Synthesis of Symmetrical and Anisotropic Core-Shell Magnetic Composite Particles and Progress in Controllable Migration of Magnetic Core in Composite Particles

by

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Synthesis of Symmetrical and Anisotropic Core-Shell Magnetic Composite Particles and Progress in Controllable Migration of Magnetic Core in Composite Particles

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In this work, a two-step method is developed to synthesize both symmetrical and anisotropic magnetic composite particles. First of all, magnetic-polymer seed particles are synthesized from iron oxide, styrene and methyl methacrylate by emulsion polymerization. Then magnetic composite particles are produced from synthesized seeds and styrene by seeded dispersion polymerization. The anisotropy of the magnetic composite particles could be achieved by the addition of a small amount of tetrahydrofuran (THF) into the alcohol-based polymerization medium. Moreover, two solvent compositions were found to be effective to swell the synthesized magnetic composite particles and enable the migration of magnetic cores inside the polymer spheres. The structure of magnetic core or the morphology and monodispersity of the composite particles were not destroyed during this swelling process. One mixture solvent contains THF, ethylene glycol (ETG), ethanol and water, with particles protected by a suitable amount of poly vinyl pyrrolidone-40 (PVP-40), and the other is a mixture of ETG and THF.

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PREFACE

I would like to express my gratitude to my research advisor Prof. Sanford A. Asher, who guided me through the course of my study and stimulated my thoughts. I also thank my thesis committee members Prof. David Waldeck and Prof. Nathaniel Rosi for their helpful suggestions during the manuscript preparation as well as discussions that helped me to finish my projects. Special thanks to my senior coworkers Dr. Dan Qu, Dr. Justin Bohn, Dr. Sasha Tikhonov, Dr. Michelle Muscatello and Dr. Sergei Bykov for their help in introducing me to the theoretical and experimental aspects of colloid science. I also thank my graduate student peers: Jia Luo, Luling Wang, Zhenmin Hong, Lu Ma, Kan Xiong and Bhavya Sharma for their participation in my research projects and creating productive environment in the group. I also appreciate Dr. Thomas Harper, Mr. Albert Stewart and Mr. Cole van Ormer for their help in the electron microscope field.

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1.0 INTRODUCTION TO POLYMER AND POLYMERIZATION

A polymer is a long molecule which contains a chain of atoms held together by covalent bonds. Polymerization is a process by which monomer molecules react together chemically to form either linear chains or a three-dimensional network of polymer chains.[1]

Polymerization could be generally divided into two large categories: chain-growth polymerization (mainly addition reaction) and step-growth polymerization (mainly condensation polymerization) by the way how the polymer chain grows. Chain-growth polymer is produced by continuously adding monomer molecule to propagating center, and step-growth polymer is formed by the stepwise reaction between functional groups of monomers. Chain-growth polymerization includes mainly anionic polymerization, cationic polymerization and free radical polymerization. In this work, we mainly use free radical polymerization as our experiment method.

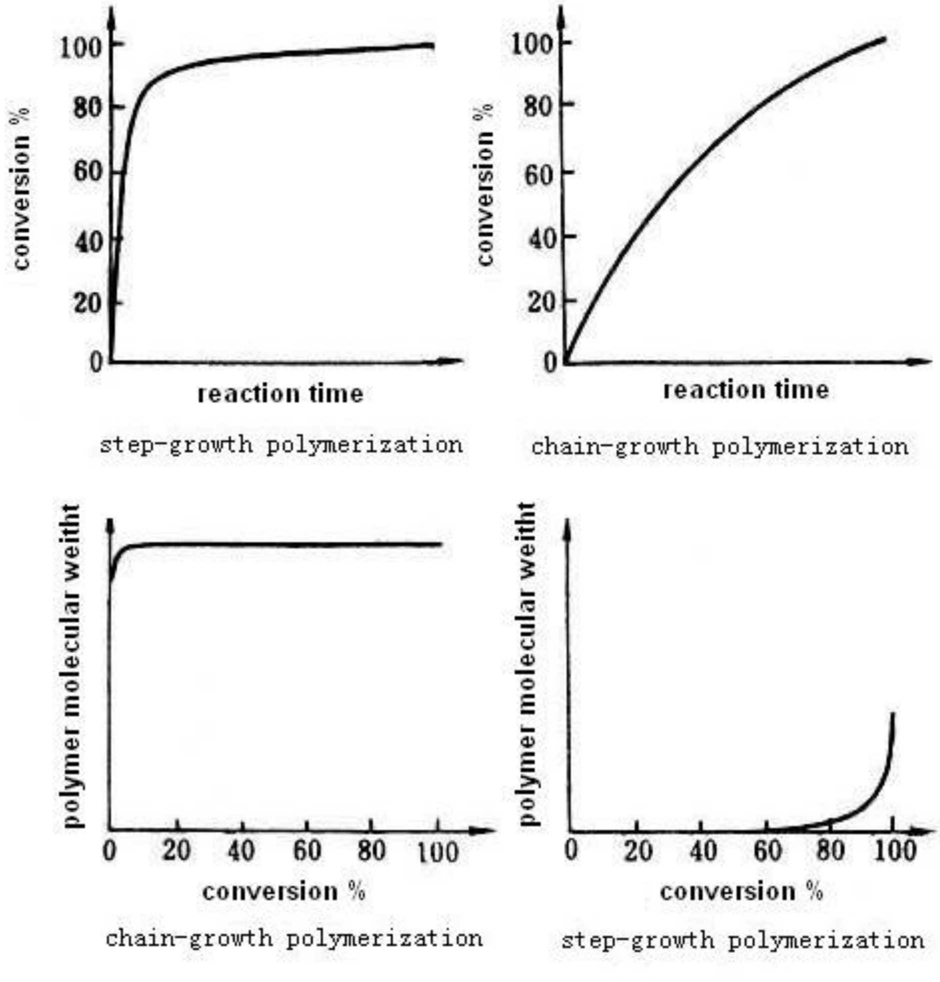


Figure 1. Difference between chain-growth polymerization and step-growth polymerization[2]

1.1 OVERVIEW OF RADICAL POLYMERIZATION

Radical polymerization is a type of polymerization in which the reactive center of a polymer chain consists of a radical. This reaction process can be divided into three stages: initiation, chain propagation and chain termination.

Initiation produces free radicals necessary for propagation. The radicals can be created from radical initiators, such as organic peroxide molecules, or some other molecules containing an OO single bond or NN double bond (azo-compound). The bond between the two oxygen atoms breaks homogeneously or the two nitrogen atoms form nitrogen gas and escape to produce two free radicals. Propagation is the rapid reaction of radical or radicalized monomer molecule with another monomer molecule, with the lone electron of the radical attacking the carbon-carbon double bond in the monomer. This reaction will generate a new radical with the new reacted monomer linked at the end of this chain. Termination occurs when a radical reacts in a way that prevents further propagation. The most common method of termination is the coupling of two radical species, forming a single molecule. Another less common method is chain disproportionation between two chain radical, generating one saturated chain and one unsaturated by exchanging one proton.

Ammonium Persulfate (APS) and 2,2'-Azobisisopropionitrile (AIBN) are two common used initiator in heat-initiation free radical polymerization. APS is a water-soluble initiator and can break into two radicals at as the reaction shown in **Figure 2**. In this work, APS is used as the initiator in the oil-in-water emulsion polymerization to synthesize magnetic seed particles. AIBN is another common initiator, but it is soluble in organic solvents. It will generate 2 tertiary carbon radicals and one nitrogen molecule after dissociation as the reaction shown in **Figure 3**. In this work, it is used as the initiator in the seeded dispersion polymerization in an alcohol-based medium to synthesize symmetrical and anisotropic core-shell magnetic composite particles.

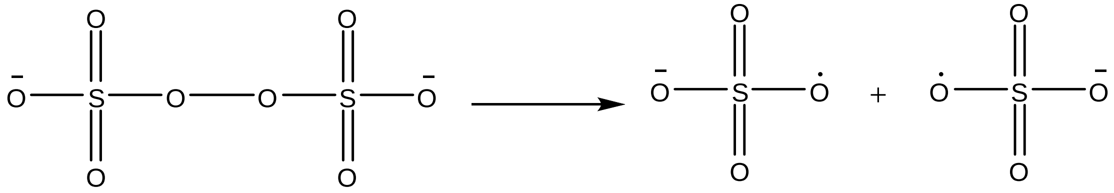


Figure 2. Dissociation reaction of APS

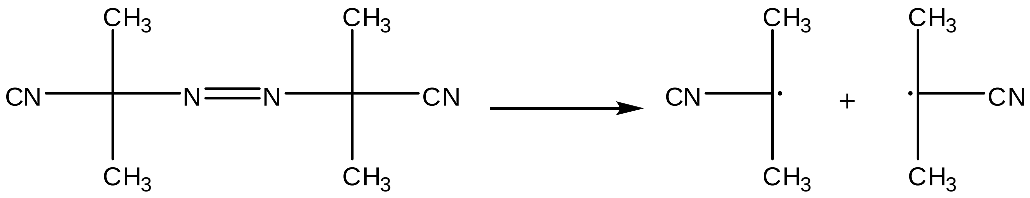


Figure 3. Dissociation reaction of AIBN

1.2 EMULSION POLYMERIZATION

Emulsion polymerization is a type of heterogeneous radical polymerization that is often used to synthesize monodisperse polymer nanoparticles. In a typical emulsion polymerization, the reaction starts with an emulsion of monomer, surfactant and reaction medium. The monomer is insoluble (or its solubility is very small) in the polymerization medium, but is emulsified with the help of the surfactant and exists mainly in the form of droplets. The initiator is soluble in the medium but not in the monomer.[3]

After the temperature is raised above the initiation temperature, reaction first starts only in the medium, forming oligomers which are either surrounded by dissolved monomer and surfactant molecules or absorbed into already existing surfactant micelles. The formed oligoradicals produce stabilized nuclei, and subsequently absorb other oligoradicals and monomer from the medium or the monomer droplet, becoming the main location of the polymerization. This reaction will continue until all monomer is consumed, leaving monodispersed latex particles dispersed in water in the form of colloid.[4]

The emulsion polymerization used in this work is oil-in-water emulsion system, which means that the monomer (styrene and methyl methacrylate) is hydrophobic, and the initiator (ammonium persulfate) is in inorganic medium phase (water). Brij-35 (Aldrich), which is a non-ionic surfactant with the structure as **Figure 4**, is used as the emulsifier in the synthesis of magnetic seed particles.

