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BLOCK COPOLYMER STABILIZED SELF-ASSEMBLED MAGNETIC NANOCOMPOSITES

by

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A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the Department of Chemistry in the College of Arts and Sciences at the University of Central Florida Orlando, Florida

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ABSTRACT

Magnetic materials are currently being developed in the areas of pharmacology and medicinal chemistry for use in applications such as drug delivery and magnetic resonance imaging. Magnetic fluids are being used in audio equipment and hard disk drives. Their suspension in a particular fluid is promoted by the adsorption or reaction of steric or electrostatic stabilizers, which are appropriate for the particular medium. Critical to the success of these magnetic fluids is the development of the steric stabilizers, which must prevent the coagulation of the metal particles. Polymeric materials are one of the most suitable nonmagnetic media to disperse the magnetic nanoparticles, forming polymeric nanocomposites in ferrofluids.

We have developed strategies in molecular nanoscience to design polymeric systems for stabilization of magnetic nanoparticles. Ring opening metathesis polymerization (ROMP) was used to prepare a series of novel, well-defined diblock copolymers of bicyclo[2.2.1]hept-5-ene 2-carboxylic acid 2-cyanoethyl ester and bicyclo[2.2.1]hept-2-ene, consisting of both anchoring and steric stabilizing blocks. Both ester and cyano groups were incorporated into the polymers to chelate and stabilize the iron oxide magnetic nanoparticles. These polynorbornene-based copolymers were characterized by GPC, along with $^1$H NMR, FTIR, DSC, and TGA.

Using diblock copolymers as stabilizers, nanostructured maghemite ($\gamma$-Fe$_2$O$_3$) magnetic ferrofluids were prepared in toluene or cyclohexanone via thermal decomposition of Fe(CO)$_5$ and then the oxidation of iron nanoparticles. Transmission electron microscopic (TEM) images showed a highly crystalline structure of the $\gamma$-Fe$_2$O$_3$ nanoparticles, with average particle size varying from 5 to 7 nm. Polymer films containing iron oxide nanoclusters were also prepared from the diblock copolymers.
For comparison, a commercial triblock copolymer (BASF Pluronic™ F127) surfactant was used to prepare stabilized ferrofluids. In addition to $\gamma$-Fe$_2$O$_3$ nanoparticles, other types of magnetic nanoparticles, such as FePt, were investigated using this triblock copolymer as a stabilizer. The results indicated that the norbornene diblock copolymers could also be used for the preparation of FePt stabilized magnetic ferrofluids in the future research work.
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INTRODUCTION

**Self-assembled Magnetic Nanoparticles and Magnetic Ferrofluids**

Nanotechnology involves the study, control and manipulation of materials at the nanoscale, typically having dimensions up to 100 nm. Nanoparticle materials have become the focus of increasing attention because their physical properties often differ significantly from those of the corresponding bulk materials.  

Materials with particle diameters in the range of 1 to 10 nm exhibit novel electronic, optical, magnetic, and chemical properties due to their extremely small dimensions.

Controlled synthesis and assembly of small magnetic nanoparticles has potential applications in ultrahigh-density magnetic recording, highly sensitive magnetic sensors, advanced nanocomposite permanent magnets, magnetic ferrofluids, refrigeration systems, and medical imaging. Particle growth is controlled by restricting particle formation to confined volumes such as micelles and vesicles or by stabilizing the growing particle with surfactant or dispersants.

Magnetic nanoparticles, such as those formed from iron, have fascinating magnetic properties that have fueled both fundamental and applied studies. Iron oxide nanoparticles, such as maghemite \((\gamma - \text{Fe}_2\text{O}_3)\) and magnetite \((\text{Fe}_3\text{O}_4)\), due to high magnetization, high magnetic susceptibility and low toxicity, are promising candidates for applications in magnetic resonance imaging and drug delivery. These iron oxides behave differently in magnetic field depending on their sizes. It has been established by several groups that abrupt changes in properties take place in the nanometer range. For instance, nanocrystalline iron oxide is
superparamagnetic (appearing no hysteresis, coercivity or remnant magnetization) when the particle sizes are sufficiently small, and they behave as ferromagnetic (providing a hysteresis loop with nonzero values of remnant magnetization) when the grain size is in micrometer range.\textsuperscript{20-22} Hard magnetic FePt materials are more stable than other well known hard magnetic materials such as CoSm, NdFeB, and have very high magneto-crystalline anisotropy. Recent advances in magnetic recording technology have indicated that, if self-assembled in a tightly packed, exchange-decoupled array with controlled magnetic easy axis direction, these FePt nanoparticles could support high-density magnetization reversal transition and would be a candidate for future ultrahigh density data storage media.\textsuperscript{23}

Iron nanoparticles are normally prepared by the thermal or sonochemical decomposition of iron pentacarbonyl, and aggregation of the particles is often minimized by adding surfactant/dispersants.\textsuperscript{17} Suslick \textit{et al.}\textsuperscript{24} found that the presence of oleic acid during sonochemical decomposition of iron pentacarbonyl leads to the formation of stable colloidal dispersions of iron nanoparticles. Sun \textit{et al.}\textsuperscript{14} were able to produce monodisperse FePt nanoparticles by coupling the thermolysis of iron pentacarbonyl with the reductive decomposition of Pt(acac)\textsubscript{2} in the presence of oleic acid and oleylamine.

Suspensions of small magnetic particles with a mean diameter of about 10 nm in appropriate carrier liquids are called magnetic fluids or ferrofluids. The particles contain only a single magnetic domain and, thus, can be treated as small thermally agitated permanent magnets in the carrier liquid.\textsuperscript{25,26} One of the special features of the ferrofluids is the combination of normal liquid behavior with superparamagnetic properties, which enables the use of magnetic forces for the control of properties and flow of the liquids (Figure 1).\textsuperscript{25}
The recent development of a large variety of ferrofluids has led to a range of new biomedical and diagnostic applications. A major drawback for many applications remains the lack of well-defined and well-characterized particles. Growing attention is paid to iron oxide nanoparticles embedded in a polymer matrix. The matrix fulfills several demands: on one hand it acts as a stabilizer or even controls the particle size; on the other hand it determines the physicochemical properties of the material or allows surface functionalization.\textsuperscript{27} Iron oxides including $\gamma$-Fe$_2$O$_3$ and Fe$_3$O$_4$ have been synthesized by using micro-emulsion, sonication and other methods. However, particle size uniformity and crystallinity of these nanoparticles are comparatively poor. Hyeon \textit{et al.}\textsuperscript{28} recently reported a novel non-hydrolytic synthetic method of fabricating highly crystalline and monodisperse $\gamma$-Fe$_2$O$_3$ nanocrystalline particles. High-temperature (300 $^\circ$C) aging of iron-oleic acid metal complex, which was prepared by the thermal decomposition of iron pentacarbonyl in the presence of oleic acid at 100 $^\circ$C, was found to generate monodisperse iron nanoparticles. The resulting iron nanoparticles were transformed to monodisperse $\gamma$-Fe$_2$O$_3$ nanocrystallites by controlled oxidation by using trimethylamine oxide as a mild oxidant. Particle sizes can be varied from 4 to 16 nm by controlling the experimental parameters. In this research work, we focused on choosing appropriate copolymer matrix

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{magnetic_force.png}
\caption{Ferrofluids under magnetic force.}
\end{figure}
systems to prepare magnetic nanoparticle ferrofluids via modified synthetic method from Hyeon et al.

