress in elution volumes for each block copolymer addition

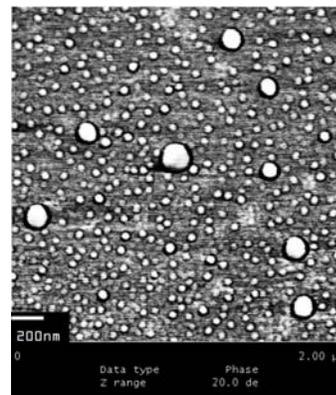


Fig. 3. AFM image of poly(tert-BMA)₁₅-(BMA)₆₄ on mica surface

Conclusions

Four different ABC amphiphilic triblock copolymers including poly((MAA)₄₆-(MMA)₁₇-(StS)₆₅₀), poly((MAA)₄₂-(MMA)₂₆-(StS)₄₆₆), poly((MAA)₁₅-(BMA)₆₄-(StS)₂₁₃) and poly((MAA)₄₃-(BMA)₂₆-(StS)₅₉₇) were prepared via ATRP. These copolymers consist of anchoring hydrophobic and hydrophilic blocks suitable for attachment, and functional encapsulation of iron nanoparticles. The ABC block copolymers were designed to provide a responsive protective encapsulation of iron particles that can inherently deliver the nanoparticles to remote sites. Where it perform reductive dechlorination of DNAPLs in underground aquifers to diminish the hazard of these materials to users of well water. Molecular weights and polydispersities for synthesized polymers were checked with GPC. DLS was used for measuring the sizes of the nanoparticles and AFM image showed distribution of hybrid nanoparticles. Practical tests in the environment are in progress.

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