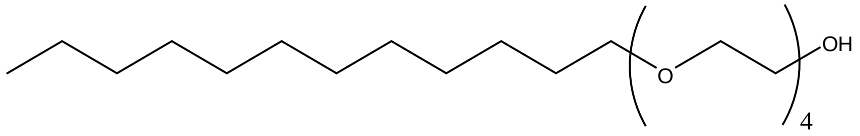


Figure 4. Structure of Brij-35

In our synthesis of magnetic seed particles, we added in oleic acid-modified iron oxide suspension into the system to introduce the magnetic component.[5, 6] Oleic acid could be adsorbed on the surface of iron oxide by the carboxylic group in a basic environment, and the carbon-carbon double bond could be copolymerized with methyl methacrylate and styrene, forming iron oxide-polymer composite particles.

1.3 DISPERSION POLYMERIZATION

Dispersion polymerization is another type of heterogeneous free radical polymerization, and it can be differentiated from emulsion polymerization by the initial state of the reaction mixture and the mechanism of the particle formation.[7]

In dispersion polymerization the monomer and the initiator are both soluble in the polymerization medium, but the medium is a poor solvent for the produced polymer. Consequently, the reaction mixture is homogeneous at the beginning, and the polymerization is initiated in homogeneous solution. Related to the solubility of the resulting macroradicals and macromoleclues in the synthesis medium, phase separation occurs at an early stage and leads to nucleation and the formation of primary particles. However, primary particles formed in dispersion polymerization are swollen by the polymerization medium and/or the monomer. As a result, polymerization proceeds largely in the individual particles, and finally forms spherical particles.

Particle dispersions produced by dispersion polymerization in the absence of any stabilizer are not sufficiently stable and may coagulate during their formation. Addition of a small amount of a suitable stabilizer to the polymerization mixture produces stable particle dispersions. Good stabilizers for dispersion polymerization are polymer and oligomer compounds with low solubility in the polymerization medium and moderate affinity for the polymer particles. [7] In our system where hydrophobic polystyrene is synthesized in alcohol-based solvents, Poly (vinyl pyrrolidone)-40 (PVP-40, molecular weight 40k, Sigma-Aldrich) as **Figure 5** is used to stabilize the particles.

Figure 5. Structure of poly (vinyl pyrrolidone)

1.4 SEEDED POLYMERIZATION

In emulsion and dispersion polymerization, the synthesized polymers first form nuclei, and then these nuclei grow by absorbing and polymerize more monomer to form the final polymer particles. In these systems, it is also possible to add in some seed particles to work as the primary particles, and even larger particles could be harvested from these seed particles.[8] In common seeded polymerization, one of the most important issues the selection of a suitable polymerization condition, under which no secondary nuclei will form; otherwise, the resulting particles suspension will include particles of two or more sizes.

In this work, the symmetrical and anisotropic core-shell magnetic particles are synthesized by a seeded dispersion polymerization. This two-step method makes it easier to obtain relative large particles. Additionally, it also helps to better control the amount of iron oxide contained in each composite particles and therefore decrease the polydispersity of magnetic cores, since the amount of iron oxide is determined by the size of the seed particles which are used in the dispersion polymerization.

1.5 THETA STATE AND POLYMER SWELLING

The theta state is defined as that state of a polymer solution at which the excess chemical potential, and correspondingly, the excess of Gibbs energy of dilution is zero. For a given polymer-solvent system, this state is obtained at a certain characteristic temperature, the theta temperature Θ, and the solvent at this temperature is called a theta solvent.[9]

The exact definition of the theta state is given by chemical thermodynamics. The chemical potential of a solvent l, $\Delta\mu_1$, can be split into an ideal term and an excess term:

$$\Delta\mu_1 = \Delta\mu_1^{\mathrm{id}} + \Delta\mu_1^{\mathrm{exc}} \qquad (1)$$

Where the excess chemical potential at the thermodynamic temperature T is given by the enthalpy of dilution, ΔH_1, and the excess of entropy of dilution, $\Delta S_1^{\mathrm{exc}}$

$$\Delta\mu_1^{\mathrm{exc}} = \Delta H_1 - T\Delta S_1^{\mathrm{exc}} \qquad (2)$$

The theta state (zero excess chemical potential $\Delta\mu_1{}^{\text{exc}}$) hence means that the terms at the right side of Equation 2 compensate each other at the theta temperature Θ.

Generally speaking, if the temperature T is higher than the theta temperature Θ for a specific polymer-solvent system of a concentration, the excess chemical potential will be negative, meaning that the diluting process by more solvent is thermodynamically favorable and that the polymer can be better dissolved. If the actual temperature is lower than Θ, the polymer will precipitate in such a solvent.

Therefore, the theta temperature may also be phenomenologically defined as the critical miscibility temperature. At the theta state, polymer-solvent interactions are just balanced by polymer-polymer and solvent-solvent interactions, a critical situation just between dissolution and precipitation. While at a temperature higher than the theta temperature, the same solvent as in the theta state becomes a good solvent, and the polymer-solvent interactions are larger than the polymer-polymer and solvent-solvent interactions. The polymer chain expands in order to minimize polymer-polymer contacts, implicating that the polymer phase is dissolved in this solvent.

Dissolution results from interactions between polymer-solvent, polymer-polymer and solvent-solvent, we can change the property of a solvent gradually by changing the composition of a mixed solvent: one is a good solvent for the polymer and the other is a poor solvent. If we carefully control the composition and temperature to just a state near the theta state, it is possible to swell the polymer particles while not completely dissolve them.

There are several solvents that have a theta temperature for styrene near or lower than room temperature, including toluene, ethyl acetate and THF etc.[9] Here THF is a better choice than the other two, since THF is water-soluble; therefore, its concentration can be easily controlled. It is also convenient to deswell particles by just diluting the THF solution to decrease its concentration. Toluene and ethyl acetate are not soluble in water, and hence a longer time is necessary for these two solvents to diffuse into the particles dispersed in water, and it is also necessary to apply a high temperature to remove these swelling solvents when the swelling process is ready.[10]

2.0 INTRODUCTION TO MAGNETISM

In physics, the term magnetism is used to describe the magnetic property of a material, and it is defined by the respondence of a material to an applied magnetic field on the microscopic level. Some are attracted to a magnetic field (paramagnetism); some are repulsed by a magnetic field (diamagnetism); others have a much more complex relationship with an applied magnetic field (including ferromagnetism, ferrimagnetism and antiferromagnetism, etc).

Magnetism mainly arises from two sources: electric currents, or more generally moving electric charges, such as the electrons' orbital angular motion around the nucleus, and nonzero "intrinsic" magnetic moments, such as the electrons' intrinsic magnetic moment. While the magnetic behavior of a material depends on its structure listed above, it is also related to the temperature, since at high temperatures, random thermal motion makes it more difficult for the electrons to maintain alignment.

2.1 FERROMAGNETISM, FERRIMAGNETISM AND ANTIFERROMAGNETISM

Ferromagnetism, Ferrimagnetism and Antiferromagnetism are all properties of magnetic materials, and the difference between them results from the arrangements of the magnetic atoms or ions.[11] (**Figure 6**)

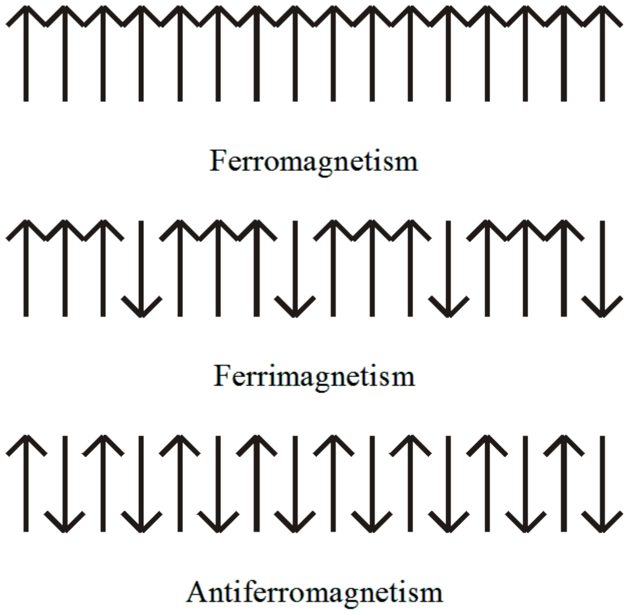


Figure 6. Illustration of ferromagnetism, ferrimagnetism and antiferromagnetism

Ferromagnetism means that in a magnetic domain, all of the magnetic atoms or ions add a positive contribution to the net magnetization. If some of the magnetic ions subtract from the net magnetization, this property is called ferrimagnetism. If the moments of the aligned and anti-aligned ions balance completely so as to have zero net magnetization, the materials is said to have antiferromagnetism. All of these alignment effects only occur at temperatures below a certain critical temperature, called the Curie temperature (for ferromagnets and ferrimagnets) or the Neel temperature (for antiferromagnets).

Magnetic domain is a concept to describe a region within a magnetic material which has uniform magnetization. The direction of magnetization inside a magnetic domain is the same, and neighboring domains have different magnetization directions. The regions separating magnetic domains are called domain walls where the magnetization directions change from one direction to the other continuously. Magnetic domain structure is responsible for the magnetic behavior of ferromagnetic and ferrimagnetic materials. When a ferromagnet or a ferrimagnet is magnetized, the directions of different magnetic domains are aligned identical, and larger domain will form from several smaller ones.

2.2 SUPERPARAMAGNETISM

Superparamagnetism is a form of magnetism, which appears in small ferromagnetic or ferrimagnetics particle, when the particle size is smaller than the size of its magnetic domain. In superparamagnets, the magnetic moments of different atoms or irons in one particle are exactly ordered (ferromagnetic) or partially ordered (ferrimagnetic), but the direction of the magnetization of each particle can randomly change due to the influence of thermal motion. In this state, an external magnetic field is able to magnetize the small particles, similarly to a paramagnet. However, their magnetic susceptibility is much larger than that of paramagnets. When an external magnetic field is applied to superparamagnetic nanoparticles, they tend to align along the magnetic field, leading to a net magnetization. And when the external field is removed, the magnetization will disappear gradually, the rate related to both the size of materials and the temperature.

Fe_3O_4 is generally a ferrimagnetic material, but it will express superparamagnetism when its size is reduced to smaller than 35 nm at normal temperature.[12] In our experiments, the size of Fe_3O_4 is smaller than 15 nm; therefore, they are superparamagnetic materials in our experiments and there is no macroscopic magnetization influencing the polymerization reaction.