**Magnetostrictive Films**

In addition to stabilize magnetic fluids, polymeric materials embedded with magnetically “hard” or “soft” particles (nanoparticles) find wide applications in magnetic data storage media, magnetic position sensors, actuators, electromagnetic shielding and touch-screen displays. By virtue of the processability afforded by their polymeric host, these materials can be formed into objects with myriad shapes and sizes. If processed in a magnetic field, these materials can process anisotropic mechanical, electrical transport, and magnetic properties due to the chain-like particle structures that result from the magnetic dipole interactions between particles,\(^\text{29}\) as shown in Figure 2. The magnetic interactions between particles depend on the orientation of each particle and their spatial relationship and the coupling of the magnetic and strain fields in term with magnetostriction.\(^\text{29}\) The magnetostrictive materials are particularly interesting in the form of thin films because they can be mass-produced and incorporated by relatively simple means into micro-electro mechanical systems (MEMS).\(^\text{30}\)

![Figure 2](image)

**Figure 2.** Comparison of undeformed with deformed magnetostrictive film.
Block Copolymer Stabilizers

A critical obstacle in assembling and maintaining nanoscale materials from nanoparticle clusters is the tendency of the latter to aggregate in order to reduce the energy associated with a high ratio of surface area to volume. By using surfactants, attempts have been made to stabilize, isolate, and prepare homogeneously dispersed metal oxide nanoparticles into organic materials.\(^4\)

Stabilized magnetic dispersions in a particular fluid are promoted by the adsorption or reaction of steric or electrostatic stabilizers, which must prevent the coagulation of the metal particles.\(^3\) Polymeric materials are one of the most suitable nonmagnetic media to disperse these magnetic nanoparticles, forming self-assembled polymer nanocomposites in ferrofluids. In these polymer-metal composites, the polymer is often only weakly bound to the metal particles. Block copolymers, with a wider variety of compositions, structures and properties, are recognized to be more efficient than homopolymers as dispersion stabilizers. Copolymers functionalized with a strongly binding head-group may be able to bind more securely and densely on the metal surface.\(^1\)

Triblock copolymers of ethylene oxide (EO) and propylene oxide (PO) were introduced commercially by BASF in the early 1950’s, which have both hydrophilic EO and hydrophobic PO blocks. They have been used in pharmaceutical formulations owing to their ability to self-aggregate, thereby displaying a rich phase behavior, forming micelles and liquid crystalline phases.\(^3\) Their unique structure allows a novel approach in the design and application of surface-active agents. It was reported that water-based magnetic fluids consisting of magnetite (Fe\(_3\)O\(_4\)) nanoparticles were coated with PEO-PPO triblock copolymer, forming micelles consisting of a hydrophobic core of PO and a hydrophilic corona of EO.\(^3\) Pluronics\(^R\) F127 is one of these commercial surfactants with PO block sandwiched between two EO blocks (Figure 3). It is a
nonionic surfactant that is relatively nontoxic. We chose this triblock copolymer surfactant at the beginning of this research work to investigate reasonable block copolymer structure and feasible synthetic methods for preparing stabilized $\gamma$-Fe$_2$O$_3$ ferrofluids in organic-based solvents.

![Structure of Pluronic F127](image)

**Figure 3.** Structure of Pluronic$^R$ F127.

Due to the unlimited freedom in block copolymer molecular design, the raw material can be tailored to satisfy specific needs and requirements. Via different synthetic methods, one can functionalize copolymers with both anchoring (binding head-group) and steric stabilizing blocks. The “iron-loving” binding head-group of block copolymers will chelate and interact with iron or iron oxides nanoparticles, and the steric stabilizing blocks will prevent metal particles from aggregation in a particular solvent system. The ideal magnetic nanoparticle and polymer stabilizer system is shown in Figure 4. Finding an appropriate copolymer stabilizer system, which has promising properties for potential applications, is important. It is also necessary to choose a polymerization method that allows for the facile functionalization of the iron-chelating group with the polymer backbone with controlled molecular weight.
Figure 4. Diblock copolymer magnetic nanoparticle stabilization.

**Ring Opening Metathesis Polymerization (ROMP)**

Polymers produced in the ROMP reaction typically have a very narrow range of molecular weight, which is very difficult to achieve by standard polymerization methods such as free radical polymerization. The polydispersity (the weight distribution MW divided by the number average MW) that may be achieved is in the range of 1.03 - 1.10. These molecular weight distributions are so narrow that the polymers are said to be monodisperse, which is suitable for use as nanoparticle stabilizers.

ROMP is a variant of the olefin metathesis reaction. The reaction uses strained cyclic olefins to produce stereoregular and monodisperse polymers and copolymers. It has attracted growing interests because of its capability of producing a wide range of functionalized polymers.
with control over polymer molecular weight and structure that are unable to be prepared by other polymerization methods.\textsuperscript{35,36}

The mechanism of the ROMP reaction\textsuperscript{34,37} involves an alkylidene catalyst and is identical to the mechanism of olefin metathesis with two important modifications. First, as the reaction involves a cyclic olefin, the “new” olefin that is generated remains attached to the catalyst as part of a growing polymer chain as is shown below with a generic strained cyclic olefin (Figure 5):

![Figure 5. General mechanism of ring opening metathesis polymerization.](image)

The second difference is that the driving force for the ROMP reaction is the relief of ring strain.\textsuperscript{34} Therefore, for such a reaction to be “living” the monomer must be highly strained, all steps must be irreversible, and the organometallic intermediates are stable over the course of the polymerization.\textsuperscript{37} Olefins such as cyclohexenes or benzene have little or no ring strain and cannot be polymerized because there is no thermodynamic preference for polymer versus monomer. Strained cyclic olefins have sufficient ring strain to make this process possible. For example, monomers based on norbornene derivatives (Figure 6) are especially popular as they can be readily synthesized from Diels-Alder reactions with cyclopentadiene.\textsuperscript{34,38} Only the unsubstituted bonds are ring opened, and it is difficult to metathesize or ROMP tri- and tetra-substituted olefins.\textsuperscript{34}
Figure 6. Examples of strained cyclic olefins of norbornene derivatives.

An important feature of this mechanism is that ROMP systems are typically living polymerizations catalyst. For example (Figure 7): one can polymerize 100 equivalents of norbornene and then add a second monomer after the first one is consumed. ROMP is a superior method for making diblock and triblock copolymers and permits one to tailor the properties of the resulting material. Such techniques are only possible if the ratio of chain initiation and chain propagation are perfectly balanced.\textsuperscript{34, 37} Under these circumstances homopolymers and block copolymers with very narrow molecular weight distribution (polydispersity approaching 1.0) can be prepared.\textsuperscript{35} Therefore, for functionalized monomers in particular, it is common to try several different catalysts, solvents, concentrations and temperatures to achieve the best results.

![Figure 7. An example of ROMP of a diblock copolymer.](image)

When the reaction is complete, in the termination process the polymer can be cleaved from the metal center by reacting with aldehyde. The mechanism is shown in Figure 8. The resulting products are a metal oxo and an olefin (or polymer) capped with the former aldehyde.
functionality. Usually a large excess (100-400equiv) of aldehyde is used. The cleaved polymer can then be separated from the catalyst by precipitation with methanol.

**Figure 8.** Termination reaction of ROMP by addition of aldehyde.

The catalysts used for ROMP are the same catalysts used for olefin metathesis. However, one has to be more careful when selecting a ROMP catalyst. If the catalyst is too active, it can metathesize the unstrained olefinic bonds in the growing polymer chain, a process called ”back-biting”, thereby reducing the molecular weight and increasing the molecular weight distribution (polydispersity). ROMP by transition metal catalysts has been known for the past four decades, but only in the last 10 years has it become possible to prepare well-defined catalysts for this reaction and therefore to control their activity closely and study details of the reaction mechanism. An important bonus is that living ROMP catalysts now are known that can tolerate a range of functionalities, many of which are likely to be destroyed in other type of living polymerizations. Therefore, new materials can be prepared with a control that has not been possible in such variety using existing living polymerization methods. Ruthenium catalysts, such as Grubbs’ catalyst (Figure 9) and Schrock’s Mo and W ROMP catalysts have found wide use in the synthesis of block copolymers, and allow control over many aspects of the polymer assembly, including molecular weight, molecular weight distribution, alkene backbone
configuration, and in some cases, tacticity. Particularly, ruthenium alkylidene complexes have significantly broadened the scope of the reaction due to their substantial tolerance of heteroatom-containing functional groups that had poisoned earlier catalysts.

![Figure 9. Structure of Grubbs 1st generation catalyst.](image)

The high tolerance of the ROMP catalyst to various functional groups along with their high activity enables facile synthesis of amphiphilic block copolymers. An amphiphilic block copolymer contains a hydrophobic block and a hydrophilic block. By exploiting the thermodynamic phase separation of amphiphilic diblock copolymers, nanodomains of hydrophilic blocks can be formed, which can then be used to incorporate metal salts. Nanoparticles obtained through the micellization of amphiphilic block copolymers have aroused considerable interest because of their increased stability and lower critical micellar concentrations as compared with low-molecular weight surfactant micelles.

Block copolymer nanoparticles have been formed by the assembly of polymers synthesized by a variety of procedures, such as anionic polymerization, group transfer polymerization, atom transfer radical polymerization, ring opening polymerization, and melt polycondensation. It turns out that ROMP provides a particularly attractive route to the formation of polymeric nanostructures of controlled dimensions. The ability to polymerize a
large number of strained cyclic olefin monomers, and the ability to hydrogenate the double bonds in the polymer backbone combine to allow a wide variety of polymers to be made.  

**Functionalized Poly(norbornene) and its Derivatives**

Norbornene based monomers are characterized with high ring strain, thus providing possibility of ROMP with high polymerization rate under mild reaction conditions. The high ring strain of the bicyclic structure may compensate to some degree for the retarding effect caused by the interaction of functional substituents with active centers of metathesis, which cannot be achieved by functionalized derivatives of low-strain cycloolefins.  

Poly(norbornene) is an amorphous polymer with high thermal stability, optical transparency and low dielectric constant. It is a promising candidate for use in information technology as advanced photoresists, optical devices, and insulators. Despite such good properties, polynorbornene has been limited in its application due to low processibility and poor mechanical properties. It contains an expanded structure that can absorb large amounts of aromatic petroleum liquids or oils, which provides a convenient handle to tune the polymer’s mechanical and thermal properties through plasticization, and has been successfully used in sound barriers, oil spill recovery and, after cross-linking, in sealants and mechanical damping. On the other hand, norbornene monomers can be synthesized with polar functional groups, and, thus, make nobornene polymers soluble in organic solvents and improve its processibility, which makes this material highly desirable for use in block copolymers and polymeric networks.

A previous study shows that the cyano group (-CN) is a good chelating group for iron oxide nanoparticles. Thus we developed strategies to functionalize norbornene with a –CN group.
as the anchoring group (more hydrophilic) (Figure 10a). Via living ROMP, well-defined diblock (Figure 10b) copolymers with low polydispersity and narrow molecular distribution are possible. The molar ratio of anchoring block and steric block (more hydrophobic) can be altered in order to study its effects on the polymer thermo stability, ferrofluids stability, magnetic nanoparticle size, and morphology.

Figure 10. Structure of (a) cyanoethyl ester norbornene derivative and (b) diblock copolymer with both anchoring and steric blocks.

**Research Objectives**

The main objectives of this research are to synthesize a series of novel block copolymers containing “iron-loving” group and study the morphology and size control of self-assembled polymeric nanocomposites in ferrofluids. An aim is also to study the effect of the different ratio of copolymer two blocks on the polymer thermal stability, glass transition temperature, and nanoparticle morphology by means of TGA, DSC, XRD, EDX, and TEM analysis. A commercial triblock copolymer surfactant Pluronic® F127, was also used in maghemite (γ-Fe₂O₃) magnetic fluids as a reference, and the results show that it is difficult to control the nanoparticle size and morphology. Hence, we developed a molecular design strategy to
synthesize diblock copolymers with a thermally stable polynorbornene expandable backbone and pendant “iron-loving” ethynitrile side chains. In addition to preparing stabilized $\gamma$ - Fe$_2$O$_3$ nanoparticle ferrofluids, our efforts were made to generate iron-platinum alloy (FePt) nanoparticles, which is another promising class of magnetic nanoparticles with high magnetic anisotropy and chemical stability.
EXPERIMENTAL

Materials

Bicyclo[2.2.1]hept-5-ene 2-carboxylic acid (98%) (mixture of endo and exo), norbornylene (99%), trimethylamine N-oxide (98%), tris(hydroxymethyl)phosphine, iron and platinum acetylacetonates, or Fe(acac)$_3$ and Pt(acac)$_2$, 1,2-hexadecanediol and bis(tricyclohexylphosphine)-benzylideneruthenium dichloride $\{\text{RuCl}_2(\text{CHPh})[\text{P(C}_6\text{H}_{11})_3]_2\}$ (Grubbs’ catalyst) were purchased from Aldrich. 3-Hydroxy propionitrile (98%), ethylene glycol (p.a.) and propylene carbonate (99.5%) were purchased from Acros. $\text{Fe(CO)}_5$ (99.5%) was purchased from Stream Chemicals. Pluronic$^R$ F127 triblock co-polymer was obtained from BASF. Polystyrene standards were purchased from Polymer Laboratories. $\text{CH}_2\text{Cl}_2$ was dried over calcium hydride and distilled before use.

Instruments and Methods

Thermogravimetric analysis (TGA) was performed with a TA Instrument model 2050 TGA instrument. The heating temperature range was from room temperature to 800 or 1000 °C at a rate of 20 °C /min, according to the different decomposition extent of the block copolymers. All the samples were dried under vacuum for two days before measurements. Differential scanning calorimetry (DSC) was conducted with a TA Instrument DSC 2920 differential scanning calorimeter. The temperature range was from −10 to 250 °C at a rate of 10 °C /min.

$^1$H NMR and $^{13}$C NMR spectra were acquired on a Varian Mercury Gemli Spectrometer at 300 and 75 MHz, respectively. Deuterated chloroform (CDCl$_3$, 99.9%, Norell) was used as the
solvent for both monomer and diblock copolymers. Fourier transform infrared (FTIR) spectra were performed with a Perkin Elmer Spectrum One Fourier transform infrared spectrometer. X-ray diffraction (XRD) (Multiplex Rigaku, $\lambda = 0.154$ nm) was used for all the powder X-ray diffraction pattern spectra. GC-MS spectra were obtained with a FINNIGAN Trace GC Ultra GC/MS in HPLC grade methanol in electron impact (EI) mode.

Transmission electron microscopy (TEM) was accomplished with a FEI Tecnai F30 instrument. The samples were prepared by depositing nanoparticle fluids on a TEM copper sample holder.

Gel permeation chromatography (GPC) was conducted with a Waters in-line degasser AF, Waters 2414 refractive index detector, Waters 2996 photodiode array and Waters 1525 binary HPLC pump. The measurements were conducted using HPLC grade THF as the mobile phase (flow rate at 0.3 mL/min). The polymer molecular weights were based on the universal calibration curve. The polystyrene standards used are listed in Table 1.

### Table 1. Molecular weights and concentrations of polystyrene standard sample.

<table>
<thead>
<tr>
<th>MW</th>
<th>Concentration (mg/10 mL THF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,000</td>
<td>10</td>
</tr>
<tr>
<td>10,200</td>
<td>10</td>
</tr>
<tr>
<td>19,000</td>
<td>10</td>
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<tr>
<td>30,230</td>
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<tr>
<td>49,170</td>
<td>7</td>
</tr>
<tr>
<td>111,800</td>
<td>7</td>
</tr>
</tbody>
</table>
Synthesis of Bicyclo[2.2.1]hept-5-ene 2-carboxylic acid 2-cyanoethyl ester