3.0 CHAPTER 3: SYNTHESIS OF CORE-SHELL COMPOSITE MAGNETIC PARTICLES AND CONTROLLABLE MIGRATION OF MAGNETIC CORE

3.1 MOTIVATION

Anisotropic particles have been a research subject of significant interest over several years. Particle anisotropy can be in the form of shape, surface property or composite internal distribution. In all of these cases, the anisotropic particles differ from isotropic particles, potentially useful in engineering biomaterials and colloid structures. Lots of approaches have been developed to synthesize such anisotropic particles[13], including micro-contact printing[14], suspension polymerization[15], miniemulsion polymerization[16, 17], soap-free emulsion polymerization[18, 19], precipitation polymerization[20], phase-separation seed polymerization[21, 22], decomposition reducing method[23], hydrothermal approach[24], and metal vapor deposition[25], etc.

On the other hand, magnetic nanomaterials also receive special attention, since the ferromagnetic, ferrimagnetic or superparamagnetic properties of these materials enable the control of these materials by a magnetic way besides other conventional ways. Consequently, they have some uncommon application, such as for drug delivery[26], magnetic biosensors[27], magnetothermo therapy[28], magnetically controllable photonic crystals[29-32] and nanoelectromechanical systems[33], etc.

Therefore, materials with both anisotropy and magnetism will have even broader potential for applications, since they will have the assets from both of these two kinds of materials. In this work we developed a method to synthesize symmetric and anisotropic core-shell magnetic composite particles and also an appropriate to move the magnetic core from one position to another inside the particle. In the future work, we will explorer more about the controllable migration of the magnetic core and use these particles as bricks to fabricate particles with multiple reactive sites and to build photonic crystals.

3.2 EXPERIMENTAL METHODS

3.2.1 Materials:

$FeCl_3$ $6H_2O$ (J. T. Baker), $FeCl_2$ $4H_2O$ (Sigma-Aldrich), NH_3 H_2O (J. T. Baker), Tetramethylammonium Hydroxide (TMAOH, Sigma-Aldrich), Hydrochloric Acid (J. T. Baker), Oleic Acid (Aldrich), Styrene (Aldrich), Methyl Methacrylate (MMA, Polysciences), Sodium p-Styrenesulfonate (NaSS, Aldrich), Ammonium Persulfate (APS, Aldrich), 2,2’-Azobisisopropionitrile (AIBN, Aldrich), Polyvinylpyrrolidone-40 (PVP-40, molecular weight 40,000, Sigma-Aldrich), Brij-35 (Molecular weight 362.5, Aldrich), Ethanol (EtOH, Pharmco-AAPER), Ethylene Glycol (ETG, J. T. Baker), Tetrahydrofuran (THF, EMD Chemicals) were all used as received.

3.2.2 Equipments:

Transmission Electron Microscope (TEM, JEOL 200CX and Philips Mogagni 268), Carboncoated Copper Grid (Ted Pella, Inc.), Dynamic Light Scattering Photometer (DLS, Brookhaven Z-90 plus)

3.2.3 Synthesis of iron oxide magnetic nanoparticles:

Nanoscale iron oxide was prepared by the coprecipitation of ferric and ferrous ions in ammonium hydroxide solution.[32, 34-37] A 5.4 g portion of $FeCl_3$ $6H_2O$ and 4.0 g $FeCl_2$ $4H_2O$ were dissolved in 25 ml water, and this resulting solution was poured into 250 ml of 1.0 M NH_3 H_2O solution while mechanically stirred at a rate of 350 rpm. After 10 minutes' stirring, the resulting black precipitate was collected with a magnet, and the supernatant was discarded. A 250 ml portion of 0.4 M TMAOH solution was added to the precipitate, and the mixture was sonicated for 1 hour. After this sonication, 1.25 g oleic acid was added into the particle suspension to modify the magnetic colloid surface properties.

3.2.4 Synthesis of magnetic composite seed particles:

Magnetic composite seed particles were synthesized by emulsion polymerization of styrene and MMA in the presence of the above iron oxide magnetic nanoparticles by modifying Xu et al's methods.[32] These particles were synthesized by using a jacketed cylindrical reaction vessel containing a reflux condenser, a Teflon mechanical stirrer, an additional funnel and a nitrogen inlet. The temperature was controlled through the jacket with the use of a circulating temperature bath. A nitrogen blanket and a stirring rate of 350 rpm were maintained throughout the polymerization.

In a typical synthesis, 10 ml of the above iron oxide suspension was diluted by 10 ml water and further modified by another 0.13 g oleic acid. Then 2.8 g 0.1g/L Brij-35 nonionic surfactant solution was added into the iron oxide suspension, and 5 ml 0.02 g/ml NaSS solution and 72 ml water were added. This suspension was well stirred and the pH of this suspension was adjusted to 12.3 by hydrochloric acid.

This modified iron oxide suspension was transferred into the jacket reactor and purged with N_2 for 30 minutes at a stir rate of 60 rpm. Simultaneously, 10 ml styrene and 1.5 ml MMA were added into the addition funnel and also purged N_2 for 30 minutes. After 30 minutes, the circulating bash was turned on to increase the reaction temperature to 50 °C, and the stir rate was raised to 350 rpm. 5 minutes after the temperature reached 50 °C, the N_2 blanketing was started, and the mixture of the MMA and styrene were added into the reactor at a constant rate. After another 10 minutes' stirring at 50 °C, the reactor temperature was increased to 70 °C. When the temperature reached 70 °C, 5 ml 16.7% (weight fraction) APS water solution was injected into the reactor to start the polymerization, and the polymerization was carried out for 4 hours. After the reaction was finished, the product suspension appeared brown. A magnet was used to collect synthesized particles containing iron oxide nanoclusters inside. The collected particles were washed with water several times to remove pure polymer particles. At last, this particle suspension was diluted to 20 ml and the weight percentage is determined to be ~1.0 % by drying this suspension.

3.2.5 Synthesis of symmetrical and anisotropic core-shell magnetic composite particles:

Symmetrical and anisotropic core-shell magnetic composite particles were synthesized by dispersion polymerization with the above composite particles as seeds in several alcohol-based solvents in the same reactors as last part. The anisotropy or symmetry could be achieved by simply adjusting the composition of the reaction medium made from water, EtOH, ETG and THF.

In a typical synthesis, 6 ml 0.05 g/ml PVP-40 ethanol solution as a particle stabilizer was added to 6 ml of the seed particle suspension, and this mixture was added into a specific alcohol-based polymerization medium (as shown in **Table 1**). This mixture suspension was transferred into the reactor, and then N_2 was purged into this suspension for 30 minutes while mechanically stirring at 120 rpm. After 30 minutes, the N_2 blanketing was started, and the stir rate was raised to 350 rpm. 3 ml styrene and 3 ml 0.01 g/ml AIBN ethanol solution were injected to the reactor. After another 20 minutes' stirring was applied to the reactor, the temperature of the reactor was increased to 60 °C to start the polymerization, and this reaction was carried out for 3 hours and 40 minutes. After the reaction was finished, the product suspension appeared pale-yellow. A magnet was used to collect synthesized particles containing iron oxide magnetic cores. The collected particles were washed with water several times to remove pure polymer particles and then diluted to 20 ml.

3.2.6 Migration of magnetic core in core-shell magnetic composite particles:

The migration of magnetic core inside core-shell magnetic composite particles was achieved by solvent swelling, with or without the presence of a magnetic field. Particles of different structure could be obtained by the change of solvent composition, swelling temperature or length of swelling time. Generally, a small amount of core-shell magnetic composite particles were dispersed at a low concentration in a mixture solvent made from water, EtOH, ETG, THF, and sometimes PVP-40 was used as stabilizer. Then this suspension was sealed in a glass vial and left still at room temperature for 1 hour to let particles reach equilibrium. Subsequently, this suspension was placed in a 60°C or 70°C oven for up to 48 hours, letting magnetic cores migrate inside particles, and at last this suspension was quenched by a large amount of water to deswell the particles and lock the position of the magnetic core. These resulting particles were washed with water and collected by a magnet for several times.

3.2.7 Structure analysis of particles:

The size and structure of particles synthesized were analyzed by TEM (200 kV for JEOL 200CX and 80 kV for Philips Mogagni 268) after drying several drops of particles suspension on a carboncoated copper grid. The size and size distribution of some of the particles were also analyzed by DLS after diluting particle suspensions in water.

3.3 RESULTS AND DISCUSSION

3.3.1 Synthesis of iron oxide magnetic nanoparticles

Figure 7 shows the TEM picture of the iron oxide magnetic nanoparticles. The iron oxide nanoparticles have a broad size distribution of 2-15 nm, and the average diameter is about 10 nm. According to Xu's work before[32], iron oxide synthesized in this coprecipitation method is superparamagnetic. These iron oxide magnetic nanoparticles are modified by oleic acid and stabilized in 0.4 M TMAOH for further use.

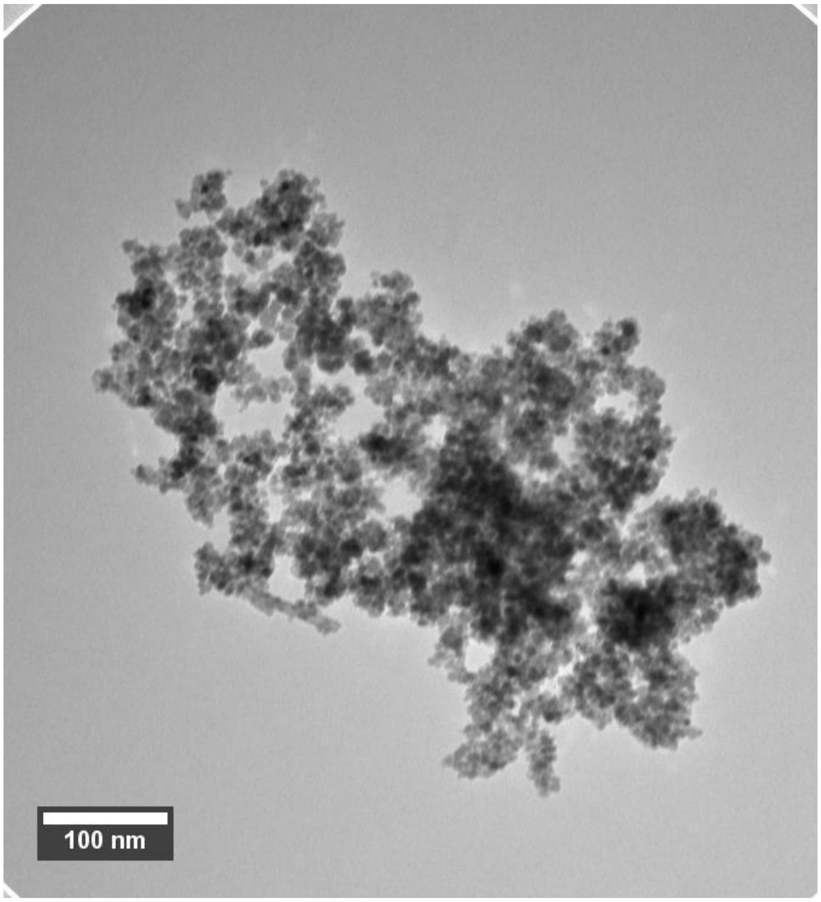


Figure 7. Transmission electron microscopy measurement of nanoscale iron oxide

3.3.2 Synthesis of magnetic composite seed particles

Figure 8 shows the TEM picture of the magnetic composite seed particles. The diameter of the particles calculated from the TEM pictures is 129 nm ± 4 nm, with a magnetic region distributing from 30 nm to 105 nm, which is made from lots of small iron oxide nanoparticles.