The preparation of bicyclo[2.2.1]hept-5-ene 2-carboxylic acid 2-cyanoethyl ester\textsuperscript{52, 53} is illustrated in Scheme 1. Specifically, the mixture of \textit{endo} and \textit{exo} bicyclo[2.2.1]hept-5-en-2-carboxylic acid and 15 mmol of thionyl chloride in dry chloroform were refluxed for 3h under nitrogen. Then, the solvent was removed under reduced pressure with a rotary evaporator and the residue was distilled at 0.75 torr (40 °C) to generate acid chloride at 80% yield. The acid chloride (10.0 g, 64 mmol) was then diluted with dry CHCl\textsubscript{3}, and added over 60 minutes to a mixture of \textit{N,N}-dimethylaniline (15.5 g, 128 mmol) and 3-hydroxypropionitrile (11.4 g, 160 mmol) at 0 °C. The mixture was stirred at room temperature for 1 h. After the addition was complete, it was heated to reflux with stirring for another 12 h. When the reaction was complete, 65 mL of 6 N H\textsubscript{2}SO\textsubscript{4} was used to quench the reaction at 0 °C. The organic and aqueous layers were separated. The aqueous layer was extracted with ether 3 times, and the organic extracts were combined. H\textsubscript{2}SO\textsubscript{4} (50 mL, 6 N) was used to wash the extract, followed by washing with 2 × 60 mL H\textsubscript{2}O. K\textsubscript{2}CO\textsubscript{3} (10%, 2 × 60 mL) was used to neutralize residual H\textsubscript{2}SO\textsubscript{4}. Saturated NaCl (30 mL) was added in order to “salt out” the organic product. The solvent was evaporated after the mixture was dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}. Reduced pressure fractional distillation was performed at 0.75 torr (114-117 °C), affording 10.1 g of colorless oil (\textit{endo} and \textit{exo} mixture of bicyclo[2.2.1]hept-5-ene 2-carboxylic acid 2- cyanoethyl ester) in 83% yield. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) 6.20-6.22 (dd, 1H, J = 3.0, 5.6 Hz, \textit{endo}-olefinic CH), 6.14-6.17 (dd, 1H, J = 2.8, 5.6 Hz, \textit{exo}-olefinic CH), 6.10-6.13 (dd, 1H, J = 2.9, 5.3 Hz, \textit{exo}-olefinic CH), 5.95-5.98 (dd, 1H, J = 2.8, 5.6 Hz, \textit{endo}-olefinic CH), 4.17-4.32 (m, 2H), 3.25 (s, 1H, \textit{endo}), 3.07 (s, 1H, \textit{exo}), 2.98-3.04 (m, 1H, \textit{endo}), 2.93 (s, 1H), 2.67-2.76 (m, 2H), 2.26-2.31 (m, 1H \textit{exo}), 1.90-1.98 (m, 1H), 1.50-1.53 (d, 1H, J = 8.3 Hz, \textit{exo}), 1.38-1.49 (br, 2H), 1.29-1.32 (d, 1H, J = 8.1 Hz, \textit{endo}).
$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ (endo) 174.3, 138.3, 132.3, 117.2, 58.8, 50.0, 46.1, 43.5, 42.9, 29.6, 18.5; $\delta$ (exo) 175.8, 138.3, 135.8, 117.1, 58.9, 47.0, 46.7, 43.3, 42.0, 30.8, 18.5. Anal. Calcd. for C$_{11}$H$_{13}$O$_2$N (191.09): C, 69.09; H, 6.85; N, 7.32. Found: C, 69.06; H, 6.75; N, 7.24. GC-MS (EI, 70eV): m/z 191.02 ($M^+$, Calcd.191.09), fragmentation m/z 121 (–OCH$_2$CH$_2$CN, 9.1), m/z 93 (–COOCH$_2$CH$_2$CN, 9.2), m/z 91 ($C_7H_7^+$, 13.6), m/z 66 ($C_5H_6^+$, 100).

**Scheme 1.** Synthesis of bicyclo[2.2.1]hept-5-ene 2-carboxylic acid 2-cyano-ethyl ester.

![Synthesis Scheme](image)

**Polymerization**

**ROMP of Diblock Copolymers**

ROMP of the cyanoethyl ester monomer with the initiator $\{RuCl_2(CHPh)[P(C_6H_{11})_3]_2\}$ was accomplished according to a literature method and shown in Scheme 2.$^{54, 55}$ Generally, a catalyst solution ($6.4 \times 10^{-3}$ M) was prepared by dissolving Grubbs' catalyst in dry CH$_2$Cl$_2$. The cyanoethyl ester monomer was diluted in dry CH$_2$Cl$_2$ to 0.24 M and purged with N$_2$. After complete degassing, the catalyst solution was injected into the monomer solution via syringe. The pink solution was stirred at room temperature under N$_2$ for 1 h. Then, the second monomer,
norbornene, was injected to the "living" reaction mixture, and the solution was stirred for another 24 hours at room temperature. The color of the solution changed from pink to dark brown. The polymerization was terminated by the addition of 500 eq ethyl vinyl ether. After termination, the solution was stirred an additional 30 min. The reaction mixture was then poured into excess methanol with stirring and the precipitates went through a further purification process causing a gray to white flaky solid (88%-93% yield). $^1$H NMR (300 MHz, CDCl$_3$) of 1:1 diblock copolymer: 5.12-5.53 (br, 4H, vinylic), 4.14-4.28 (br, 2H), 2.55-2.97 (br, 4H), 2.27-2.50 (br, 2H), 1.59-2.14 (br, 6H), 1.19-1.50 (br, 3H), 0.94-1.15 (br, 2H).

**Scheme 2.** ROMP of a series of diblock copolymers using 1$^{st}$ generation Grubbs catalyst.

![Scheme 2](image)

**Purification of Diblock Copolymers**

The purification technique used to decrease the amount of Ruthenium catalyst remaining in the block copolymer was modified from previous work.$^{56}$ A polymer solution was added to a mixture of 100 eq (based on the amount of Ru catalyst added during ROMP) of tris(hydroxymethyl)phosphine and 2 eq of triethylamine. The color of the solution changed gradually from brown to pale yellow and kept stirring for 2 h. The mixture was then concentrated
and run through a silica gel column (CH$_2$Cl$_2$:THF = 7:1). The resulting polymer solution was precipitated in methanol to generate a relatively gray to white flaky solid. Alternatively, excess silica gel can be added to the yellow polymer solution, which was already reacted with phosphine. The mixture was stirred for 6 h followed by vacuum filtration. Finally, filtered polymer solution was precipitated into methanol or hexane to obtain pure polymer.

**Preparation of Stabilized Magnetic Nanoparticle Dispersions**

**Preparation of γ-Fe$_2$O$_3$ Magnetic Dispersions**

In preparing stabilized monodisperse iron nanocrystals within block copolymer matrices, known methods$^{57}$ were modified as follows: the diblock copolymer was dissolved in cyclohexanone, 1,4-dioxane, or toluene, heated to 100 °C, followed by addition of Fe(CO)$_5$ to the polymer solution, and refluxed for 2 h. Fe(CO)$_5$ underwent thermal decomposition, creating Fe nanoparticles, and the color of the solution changed gradually from yellow orange to brown. After the solution was cooled down, trimethylamine $N$-oxide was added to oxidize the iron nanoparticles. Refluxing for another 4 h under N$_2$, the solution finally changed color to black and cooled to room temperature. Stabilized γ-Fe$_2$O$_3$ magnetic dispersions were observed. Pure polymer-stabilized γ-Fe$_2$O$_3$ magnetic nanoparticles were obtained by adding ethanol to the magnetic dispersions to yield a black powder precipitate and then separated by centrifuge.
**Preparation of FePt Magnetic Dispersions**

Pluronic$^R$ F127 (0.0625 mmol, 0.8 g) was dissolved in 5 mL propylene carbonate in a two-necked flask and then 0.125 mmol (0.044 g) of Fe(acac)$_3$ and 0.125 mmol (0.05 g) Pt(acac)$_2$ were added. Afterwards, 5 mL of ethylene glycol was added as the reducing agent. The mixture was refluxed at (~220 °C) for about 3.5 h while stirring with a magnetic stir bar, and the solution turned into black indicating the formation of FePt nanoparticles. To obtain pure FePt nanoparticles, 4 mL ethanol was added to the mixture and centrifuged it for 20 min. The dark-brown supernatant was discarded and the precipitate was collected. This procedure was done twice. The precipitate was washed with ethanol and dried in an oven under vacuum overnight to get rid of remaining solvent, affording the pure dry FePt nanoparticles.

Furthermore, particles were synthesized using 1, 2-hexadecanediol as the reducing agent, as reported in the literature.$^{14}$ A similar procedure was followed as when ethylene glycol was used. First, Pluronic$^R$ F127 was dissolved in 10 mL of propylene carbonate in a two-necked flask, and 0.375 mmol (0.097 g) of 1,2-hexadecanediol was added. It took time for 1, 2-hexadecanediol to completely dissolve in the reaction mixture. Then 0.125 mmol of Pt(acac)$_2$ and 0.125 mmol Fe(acac)$_3$ were added to the solution. This was refluxed for another 3.5 h resulting black stabilized FePt magnetic nanoparticle dispersions.

**Preparation of Diblock Copolymer Films Containing Iron Oxide Nanoclusters**

One equivalent of iron (III) chloride (FeCl$_3$) was added to three equivalents cyanoethyl ester (NORCOOCH$_2$CH$_2$CN) in 2-4 wt% diblock copolymer solutions in THF.$^{58}$ Static casting was done in the glove box with a constant N$_2$ purge to slowly remove solvent over a period of 3-
5 days followed by drying the thin films under vacuum for at least 2 days.\textsuperscript{59} To make iron oxide nanoclusters, polymer films containing FeCl$_3$ were gently stirred in 2M NaOH solution at room temperature for 24 h until the color of the films finally changed from yellowish to red-brown. The films were then gently stirred in deionized water to complete the oxidation of iron hydroxide by ambient O$_2$ and wash away residual NaOH and NaCl, followed by drying under vacuum.\textsuperscript{58}
RESULTS AND DISCUSSIONS

**Synthesis of Norbornene Nitrile Derivative Monomer**

Synthesis of bicyclo[2.2.1]hept-5-ene 2-carboxylic acid 2-cyanoethyl ester was illustrated in Scheme 1. The first step of the synthesis was to generate the acid chloride intermediate. Treatment of bicyclo[2.2.1]hept-5-ene 2-carboxylic acid (or norbornene 2-carboxylic acid) with thionyl chloride directly at reflux using dry chloroform as solvent facilitated the reaction under a relatively mild conditions, minimizing side product formation. The reaction was monitored by TLC with a mixture of 3:1 cyclohexane and ethyl acetate. After fraction distillation, the monomer was dried under vacuum for 24 h, which was pure enough for ROMP. Elemental analysis results of the monomer are listed in Experimental Section. The mass found from GC-MS spectrum was 191 g/mol (Figure 17b), matching the calculated value.

Figure 12 shows the $^1$H NMR spectrum of bicyclo[2.2.1]hept-5-ene 2-carboxylic acid 2-cyanoethyl ester. Compared with the starting material, norbornene 2-carboxylic acid (Figure 11), we found that the –OH group disappeared from the product $^1$H NMR spectrum and two –CH$_2$ proton peaks appeared at 4.30 ppm and 2.75 ppm. The characteristic norbornene vinyl proton peaks were present in both spectra (6.00–6.25 ppm). The $^{13}$C NMR spectrum (Figure 14) showed three new peaks at 117.2 ppm, 58.8 ppm, and 18.5 ppm, due to the functionalized cyanoethyl ester group on the 2-carboxylic acid (Figure 13).
Figure 11. 300 MHz $^1$H NMR spectrum of bicyclo[2.2.1]hept-5-ene 2-carboxylic acid.

Figure 12. 300 MHz $^1$H NMR spectrum of bicyclo[2.2.1]hept-5-ene 2-carboxylic acid 2-cyanoethyl ester.
Figure 13. $^{13}$C NMR spectrum of bicyclo[2.2.1]hept-5-ene 2-carboxylic acid.

Figure 14. $^{13}$C NMR spectrum of bicyclo[2.2.1]hept-5-ene 2-carboxylic acid 2-cyanoethyl ester.
FTIR spectra (Figures 15 and 16) confirmed the presence of the main functional groups of both starting material and final product. We clearly saw that the alcohol functional group of the norbornene carboxylic acid disappeared from the product spectrum and a new peak appeared at 2370 cm$^{-1}$, corresponding to the –CN stretch.

The starting material norbornene 2-carboxylic acid is a mixture of endo and exo isomers (ca. 2:1 endo/exo). Thus, the final product was a 2:1 mixture of endo and exo isomers, estimated from $^1$H NMR analysis. However, the integration of the two product isomer peaks from the GC-MS spectrum (Figure 17a) showed that the molar ratio between these two isomers (endo/exo) was nearly 1:1 (Table 3). The difference between these two ratios was that two different monomer fractions (from distillation) were used for the $^1$H NMR and GC-MS measurements. The fractions contained different amounts of endo/exo products due to their different boiling points.

Table 2. Retention time (RT), % area and % height of two isomer peaks of bicyclo[2.2.1]hept-5-ene 2-carboxylic acid 2-cyanoethyl ester from GC-MS spectrum.

<table>
<thead>
<tr>
<th>Apex RT</th>
<th>Start RT</th>
<th>End RT</th>
<th>%Area</th>
<th>% Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.45</td>
<td>5.40</td>
<td>5.68</td>
<td>47.27</td>
<td>33.62</td>
</tr>
<tr>
<td>5.74</td>
<td>5.72</td>
<td>5.97</td>
<td>52.73</td>
<td>66.38</td>
</tr>
</tbody>
</table>
Figure 15. FTIR spectrum of bicyclo[2.2.1]hept-5-ene 2-carboxylic acid.

Figure 16. FTIR spectrum of bicyclo[2.2.1]hept-5-ene 2-carboxylic acid 2-cyanoethyl ester.
Figure 17. GC-MS spectrum of bicyclo[2.2.1]hept-5-ene 2-carboxylic acid 2-cyanoethyl ester.
**Synthesis of Diblock Copolymers**

Five diblock copolymers with different molar ratios between anchoring and steric blocks were synthesized according to the feed listed in Table 3. Under mild conditions (room temperature), Grubbs catalyst was used for ROMP according to the similar procedure described in the Experimental Section and Scheme 2. The key factors to characterize living ROMP are the effective initiation and consumption of monomer, the generation of polymers with controlled molecular weights, and the ability to form block copolymers.⁴¹

Grubbs’ catalyst is an air and water-sensitive metal complex. To get high effective initiation, the reaction must be kept in a dry and N₂ or Ar-protected environment. All of the glassware was dried in the oven overnight and methylene chloride was distilled over anhydrous calcium hydride just before use. The reaction was kept under N₂ until termination. To ensure the reaction was “living”, the rate of propagation ideally should be approximately the same order of magnitude as the rate of initiation.³⁴ If propagation starts after full initiation of monomers, the number of polymer chains will be equal to the molar ratio of monomer to initiator [M] / [I].⁶⁰ In case of entry 1 (Table 3), in the first stage of polymerization, the molar amount of norbornene cyanoethyl ester monomer [NORCOOCH₂CH₂CN] was 200 times that of the initiator. Theoretically, the degree of polymerization (m) for the first block should be 200, which is expressed as [NORCOOCH₂CH₂CN]₂₀₀. According to [NOR] / [I] = 20, the target diblock copolymer was obtained as [NORCOOCH₂CH₂CN]₂₀₀ [NOR]₂₀.
Table 3. Target block ratio (m:n) of five diblock copolymers ([NORCOOCH₂CH₂CN]ₘ [NOR]ₙ), related molar feed ratio of monomers and catalyst, and reaction yield

<table>
<thead>
<tr>
<th>Entries</th>
<th>[NORCOOCH₂CH₂CN] / [I]</th>
<th>[NOR] / [I]</th>
<th>Block ratio (target)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>200</td>
<td>20</td>
<td>200 : 20</td>
<td>88</td>
</tr>
<tr>
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<td>100</td>
<td>20</td>
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<td>92</td>
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<td>100</td>
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<td>91</td>
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<tr>
<td>4</td>
<td>100</td>
<td>200</td>
<td>100 : 200</td>
<td>90</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>700</td>
<td>100 : 700</td>
<td>93</td>
</tr>
</tbody>
</table>

Reactions were run at room temperature for 24-52 hours.

Not unexpectedly that concentration of monomer solution has some effect on the rate of propagation. As we injected catalyst solution to 0.6 M monomer solution in the first stage polymerization, the polymer solution became very viscous within half an hour indicating a rapidly increase of the rate of propagation before the full initiation of monomer. When we decreased the monomer concentration three times to 0.24 M, no obvious increase in viscosity was observed in the first stage of polymerization. The probable reason is that the initiated monomer needs a longer time to propagate polymer chains in a less concentrated monomer solution.

Using TLC (thin layer chromatography) cyclohexane:ethyl acetate = 3:1 as the mobile phase, the degree of monomer consumption was monitored. From ¹H NMR spectrum we can determine whether all the monomer was polymerized or not. The completion of the polymerization was indicated by the total disappearance of monomer olefin proton peaks at 6.05-6.25 ppm and appearance of polymer backbone double bond proton peaks at 5.18-5.55 ppm. We
found that it took a longer time to complete the reaction as we increased the amount of cyanoethyl ester monomer in the first step of ROMP. After all the first block monomer was consumed, norbornene was added as the second block to the still living polymer mixture. It took the same time to complete the second stage of polymerization.