In the synthesis of these magnetic seed particles, it is very critical to add in MMA to copolymerize with styrene, and it is almost impossible to make such composite particles without MMA. The possible reason to this phenomenon is that poly-MMA (PMMA) has a stronger affinity to iron oxide than polystyrene does according to Xia's work[38], and the reason to this larger attraction might result from the more hydrophilic branch chain in PMMA.

This synthesis is also very sensitive to the amount of Brij-35 used, which is a nonionic surfactant and works as the emulsifier in this reaction: the structure of the particles would be destroyed by even a 5 % change of this surfactant amount. If the concentration of surfactant is too high, most of the particles will be formed from the micelles, generating only pure polymer particles. If the concentration of surfactant is too low, the iron oxide nanoparticles will form aggregates.

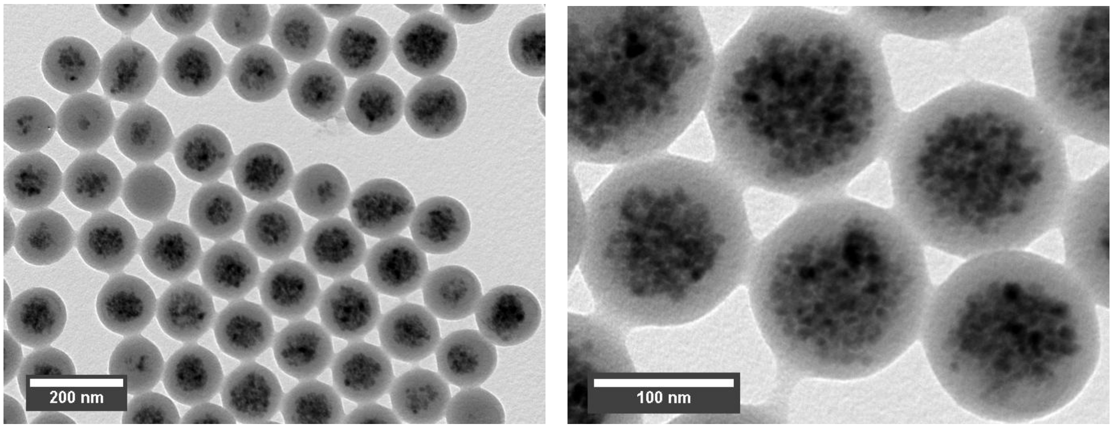


Figure 8. Transmission electron microscopy measurement of magnetic composite seed particles at different magnifications (left: low magnification; right: high magnification)

3.3.3 Synthesis of symmetrical and anisotropic core-shell magnetic composite particles

Figure 9-11 show the TEM pictures of three samples of core-shell magnetic composite particles synthesized by seeded dispersion polymerization in similar conditions except for different polymerization medium. The compositions of three synthesis media are listed in **Table 1**.

Table 1. Composition of solvents used in dispersion polymerization of core-shell magnetic particle synthesis and corresponding particle morphologies

Sample Name	Solvent composition	Resulting particle morphology
pis-072909	11 ml water, 34 ml EtOH, 40 ml ETG	Symmetrical, monodisperse
pis-080709	11 ml water, 34 ml EtOH, 40 ml ETG, 10 ml THF	Anisotropic, monodisperse
pis-082009	27 ml water, 57 ml EtOH, 10 ml THF	Anisotropic, not monodisperse

As shown in **Table 1** and **Figure 9-11**, three samples synthesized in different media showed different structures and polydispersities, even they were made from the same seed particle and under identical other experimental conditions. All these three samples have in the polymer sphere a concentrated magnetic core, which is made from lots of small iron oxide nanoparticles and whose size is directly determined by the iron oxide content contained in the seed composite particles.

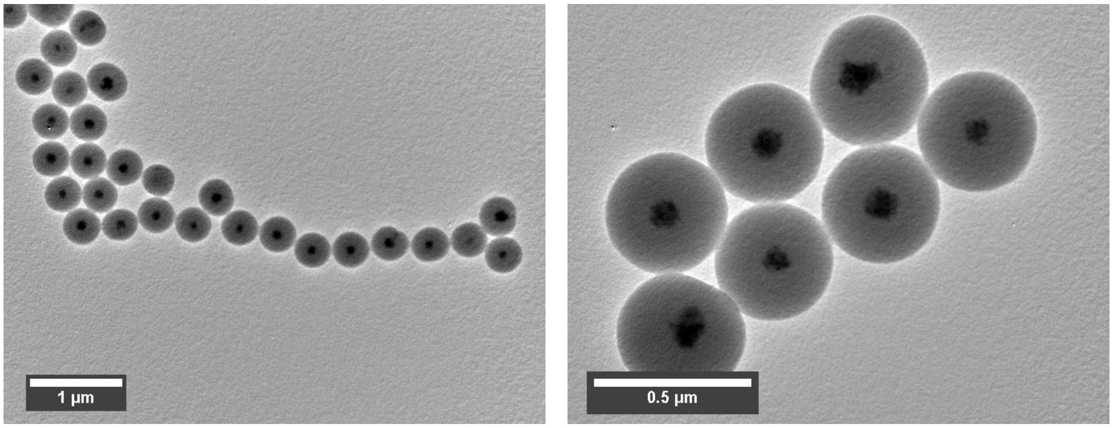


Figure 9. Transmission electron microscopy measurement of symmetrical core-shell magnetic composite particles pis-0729009 at different magnifications (upper left: low magnification; upper right: medium magnification, bottom, high magnification to show magnetic core)

The particle sample pis-072909 has a symmetrical structure (**Figure 9**), with the magnetic core at the center of the polymer sphere. These particles are also monodispersed generally, with the average diameter 381 nm ± 20 nm determined from TEM picture. The solvent used in the synthesis of this sample is mixture of 11 ml water, 34 ml ethanol and 40 ETG, which is not a good solvent for polystyrene nor PMMA. Consequently, the seed particle polymer matrix remains its original structure during the polymerization, and the magnetic core remains at the center of the particle with new-formed polystyrene growing at the surface of the outer shell homogeneously.

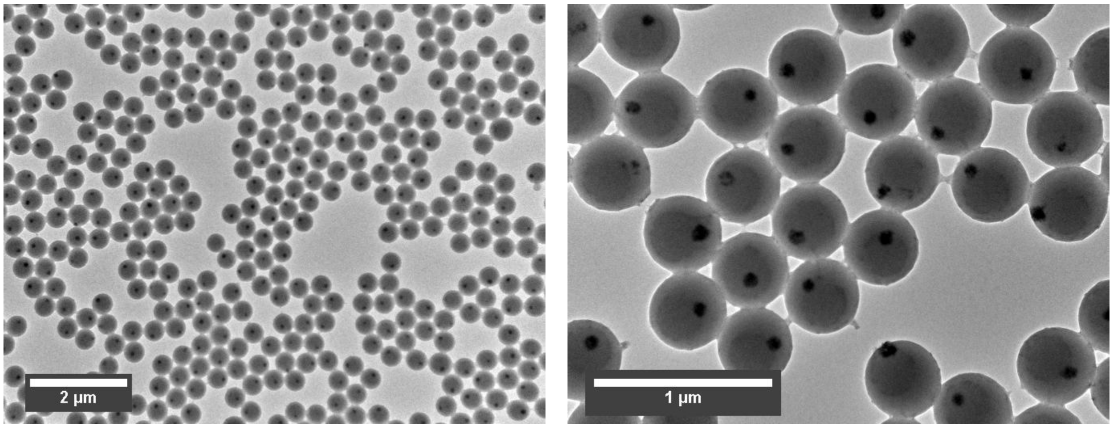


Figure 10. Transmission electron microscopy measurement of anisotropic core-shell magnetic composite particles pis-080709 at different magnifications (left: low magnification; right: high magnification)

The particle sample pis-080709 (**Figure 10**) is also monodisperse, with the average diameter 402 nm ± 11 nm, but they have anisotropic structures, with the magnetic core at the edge of the polymer sphere. The only difference in this synthesis from sample pis-072909 is the polymerization medium: another 10 ml THF, which is a very good solvent for polystyrene, was added into the medium besides 11 ml water, 34 ml ethanol and 40 ml ETG. Therefore, in a solvent with a small fraction of THF, the seed particles could be swollen or partially dissolved to enable the phase separation between the iron oxide and the polymer to happen, and this small concentration of THF will not completely dissolve the particle.

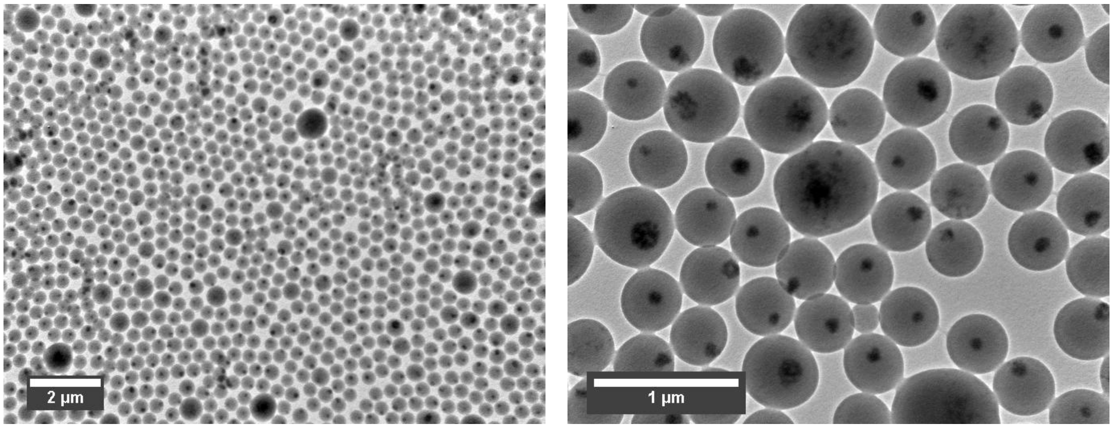


Figure 11. Transmission electron microscopy measurement of anisotropic core-shell magnetic composite particles pis-082009 at different magnifications (left: low magnification; right: high magnification)

The particle sample pis-082009 is also anisotropic (**Figure 11**), but the polydispersity is not as good as the former two. Most of the resulting particles are of the same size around 400 nm, but a small part of the particles are very large (up to 900 nm). This polymerization medium also contains THF, but no ETG is used, and the water-alcohol ratio is larger.