One of the biggest problems in the synthesis of this series of diblock copolymers was how to remove the high-colored ruthenium catalyst from the products. The residual ruthenium can cause problems such as olefin isomerization during distillation of the product, decomposition over time and the increased toxicity of the final materials. After we precipitated the polymer mixture into the vigorously stirred cold methanol, in most cases we obtained brown crude polymers that contained Ru catalyst. Even if we repeated precipitation several times, it was still difficult to get rid of the ruthenium catalyst. We found only a few literature references that mentioned using chromatography (short column of silica gel) to remove some impurities from ROMP. According to the solubility of our diblock copolymers, CH$_2$Cl$_2$:THF = 4:1 was chosen as the mobile phase for elution of the polymer solution through the short column. It turned out that it took a longer time to elute out all the polymers when part of the catalyst remaining. An alternative technique for the removal of ruthenium from olefin metathesis reaction products was explored reported for the ring-closing metathesis (RCM) products (small molecules). We found this was also useful for ROMP products (polymers).

Tris(hydroxymethyl)phosphine is a moderately air stable and water soluble phosphine. It has been reported that this phosphine can readily coordinate to the ruthenium resulting in a complex soluble in water. When the crude product containing ruthenium was added to a solution of the phosphine and triethylamine in methylene chloride, the color of the solution change from black-brown to pale yellow within several minutes, indicating that phosphine has
been coordinated to the ruthenium.\textsuperscript{56} Due to the insolubility of our diblock copolymers in water, we could not simply add water to the polymer mixture to remove the water-soluble phosphine-ruthenium complex. It was also known that phosphine is polar and is able to graft onto silica gel.\textsuperscript{64} By running the polymer solution through a short silica gel column or stirring the polymer solution with silica gel, we were able to remove most of the ruthenium catalyst. It turned out that the latter method gave better results as it was indicated in the literature.

**Characterization of Diblock Copolymers**

\textsuperscript{1}H NMR spectra of five diblock copolymers are shown in Figures 18-22. The vinylic proton peaks at 6.00 and 6.25 ppm for norbornene and its cyanoethyl ester derivative disappeared and the diblock copolymer had new vinyl protons in the range 5.18-5.55 ppm. From \textsuperscript{1}H NMR, the ratio between m and n was estimated which is equal to the ratio of two blocks’ vinyl proton integration. For example, in Figure 18, the new vinyl proton peak at 5.25-5.52 ppm indicated four proton units resulting from both blocks of the copolymer backbone. The methylene peak (two proton units) at 4.21-4.41 ppm was due to the cyanoethyl ester pedant chain, which is equal to the integration area of the two-vinyl proton units from the same block backbone. It was found that the integration of the vinyl peak and the methylene peak was 1.05 and 0.92, respectively. Thus, the vinyl integration from the first block was 0.92, the same as its methylene peak integration. The second block vinyl integration was 1.05–0.92 or 0.13, resulting in m:n = 0.92:0.13 = 7:1. Using same method we were able to find actual m to n values for all five diblock copolymers (Table 4).
Figure 18. $^1$H NMR estimation of block ratio for 7:1 diblock copolymer.

Figure 19. 300 MHz $^1$H NMR spectrum of 3:1 diblock copolymer.
Figure 20. 300 MHz $^1$H NMR spectrum of 1:1 diblock copolymer.

Figure 21. 300 MHz $^1$H NMR spectrum of 1:3 diblock copolymer.
Figure 22. 300 MHz $^1$H NMR spectrum of 1:10 diblock copolymer.

Table 4. Block ratio and molecular weight of diblock copolymers.

<table>
<thead>
<tr>
<th>Block ratio (target)</th>
<th>m:n (target)</th>
<th>$M_n^a$ (theo)</th>
<th>m:n$^b$ (NMR)</th>
<th>$M_n^c$ (GPC)</th>
<th>Block ratio$^d$ (calculated)</th>
<th>PDI$^c$ ($M_w/M_n$)</th>
</tr>
</thead>
<tbody>
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<td>193 : 28</td>
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<tr>
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<td>3 : 1</td>
<td>55,470</td>
<td>250 : 82</td>
<td>1.59</td>
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<tr>
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<td>27,720</td>
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</tr>
<tr>
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<td>1 : 2</td>
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<td>1 : 3</td>
<td>35,770</td>
<td>76 : 227</td>
<td>1.27</td>
</tr>
<tr>
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<td>1 : 7</td>
<td>84,900</td>
<td>1 : 10</td>
<td>71,230</td>
<td>63 : 630</td>
<td>1.37</td>
</tr>
</tbody>
</table>

a. Theoretical molecular weights were calculated according to [monomer]/[initiator] ratio.
b. m : n calculated from $^1$H NMR.
c. Number average molecular weight ($M_n$) and Polydispersity Index (PDI) determined by GPC in THF and reported relative to polystyrene standards.
d. Based on the m : n ratio found from $^1$H NMR and $M_n$ found from GPC, polymer block ratio was calculated.
Molecular weights were determined by GPC using a universal calibration curve obtained from the polystyrene standard. The actual molecular weight values were close to the calculated theoretical molecular weights $M_{n, \text{theo}}$ (Table 5). $M_{n, \text{theo}}$ was calculated in accordance with the target block ratios. For instance, we know the molecular weights of the first and the second repeat unit are 191 and 94, respectively; if the target block ratio is 200 : 20, then: $M_{n, \text{theo}} = 191 \times 200 + 94 \times 20 = 40,080$.

We know that monomer concentration has an effect on the rate of propagation in the first stage in our ROMP. We also found that the specific functional group of the norbornene monomer affected the PDI of ROMP polymers. It was reported that the homopolymer of norbornene had a polydispersity index (PDI) of 2.0 when initiated with Grubbs catalyst in ROMP. After adding the initiation catalyst, in just a few minutes, the norbornene solution became viscous, and polymerization was completed in an hour. The rapid increase in viscosity indicated that norbornene had a higher rate of propagation than that of initiation (propagation started before full initiation of norbornene), which resulted in a high PDI. Under controlled monomer concentration, after completely polymerizing the cyanoethyl ester norbornene monomer, we added the unfunctionalized norbornene as the second block. We found that synthesized diblock copolymers had lower PDI (Table 5) than the norbornene homopolymer, which means that adding functionalized cyanoethyl ester norbornene monomer as the first block apparently lowers the rate of propagation in the unfunctionalized norbornene second block polymerization.

The thermal stability of synthesized diblock copolymer was evaluated by TGA. The results are shown in Figure 23-27. Different ratios between the two blocks have effects on the thermal stability of the copolymers. We found that pendant cyanoethyl ester chains decompose before the norbornene backbone. The first peak on the TGA indicated the decomposition of
cyanoethyl ester sidechain, and the second peak indicated the polymer backbone decomposition. When we decreased the amount of the cyanoethyl ester group in the copolymer, the first decomposition peak appeared at a higher temperature, indicating higher stability of the copolymer. For example, the cyanoethyl ester rich copolymer (7:1) had an early decomposition temperature at 320 °C and increased to a maximum at 470 °C; but the norbornene rich copolymer (1:10) had a thermal decomposition at 450 °C and 600 °C, respectively.

**Figure 23.** TGA analysis of 7:1 diblock copolymer.
Figure 24. TGA analysis of 3:1 diblock copolymer.

Figure 25. TGA analysis of 1:1 diblock copolymer.
Figure 26. TGA analysis of 1:3 diblock copolymer.

Figure 27. TGA analysis of 1:10 diblock copolymer.
Experimentally, the homopolymer of norbornene had a $T_g$ of 40 °C and the homopolymer of norbornene with pendant cyanoethyl ester sidechain had a $T_g$ of 50 °C. DSC analysis (Figures 28-32) shows that diblock copolymers 7:1, 3:1, 1:1, 1:3 and 1:10 have $T_g$’s at 50, 47, 45, 44 and 42 °C, respectively, which match well with the calculated $T_g$ value (49, 48, 46, 44 and 41 °C, respectively) from the Fox Equation:

$$1 / T_g = W_a / T_{g,a} + W_b / T_{g,b}$$  \hspace{1cm} (1)

Where $T_{g,a}$ and $T_{g,b}$ are the glass transition temperatures of the homopolymers a and b. $W_a$ and $W_b$ are the weight fractions of polymers a and b. Figure 33 is a $T_g$ comparison of all five diblock copolymers. The $T_g$ gradually increased with an increasing number of cyanoethyl ester blocks and a decreasing number of norbornene blocks (Table 5).

![DSC analysis of 7:1 diblock copolymer.](image)

**Figure 28.** DSC analysis of 7:1 diblock copolymer.
Figure 29. DSC analysis of 3:1 diblock copolymer.

Figure 30. DSC analysis of 1:1 diblock copolymer.
Figure 31. DSC analysis of 1:3 diblock copolymer.