In all these three particle polymerizations, no cross-linker was used, and therefore, all the polymers are linear chains. By comparing the conditions and results of these samples, we can reach a conclusion that the addition of THF to the dispersion polymerization medium is critical to generate the anisotropy in these particles. The assumed reason to this phenomenon is the solubility of polystyrene in THF. THF is a good solvent for polystyrene, with a theta temperature of 25°C (THF/water (v/v: 92.3/7.7))[9]. While in our experiments, the reaction temperature was 60°C, and the THF volume was reduced to about 10%. The higher temperature would increase the solubility and the lower concentration of THF would decrease the solubility. The theta temperature of the mixture solvent is still expected around 60°C, since the polystyrene is swollen to enable the phase separation between the iron oxide phase and the polymer phase, but the particles still remains spherical and not destroyed.

From these experiments, we can also obtain some conclusion about the polydispersity. The dispersion polymerization without ETG in the medium gave out a result of a poor polydispersity. The mechanism of ETG's effect here is not clear, but one possible explanation to this phenomenon could be attributed to the lower dielectric constant of ETG. The high concentration of ETG in the polymerization medium results in lower dielectric constant of the medium, and it therefore allows higher electronic repulsive force (inverse proportional to the dielectric constant) between individual particles to prevent them from approaching one another.

3.3.4 Swelling of symmetrical core-shell magnetic composite particles

One objective of this project is to magnetically control the magnetic core migration of the composite particles. And this part is a preparatory work to the total objective, since it will give a condition under which the polymer properties of the magnetic composite particles can be changed enough to enable such migration and under which the magnetic core made from small iron oxide clusters would not be destroyed.

THF is selected as the effective part of the mixture solvent, since it is a good solvent for polystyrene, and the theta condition for this pair[9] is: THF/water (v/v: 92.3/7.7), theta temperature: 25°C. Some work has been done on the swelling effect of styrene by THF, such as in [39], styrene particles can be best swollen by 50% THF water solution at room temperature, with the diameter largest measured by DLS. If the THF concentration is lower, the polystyrene particles would be less effectively swollen, and if the THF concentration is higher, the polystyrene chains would be removed from the particle into the solvent, causing the dissociation of the particles. After the swelling, it is also very convenient to deswell the particles by just diluting the solvent to decrease THF concentration, making the particles contract to almost the original size. Since the temperature used in this lab is a little higher, a lower concentration of THF might also work.

(1) Swelling by THF water solution

In this part, THF water solutions with THF volume fraction 50%, 40%, 30% and 20% were used. At each concentration, two parallel particle samples were swollen under magnetic field and without magnetic field. The temperature of the swelling is 70 °C and the swelling duration is 48 hours. After 48 hours, the particles were deswollen by adding large amount of water into the particle suspension. Later, particles are collected by a magnet, and washed several times with water.

From the TEM picture of all the four sets samples (**Figures 12-15**), it can be seen that the magnetic core of the composite magnetic particles moved from the center to the outside of the polymer sphere. The shape of the magnetic core were kept, and the size of the magnetic region became a little smaller than in the magnetic seed particles. Generally, there is a one-to-one linkage between migrated magnetic core and its original polymer particle in most of the samples (the only exception is in 50% THF solution, under magnetic field), and this linkage was strong, since the magnetic core kept its position even under the very strong surface tension when drying on TEM grid and in the high vacuum of TEM measurements.

The mechanism of this core movement is not clear, but one possible reason could be attributed to the minimization of interfacial free energy between different phases: polystyrene/PMMA, polystyrene/solvent and PMMA/solvent. The formation of the original composite core-shell particles might be a kinetic process: polystyrene grows continuously on the surface of existing particles, and therefore, the structure might not be at the global minimum of the free energy (only interfacial energy is considered here). When a good solvent of the polymer is added, the polymers are swollen and become flowable. Consequently, the phase separation between the polystyrene phase and PMMA phase could happens, and it will stop only when the interfacial energy (the sum of surface energy between polystyrene/PMMA, polystyrene/solvent and PMMA/solvent) reaches the thermodynamic minimum. The final morphology of the particle is a function of the solvent used to swell the particle, and therefore, it is possible to control the this morphology by changing the composition of the solvent, or introducing surfactants into the system. Saito's paper[40] detailedly described this process in a similar system.

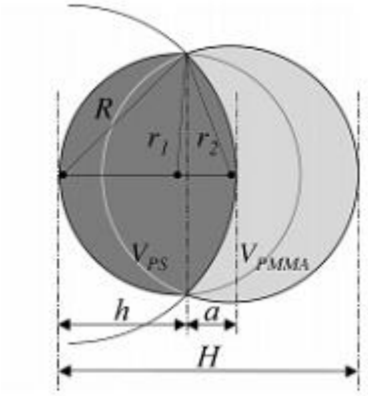


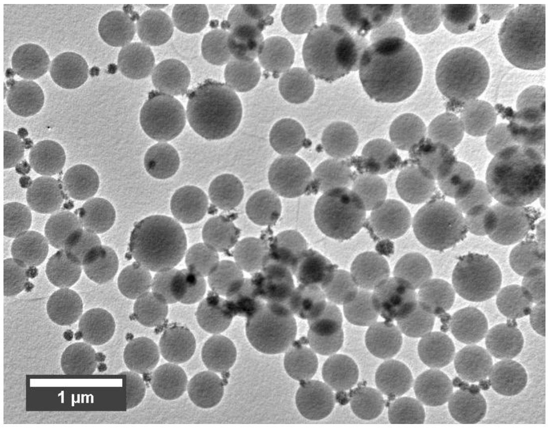
Figure 12. Three interfaces of PS/PMMA composite particles suspended in a solvent. (Reprinted with permission from [40]. Copyright 2007 American Chemical Society).

In all of these THF concentrations, the migration of magnetic cores is not very sensitive to the concentration of THF. Only in the 20% THF trial, there are magnetic cores which just moved half-way and remained inside (not necessarily at the edge), forming an asymmetrical particle, but this phenomenon still happens in a small probability. Therefore, it seems impossible to control the extent the magnetic core moves by the concentration of THF in water, since magnetic cores could be both outside the sphere and near the center in the same sample.

The concentration of THF has some effect on the polydispersity of the particles at this concentration range, but it is not very remarkable. At higher THF concentration (50%), some particles may fuse and form larger ones, while at lower (20% or 30%), most particles are still of their original size.

The magnetic field applied to the particles suspensions during the swelling process had almost no effect to the final results. Almost no difference could be recognized between the samples swollen with and without magnetic field, and the only one that can be found is that at high concentration (50%), the samples swollen under field did not show an exact one-to-one magnetic core – polymer sphere ratio.

This part is also an evidence of the strong repulsive interaction between individual particles. When the particles were swollen under magnetic field, they were all attracted to the wall soon, forming a yellow block at the wall of the glass vial and leaving clear supernatant. However, even at the highest concentration (50% THF, where particles are fully swollen), the particles did not fuse together or form a huge polymer clump even after 48 hours at 70 ℃ and can be redispersed into particle suspension by simple shaking for several seconds, which is a definite evidence of the existence of high repulsive forces between particles.



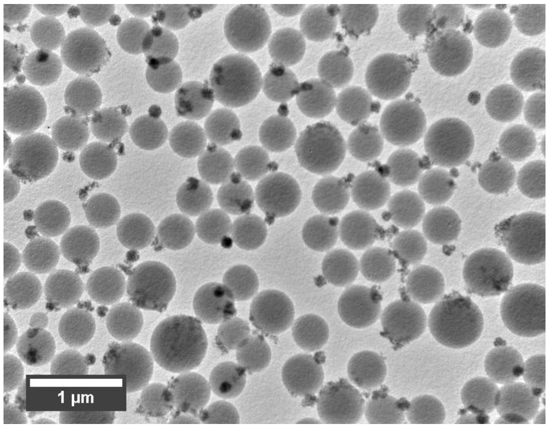


Figure 13. Transmission electron microscopy measurement of symmetrical core-shell magnetic composite particles pis-072909 swollen by 50% (v/v) THF water solution (left: swollen under magnetic field; right: swollen without magnetic field)

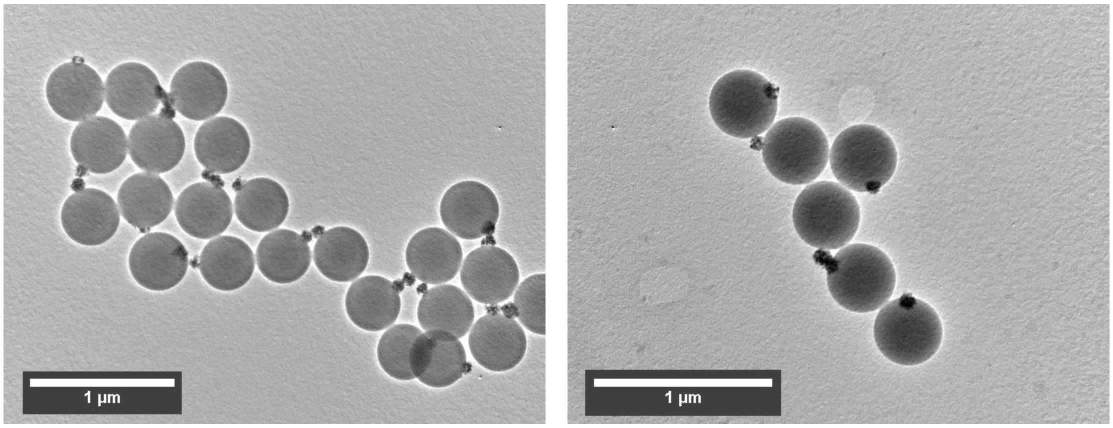
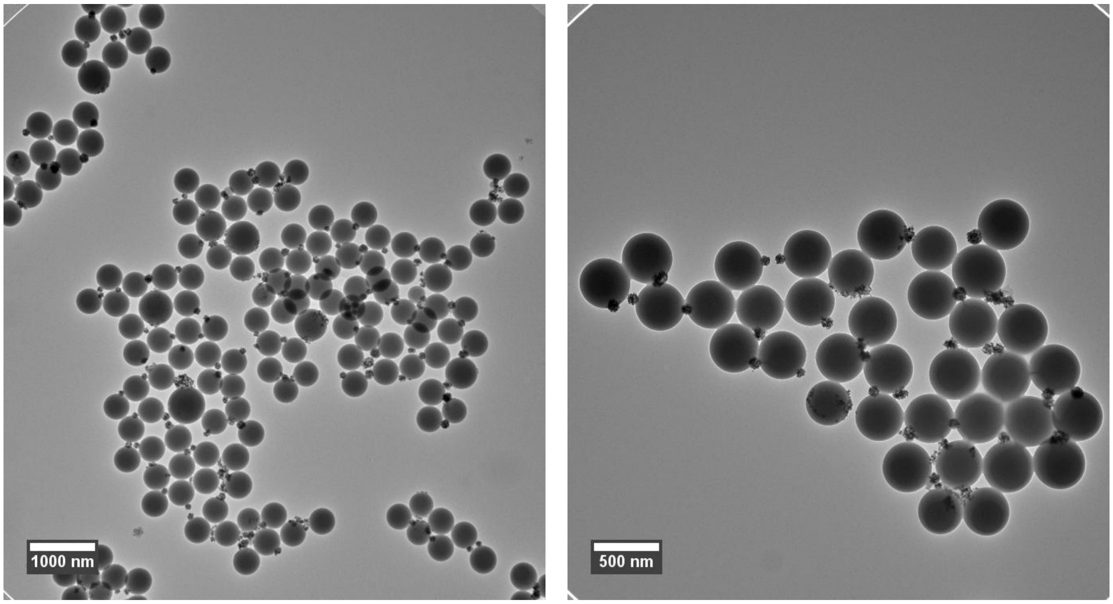