Figure 32. DSC analysis of 1:10 diblock copolymer.
Figure 33. $T_g$ comparison of five diblock copolymers in same scale.

Table 5. Summary of $T_g$ results for five diblock copolymers.

<table>
<thead>
<tr>
<th>Diblock copolymer m:n (NMR)</th>
<th>$T_g$ °C (observed)</th>
<th>$T_g$ °C (calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 : 10</td>
<td>42</td>
<td>41</td>
</tr>
<tr>
<td>1 : 3</td>
<td>44</td>
<td>44</td>
</tr>
<tr>
<td>1 : 1</td>
<td>45</td>
<td>46</td>
</tr>
<tr>
<td>3 : 1</td>
<td>47</td>
<td>48</td>
</tr>
<tr>
<td>7 : 1</td>
<td>50</td>
<td>49</td>
</tr>
</tbody>
</table>
Synthesis of Maghemite (γ-Fe₂O₃) Magnetic Nanoparticle Dispersions

We chose Pluronic® F127 as a reference copolymer surfactant to prepare stabilized magnetic nanoparticle dispersions due to its amphiphilic properties. We knew that PEO-PPO-PEO could form micelles in aqueous solution and was used to prepare water-based magnetite magnetic fluids. We tried to use this triblock copolymer surfactant to stabilize maghemite nanoparticles in organic solvents. The synthetic steps included synthesis of iron nanoparticles by thermal decomposition of iron pentacarbonyl followed by oxidizing iron nanoparticles to γ-Fe₂O₃ nanocrystallites (Scheme 3). According to the solubility of PEO-PPO-PEO, we chose toluene as the dispersion solvent, whose boiling point is 110 °C, above the decomposition temperature of Fe(CO)₅ (100 °C).

\[
\text{Fe (CO)}_5 \xrightarrow{100 \, ^\circ\text{C}} \text{Fe} + 5 \text{CO} \\
2 \text{Fe} + 3 (\text{CH}_3)_3\text{NO} \rightarrow \text{Fe}_2\text{O}_3 + 3 (\text{CH}_3)_3\text{N}
\]
Scheme 3. Preparation of stabilized $\gamma$-Fe$_2$O$_3$ magnetic nanoparticle dispersions.

F127 in Toluene

or

Diblock copolymer in toluene or cyclohexanone

Add Fe(CO)$_5$

at 100 °C

Orange dispersion

Reflux 2 hrs

Under N$_2$

Brown dispersion

(1) Cool down to r.t.

(2) Add (CH$_3$)$_3$NO

(3) Reflux 4 hrs under N$_2$

Black dispersion

Cool down to r.t

Stabilized magnetic nanoparticle dispersion
Transmission electron microscopy (TEM) was used to study and characterize nanoparticle morphology and nanostructure. The low-resolution TEM image in Figure 34 is an overview of the morphology of the $\gamma$-Fe$_2$O$_3$ ferrofluids. It shows that spherical magnetic nanoparticles were stabilized in toluene by surfactant Pluronic$^R$ F127. We found some micelles with magnetic nanoparticles inside were formed even in organic solvent (Figures 35-38). From high-resolution TEM images (Figures 36 and 38), we saw some aggregation of magnetic nanoparticles and the control of particle size and morphology was not good using the Pluronic$^R$ F127 triblock copolymer. We also studied the effects of amount of iron in ferrofluids on the stability of particles. As we increased the Fe(CO)$_5$ from 0.2 mL to 0.4 mL in the reaction feed, more aggregation was observed (Figures 35 and 37).
Figure 34. Low-resolution TEM of maghemite ($\gamma$-Fe$_2$O$_3$) nanoparticle dispersions stabilized by Pluronic$^R$ F127 in toluene (0.2 mL Fe(CO)$_5$).
Figure 35. Low-resolution TEM of maghemite ($\gamma$-Fe$_2$O$_3$) nanoparticle dispersions stabilized by Pluronic$^R$ F127 in toluene (0.2 mL Fe(CO)$_5$).
Figure 36. High-resolution TEM of maghemite (γ-Fe₂O₃) nanoparticle dispersions stabilized by Pluronic® F127 in toluene (0.2 mL Fe(CO)₅).
Figure 37. Low-resolution TEM of maghemite ($\gamma$-Fe$_2$O$_3$) nanoparticle dispersions stabilized by Pluronic® F127 in toluene (0.4 mL Fe(CO)$_5$).
Figure 38. High-resolution TEM of maghemite (γ-Fe₂O₃) nanoparticle dispersions stabilized by Pluronic® F127 in toluene (0.4 mL Fe(CO)₅).
The synthetic procedure for \( \gamma\text{-Fe}_2\text{O}_3 \) nanoparticle dispersions using our synthesized norbornene diblock copolymers were similar to the steps used for Pluronic\(^{R}\) F127 triblock copolymer (Scheme 3). Stabilized \( \gamma\text{-Fe}_2\text{O}_3 \) nanoparticle ferrofluids were synthesized with five diblock copolymers. Figure 39b shows that the nanoparticle precipitated out when we dispersed them in pure solvent. As a comparison, “homogeneous” ferrofluids were generated when adding norbornene diblock copolymer as a stabilizer (Figure 39a).

High-resolution and low-resolution TEM images (Figures 40-49) show better control of nanoparticle morphology and size using the synthesized norbornene diblock copolymers with anchoring and steirc blocks than that using the commercial triblock copolymer Pluronic\(^{R}\) F127. The spherical magnetic nanoparticles with average diameter of 5-7 nm were found in all the ferrofluids. Generally, nanoparticles stabilized by cyano CN-rich diblock copolymers exhibited less aggregation than that with norbornene-rich diblock copolymers. For example, \( \gamma\text{-Fe}_2\text{O}_3 \) nanoparticles were better dispersed by 7:1, 3:1, and 1:1 diblock copolymers than when 1:3 and 1:10 diblock copolymers were used that possess fewer anchoring groups (-CN). However, this doesn’t mean that the richer the polymer in –CN groups, the better the dispersions. It has an ultimate ratio between copolymer two blocks. When magnetic fluids formed by 7:1, 3:1, and 1:1 cyano-rich diblock copolymers were compared, it was found that the 1:1 diblock copolymer provided the best stabilization of magnetic nanoparticles.

Different solvents were used in the reaction, such as 1,4-dioxane, toluene and cyclohexanone. It was found that \( \gamma\text{-Fe}_2\text{O}_3 \) nanoparticles synthesized in higher boiling point solvent, cyclohexanone, afforded nanoparticles with a nice crystal lattice structure (Figure 41). This is likely due to the fact that after each reflux step we need to cool down the reaction mixture.
to room temperature, the higher the temperature of the mixture, the longer the time to allow nanoparticle crystal formation.

Figure 39. Comparison of the $\gamma$-Fe$_2$O$_3$ nanoparticles stabilized by diblock copolymer in solvent (a) with nanoparticles dispersed in pure solvent (b). The polymer-nanoparticle solution (a) created was 1.25% weight percent of diblock copolymer and 0.23% iron oxide nanoparticles.
**Figure 40.** Low-resolution TEM image of maghemite ($\gamma$-Fe$_2$O$_3$) nanoparticle dispersions stabilized by 7:1 diblock copolymer in cyclohexanone (0.2 mL Fe(CO)$_5$).
**Figure 41.** Clear crystal lattice structures in high-resolution TEM image of maghemite (γ-Fe$_2$O$_3$) nanoparticle dispersions stabilized by 7:1 diblock copolymer in cyclohexanone (0.2 mL Fe(CO)$_5$).
Figure 42. High-resolution TEM image of maghemite (γ-Fe₂O₃) nanoparticle dispersions stabilized by 3:1 diblock copolymer in cyclohexanone (0.2 mL Fe(CO)₅).
Figure 43. High-resolution TEM image of maghemite ($\gamma$-Fe$_2$O$_3$) nanoparticle dispersions stabilized by 3:1 diblock copolymer in cyclohexanone (0.2 mL Fe(CO)$_5$).
Figure 44. High-resolution TEM image of maghemite ($\gamma$-Fe$_2$O$_3$) nanoparticle dispersions stabilized by 1:1 diblock copolymer in cyclohexanone (0.2 mL Fe(CO)$_5$).
Figure 45. High-resolution TEM image of maghemite (γ-Fe₂O₃) nanoparticle dispersions stabilized by 1:1 diblock copolymer in cyclohexanone (0.2 mL Fe(CO)₅).
Figure 46. Low-resolution TEM image of maghemite ($\gamma$-Fe$_2$O$_3$) nanoparticle dispersions stabilized by 1:3 diblock copolymer in cyclohexanone (0.2 mL Fe(CO)$_5$).
Figure 47. High-resolution TEM image of maghemite (γ-Fe$_2$O$_3$) nanoparticle dispersions stabilized by 1:3 diblock copolymer in cyclohexanone (0.2 mL Fe(CO)$_5$).
Figure 48. Low-resolution TEM image of maghemite ($\gamma$-Fe$_2$O$_3$) nanoparticle dispersions stabilized by 1:10 diblock copolymer in cyclohexanone (0.2 mL Fe(CO)$_5$).
Figure 49. High-resolution TEM image of maghemite ($\gamma$-Fe$_2$O$_3$) nanoparticle dispersions stabilized by 1:10 diblock copolymer in cyclohexanone (0.2 mL Fe(CO)$_5$).
Purified polymeric $\gamma$-$\text{Fe}_2\text{O}_3$ nanocomposites and stabilized ferrofluids generated by diblock copolymers were placed under magnetic force. Obvious movement (Figures 50 and 51) was observed even with a weak magnetic force, which indicated high magnetism of the $\gamma$-$\text{Fe}_2\text{O}_3$ nanoparticles.