Figure 14. Transmission electron microscopy measurement of symmetrical core-shell magnetic composite particles pis-072909 swollen by 40% (v/v) THF water solution (left: swollen under magnetic field; right: swollen without magnetic field)



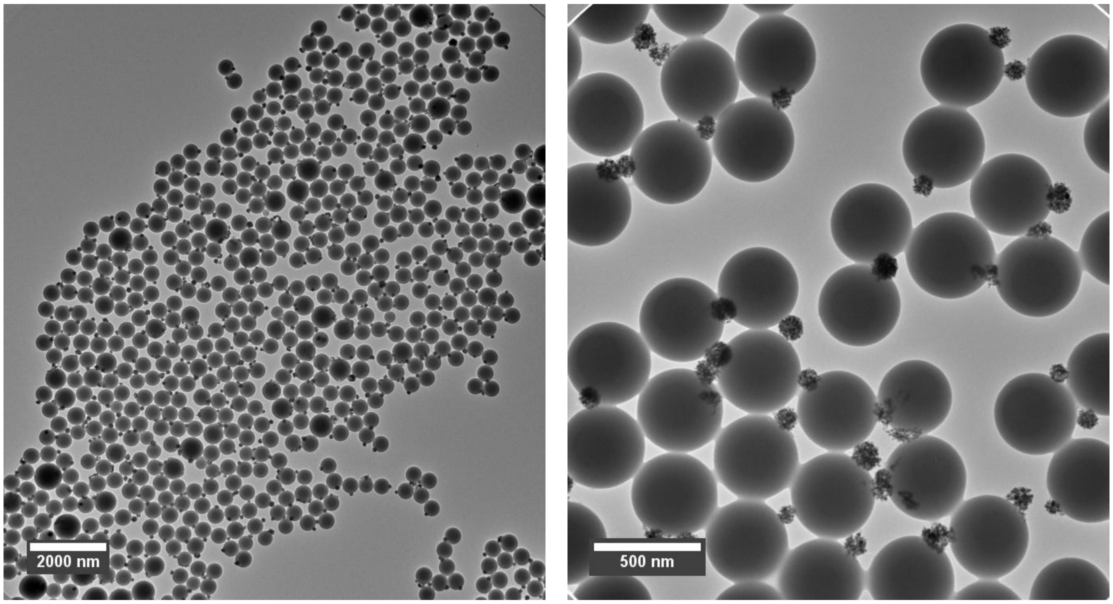
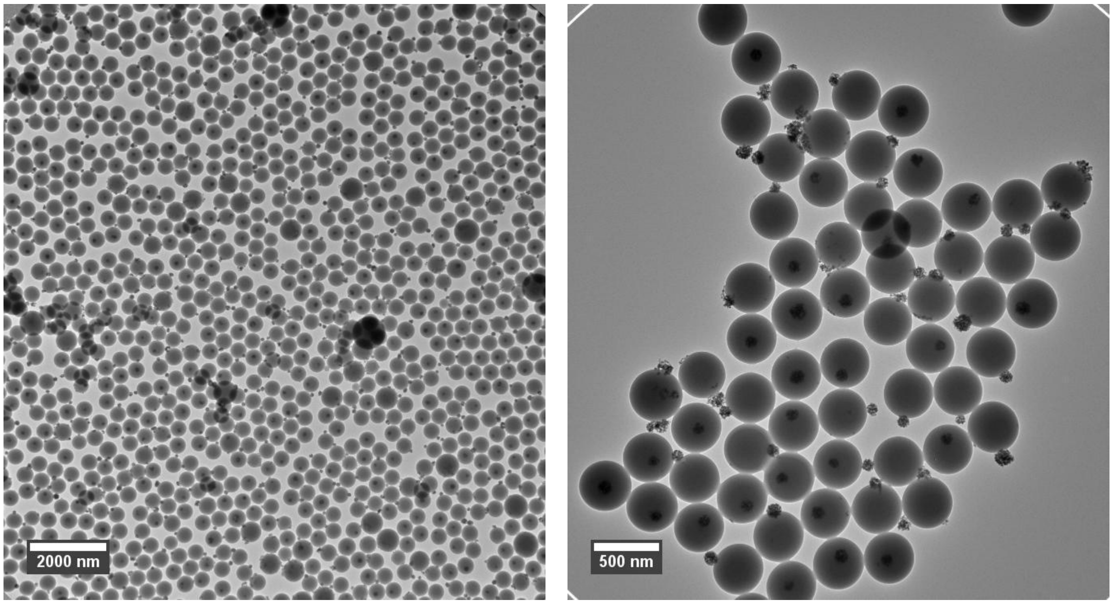


Figure 15. Transmission electron microscopy measurement of symmetrical core-shell magnetic composite particles pis-072909 swollen by 30% (v/v) THF water solution (top 2: swollen under magnetic field; bottom 2: swollen without magnetic field)



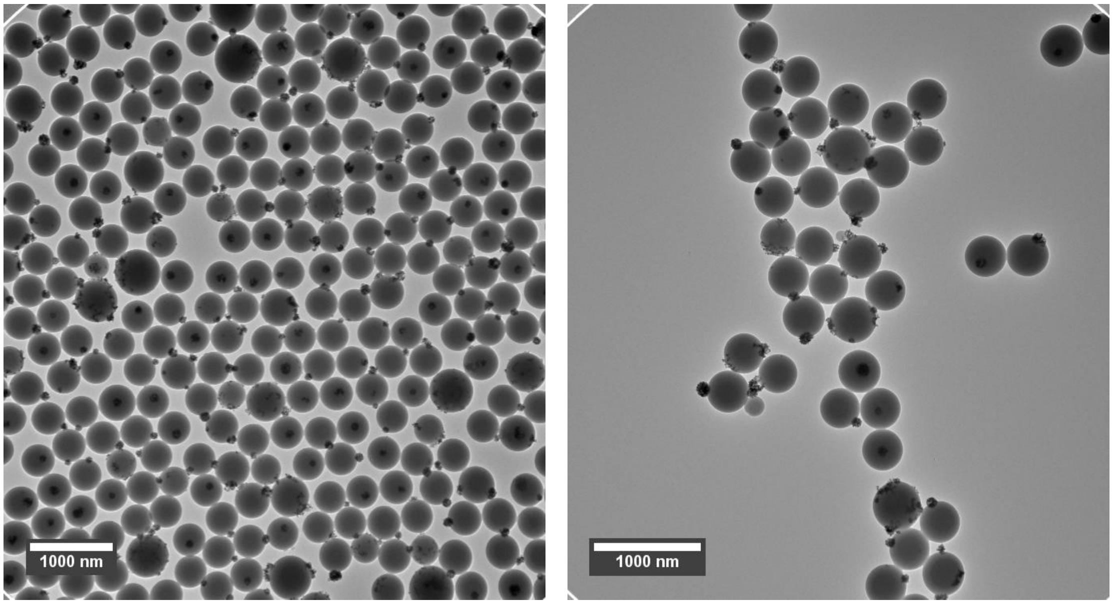


Figure 16. Transmission electron microscopy measurement of symmetrical core-shell magnetic composite particles pis-072909 swollen by 20% (v/v) THF water solution (top 2: swollen under magnetic field; bottom 2: swollen without magnetic field)

(2) Swelling by a solvent similar to dispersion polymerization medium

As discussed in last part, in the swelling process by THF water solution water might play an important role to the formation of the structure that the magnetic core moved outside the polymer sphere. While during the synthesis of anisotropic magnetic composite particle pis-080709, a mixture solvent containing THF was used, but the resulting particles are in a good spherical shape, with all magnetic cores inside the polymer sphere. Therefore, an alcohol-based THF solution is tried to move the magnetic core when also keeping it inside the polymer sphere.

In this part, a mixture solvent with the same composition as the medium in synthesis of pis-080709 was used, and then different amount of THF was added as shown in **Table 2**. This swollen process was carried out for 24 hours, and the temperature was kept 60°C to be consistent with the synthesis environment of pis-080709. No magnetic field was applied to the sample since no specific effect of field was found in last part. After swelling, the particles were deswollen by adding large amount of water to decrease the THF concentration, and then the particles were collected by a magnet and washed by water for several times.

Table 2. Particles swollen by solvents similar to dispersion polymerization media

Sample Name	Composition	THF vol. %
pis-082609-01	110 µl pis-072909, 340 µl EtOH, 400 µl ETG, 100 µl THF	10.5%
pis-082609-02	110 µl pis-072909, 340 µl EtOH, 400 µl ETG, 200 µl THF	19.0%
pis-082609-04	110 µl pis-072909, 340 µl EtOH, 400 µl ETG, 400 µl THF	32.0%
pis-083109-01	110 µl pis-072909, 340 µl EtOH, 400 µl ETG, 600 µl THF	41.4%
pis-083109-02	110 µl pis-072909, 340 µl EtOH, 400 µl ETG, 800 µl THF	48.5%

After the composite magnetic particles are swollen and deswollen back, TEM pictures (**Figure 16-20**) of the particles were taken to check how the magnetic core behaved. Generally, the magnetic cores moved more remarkably to the edge when the THF concentration was higher. When the THF concentration is lower than 32%, there is almost no magnetic core in the particles moving. When the THF concentration is 41.4%, some of the magnetic cores moved to the edge, but some of the cores remained near the centre of the particles. When the THF concentration was raised to 48.5%, almost all the magnetic cores moved to the edge of the particles, and different from the results in THF water solution, none of the particles moved outside the particles, and the particles after swollen is still spherical. However, the problem is, the monodispersity of the particles become worse at a high THF concentration. Some large particles formed, possibly from the fusion of several original particles.

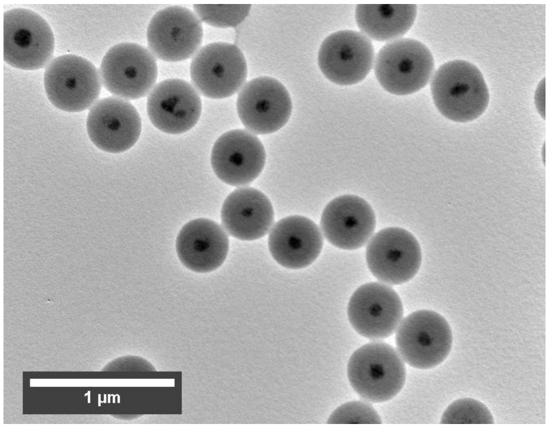


Figure 17. Transmission electron microscopy measurement of swollen magnetic composite particles pis-082609-01

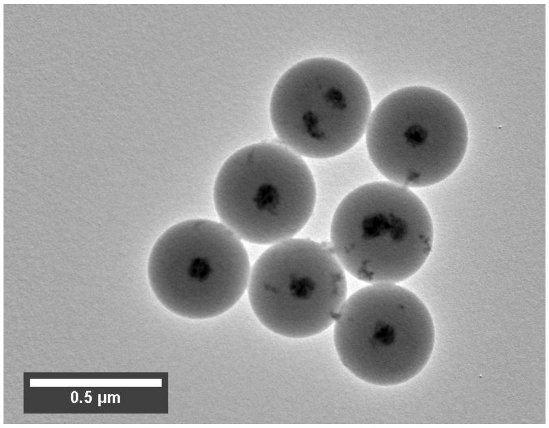


Figure 18. Transmission electron microscopy measurement of swollen magnetic composite particles pis-082609-02

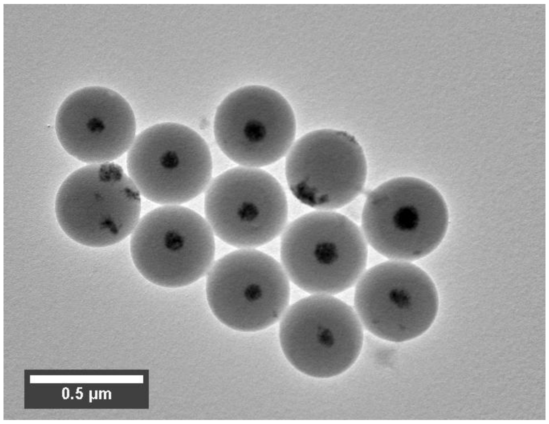


Figure 19. Transmission electron microscopy measurement of swollen magnetic composite particles pis-082609-04

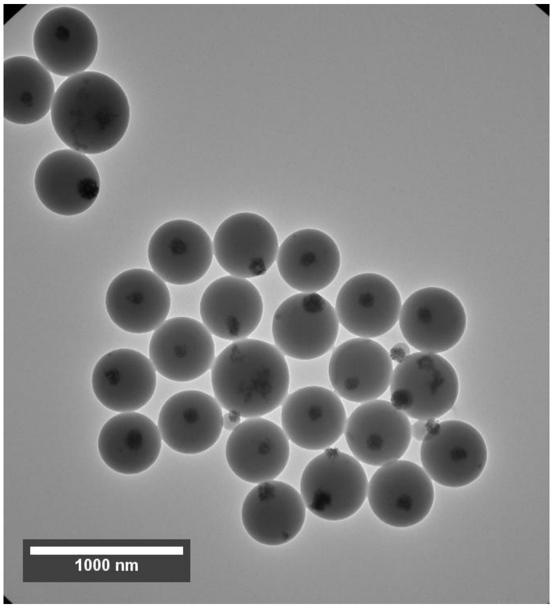


Figure 20. Transmission electron microscopy measurement of swollen magnetic composite particles pis-083109-01

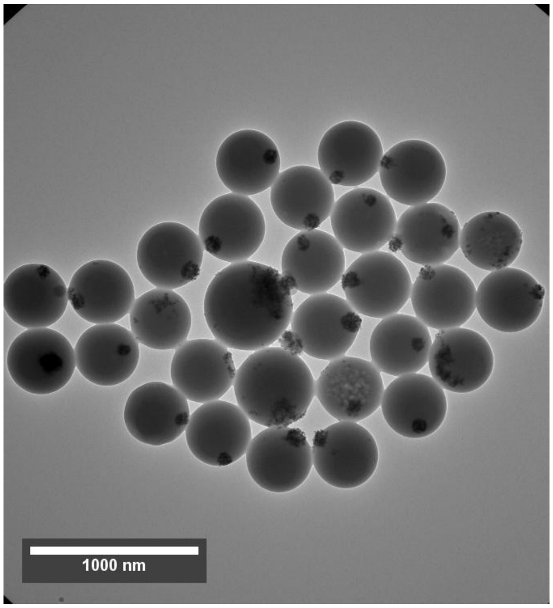


Figure 21. Transmission electron microscopy measurement of swollen magnetic composite particles pis-083109-02

(3) Swelling by non-water solvent

In this part, 110 μl symmetrical magnetic composite magnetic particle suspension pis-072909 (about 1.0% in weight) was used in each of the sample. Then particles were collected by a magnet, supernatant water was removed, and collected particles were redispersed in 850 μl of ethanol, ETG and 34/40 (v/v) ethanol/ETG solvents in order to achieve solvent replacement, respectively. 800 μl THF was added to each of the three samples, and the samples were kept in 60 °C for 24 hours. The particles were deswollen back by adding large amount of water into the suspension to decrease the THF concentration, and then the particles were collected by a magnet and washed by water for several times.

As show in **Figure 21-23**, the migration of the magnetic cores in this set of experiment is satisfactory, since almost all the magnetic cores moved to the edge of the polymer sphere, but none of them went too far to the outside. However, the monodispersity of these three samples was not as good as that of the original samples. But there is a trend that the larger fraction of ETG, the better monodispersity the result is. In fact, in the pure ETG solvent together with THF, the monodispersity and the migration of magnetic core are both all right, and this composition of solvent could be used for further swelling purpose.

In (1) and (3) of this swelling experiment, we can reach the conclusion that both water and ETG have a positive effect on the maintenance of the monodispersity of the particles, but possibly in different mechanisms. Higher water concentration is related to higher ionization rate of sulfate group in the polymer chain, therefore generating more charge and larger electronic repulsive forces, but it will cause the magnetic more move too much. In a non-water environment, ETG has a low permittivity compared to ethanol, and also produces an environment of larger electronic repulsive force if the particles have the same charge. Ethanol has neither of these two properties and therefore is not a good component choice in the swelling solvent.

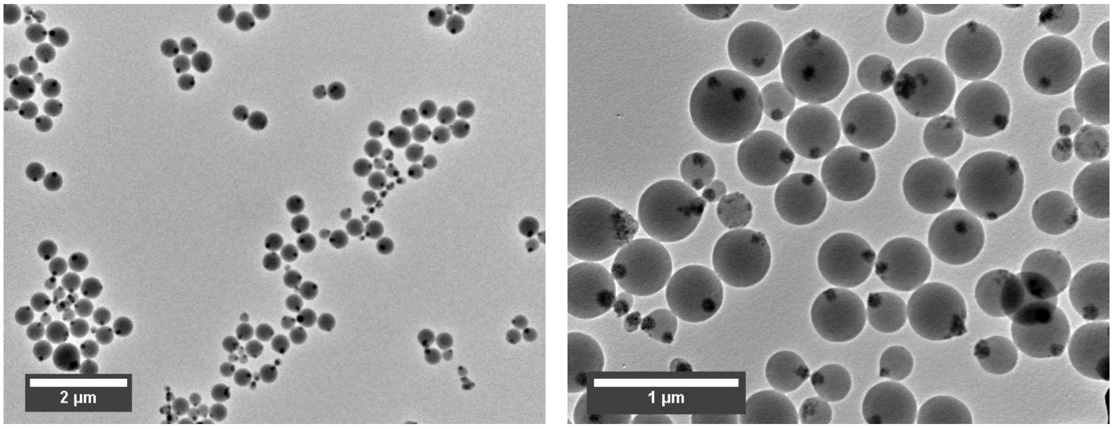


Figure 22. Transmission electron microscopy measurement of symmetrical core-shell magnetic composite particles pis-072909 swollen by 850 µl ethanol and 800µl THF

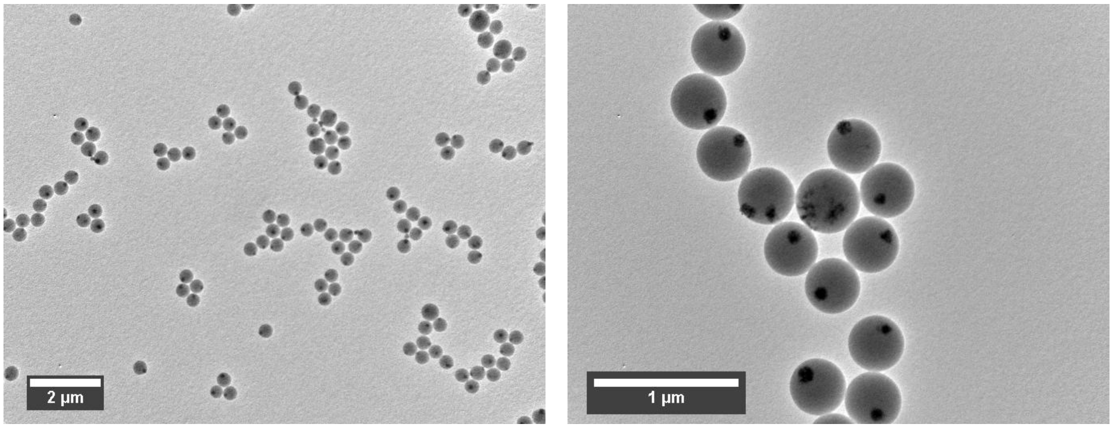


Figure 23. Transmission electron microscopy measurement of symmetrical core-shell magnetic composite particles pis-072909 swollen by 850 µl ETG and 800µl THF

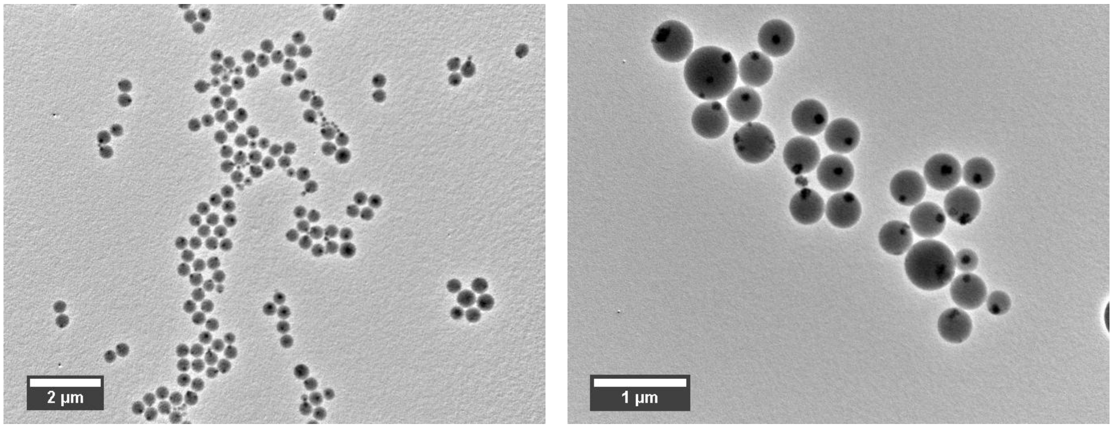


Figure 24. Transmission electron microscopy measurement of symmetrical core-shell magnetic composite particles pis-072909 swollen by 850 µl (34/40 v/v) ethanol/ETG solution and 800µl THF

(4) Swelling by alcohol-based THF solution while protected by PVP-40 as stabilizer

In the last several parts, it has been proved that mixture solvent of water, ethanol, ETG and THF could effectively swell the magnetic composite particles and enable the magnetic core to migrate to the edge from the center. In order to solve the problem that the fusion happened between particles when they were swollen by high concentration of THF, another method is tested. PVP-40 was used as stabilizer to protect particles from getting too close to one another, forming new larger particles and therefore further destroying the monodispersity.

In this part, 110 μl symmetrical magnetic composite particle pis-072909 suspension (about 1.0% in weight) was used in each of the sample, and then 340 μl ethanol and 400 μl ETG were added in. Then 20, 50, 100 and150 μl 0.05 g/ml PVP-40 ethanol solution were added into the four samples, respectively. All swelling processes were carried out at 60 °C for 24 hours, and then the particles were deswollen back by adding large amount of water into the suspension to decrease the THF concentration. Then the particles were collected by a magnet and washed by water for several times.

The result of this experiment (**Figure 24-27**) showed that PVP-40 was effective in preventing particles fusing together, but it did not interfere the migration of magnetic cores, when the concentration of PVP-40 was high enough compared to that of particles. When the volume of PVP-40 is 20 μl, large particles could still be found. When the volume of PVP-40 was raised to 50 μl, the number of larger particles was smaller, and the volume of large particles was also smaller. When the volume of PVP-40 was increased to 100 and 150 μl, almost all particles stayed in their original sizes, both with magnetic core migrating to the edge. No remarkable differences could be found between these two samples.

In this part, it is proved that PVP-40 does have effect on preventing the formation of large polymer particles; therefore, this method can also be applied to swell particles later. If assuming the density of magnetic composite particles is 1.15 g/cm^3, and the weight percentage of particle suspension is 1.0%, the density of PVP-40 absorbed on particles surface is calculated to be 4000-6000 PVP-40 molecules per particle, corresponding to the 100 µl and 150µl PVP-40 stock solution added, respectively.

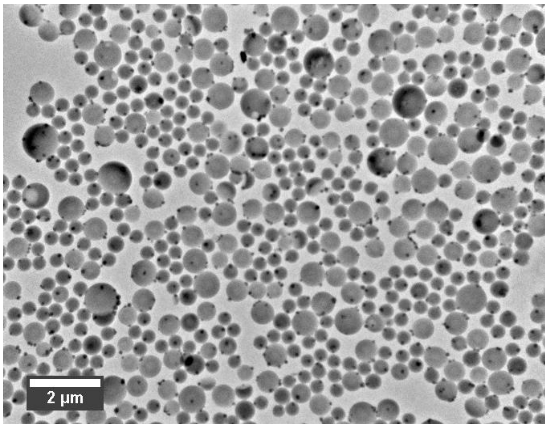


Figure 25. Transmission electron microscopy measurement of symmetrical core-shell magnetic composite particles pis-072909 protected by PVP-40: 110 µl particle suspension and 20 µl 0.05 g/ml PVP-40 solution

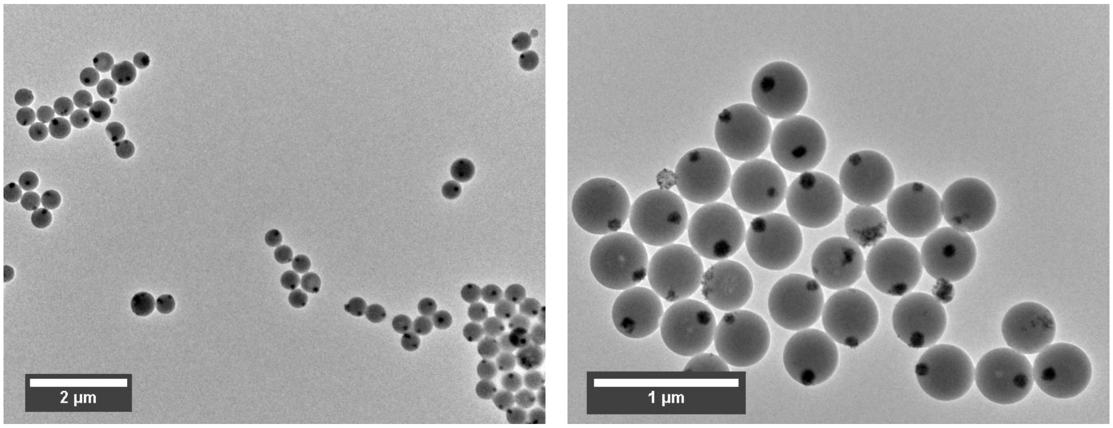


Figure 26. Transmission electron microscopy measurement of symmetrical core-shell magnetic composite particles pis-072909 protected by PVP-40: 110 µl particle suspension and 50 µl 0.05 g/ml PVP-40 solution

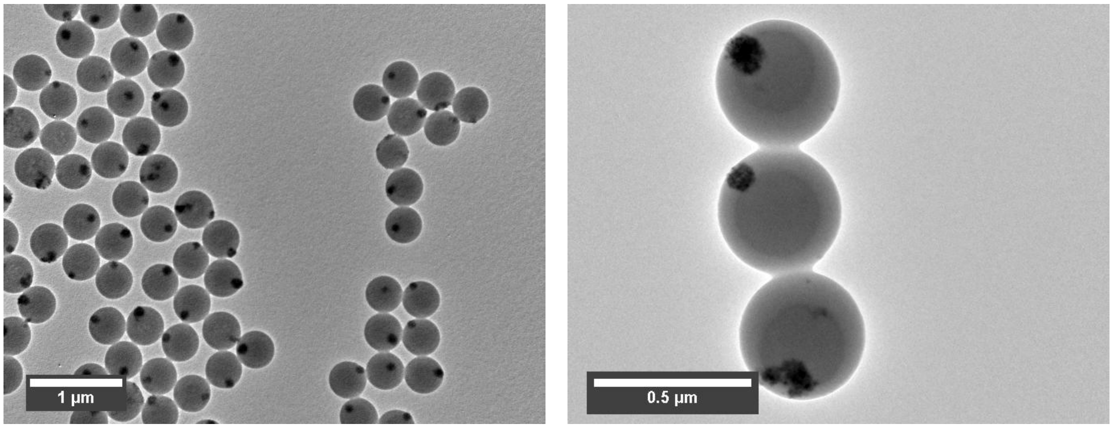


Figure 27. Transmission electron microscopy measurement of symmetrical core-shell magnetic composite particles pis-072909 protected by PVP-40: 110 µl particle suspension and 100 µl 0.05 g/ml PVP-40 solution

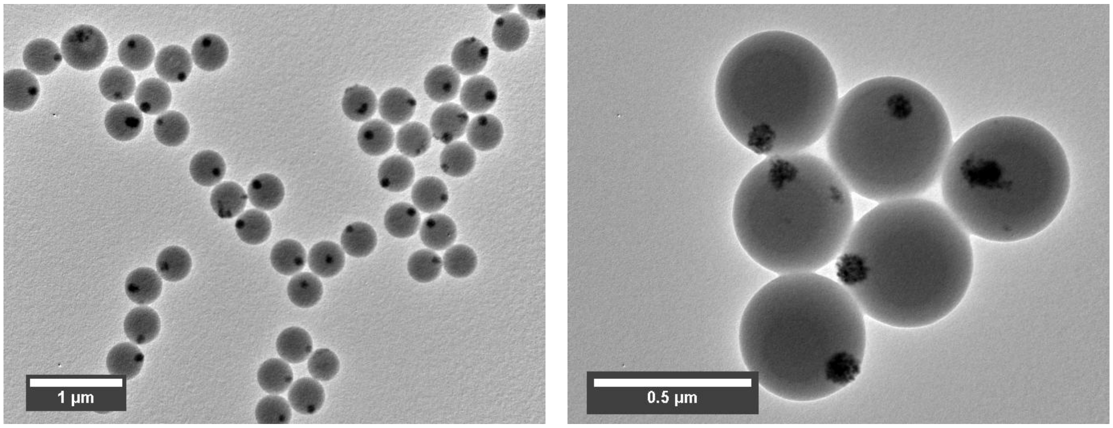


Figure 28. Transmission electron microscopy measurement of symmetrical core-shell magnetic composite particles pis-072909 protected by PVP-40: 110 µl particle suspension and 150 µl 0.05 g/ml PVP-40 solution

3.4 CONCLUSIONS

In this work, a two-step method, first emulsion polymerization and then seeded dispersion polymerization, was developed to synthesize symmetrical and anisotropic magnetic core-shell composite particles. The anisotropy of the resulting particles can be easily controlled by the addition of a small amount (~10%) of THF in dispersion polymerization medium. And further, two compositions of solvents were found to effectively swell the synthesized magnetic composite particles and enable the migration of magnetic core inside the polymer sphere, without destroying the structure of magnetic core or the morphology and monodispersity of the composite particles. One recipe is a mixture solvent made from THF, ETG, ethanol and water, with particles protected by a suitable amount of PVP-40, and the other is just a mixture of ETG and THF.

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