Electron energy loss spectroscopy (EELS) in the transmission electron microscope was used to identify specific energy loss peaks for stable elements. The potential of EELS combined with TEM for studying samples of geophysical interest has recently been demonstrated. An important application of EELS is the determination of mineralogical parameters such as redox states and crystallographic sites of chemical elements in samples where nanometric spatial resolution is required. We found characteristic peaks of oxygen K edges at 525 eV and iron L$_2$, 3 edge (excitations from the 2$p$ subshell) at about 710 eV (Figure 52), which are in good agreement with the literature results.

The energy dispersive X-ray (EDX) spectrum (Figure 53) showed the iron and oxygen peaks confirming that the nanoparticles are iron oxide. The copper peaks present were due to the TEM sample holder. The X-ray powder diffraction pattern (Figure 54) and electron diffraction pattern (Figure 55) of nanoparticles exhibited a high crystalline structure of maghemite ($\gamma$-$\text{Fe}_2\text{O}_3$) consistent with that reported in the literature.

Comparing the TEM images of $\gamma$-$\text{Fe}_2\text{O}_3$ prepared from commercial triblock copolymer with our norbornene diblock copolymers, it was demonstrated that we were able to better control the morphology and size of nanoparticles. With the latter copolymers, which have iron-chelating pedant chains (-COOCH$_2$CH$_2$CN) and steric norbornene blocks, stabilized ferrofluids can be produced with monodisperse magnetic nanoparticles, possessing a relatively regular particle geometry and a particle size of 5-7 nm.
**Figure 50.** Pure polymeric $\gamma$-Fe$_2$O$_3$ nanocomposites from diblock copolymer magnetic fluids under magnetic force.

**Figure 51.** $\gamma$-Fe$_2$O$_3$ nanoparticles magnetic fluids stabilized by diblock copolymer under magnetic force.
Figure 52. Electron energy loss spectra (EELS) of $\gamma$-Fe$_2$O$_3$ magnetic nanoparticles.

Figure 53. Energy dispersive X-ray (EDX) of $\gamma$-Fe$_2$O$_3$ magnetic nanoparticles.
Figure 54. X-ray diffraction (XRD) pattern of $\gamma$-Fe$_2$O$_3$ magnetic nanoparticles.

Figure 55. Electron diffraction pattern of $\gamma$-Fe$_2$O$_3$ magnetic nanoparticles.
FePt Magnetic Nanoparticle Stabilized by F127 Surfactant

FePt synthesis was performed via a polyol reduction process, in which organometallic salts are reduced. Magnetic nanocomposites are formed by self-assembly of the FePt nanoparticles into triblock copolymer (Pluronic® F127) matrix. We used two different reducing agents in synthetic procedures, one was ethylene glycol and the other was 1,2-hexadecanediol. It turned out that FePt nanoparticles generated using long-chain 1,2-hexadecanediol had less aggregation, better morphology, and smaller particle size (Figures 60 and 61). The EDX profile confirmed that these magnetic particles were FePt (Figure 59). Copper peaks were also from the TEM sample holder.

The synthesis typically produces low-anisotropy face-centered cubic (FCC) FePt nanoparticles, which are disordered with weakly magnetic field. However, through thermal annealing at temperatures 580-650°C, a phase transformation occurs, which turns them into high-anisotropy face-centered tetragonal (FCT) particles with ordered and displayed strong magnetic properties. This can be proved from X-ray diffraction pattern. Figures 56 and 57 show that, for all unannealed particles, the peaks were broad and weak with no ordered superlattice peaks present, which is characteristic for the chemically disordered FePt alloy with FCC phase. The lack of separate peaks of Fe and Pt suggested the alloy structure of Fe and Pt. The peak at 24° in Figure 56 is an amorphous carbon peak of the surfactant. After annealing at 600 °C for 30 min in Ar atmosphere, the XRD (Figure 58) showed superlattice peaks revealing the FCT phase of the FePt alloy. The triblock surfactant has a decomposition temperature that is well below the annealing temperatures, so attempting to anneal the FePt particles with surfactant will destroy the copolymer and result in only particles. This is the reason that no amorphous carbon peak was
detected from XRD of annealed samples. Anneal the FePt particles in Ar prevented the oxidation reaction. Although Pt is a noble metal, Pt oxide is not stable, and Fe can be oxidized to FeO, Fe$_3$O$_4$, and Fe$_2$O$_3$.\textsuperscript{71}

It was reported that fluorescence spectroscopy can be used to characterize nanoparticles in solution.\textsuperscript{74} Very little information in the literature gave the explanation about the role of nanoparticles on peak shifts and intensity changes. We prepared three samples in H$_2$O. According to Figure 64, the solution made of the surfactant and dye and the solution made of the particles and dye both had similar fluorescence profiles with a slight bathochromic shift to longer wavelength for the particle solution. However, when the particles were in the presence of the dye and surfactant, the fluorescence intensity was greatly enhanced with a more significant bathochromic shift towards longer wavelength. This may be due to a new interface interaction between the nanoparticles and polymer surfactant Pluronic$^R$ F127, forming micelles in water.
Figure 56. X-ray diffraction pattern of unannealed FePt nanoparticles stabilized by Pluronic® F127 using ethylene glycol as a reducing agent.

Figure 57. X-ray diffraction pattern of unannealed FePt nanoparticles stabilized by Pluronic® F127 using 1,2-hexadecanediol as a reducing agent.
Figure 58. X-ray diffraction pattern of annealed FePt nanoparticles.

Figure 59. Energy dispersive X-ray of FePt magnetic nanoparticles.
Figure 60. High-resolution TEM image of FePt magnetic nanoparticle dispersions stabilized by Pluronic® F127 (using ethylene glycol).
Figure 61. High-resolution TEM image of FePt magnetic nanoparticle dispersions stabilized by Pluronic® F127 (using 1,2-hexadecanediol).
Figure 62. High-resolution TEM image of annealed FePt redispersed in 1, 4-dioxane.
Figure 63. Enlarged (no scale) TEM image of annealed FePt nanoparticles with clear lattice structure.
Figure 64. FePt nanoparticle influence on UV Fluorescence spectroscopy.

Diblock Copolymer Film Containing Iron Oxide Nanoclusters

We conducted preliminary studies to generate magnetostrictive elastomers (films), and an experiment was conducted to prepare of polymer film containing magnetic nanoparticles. Using static casting, we made a polymeric thin film from 3:1 norbornene diblock copolymer THF solution. We found that FeCl₃ could be dispersed well within the polymer film and, after treatment with NaOH, iron oxide nanoclusters appeared throughout the polymer thin film. Without iron oxide, the polymer film had a nitrile peak 2253 cm⁻¹ and a strong carbonyl group peak at 1733 cm⁻¹ in the FTIR spectrum (Figure 65). The nanocluster-containing polymer film exhibited two new peaks at 2162 and 1557 cm⁻¹ (Figure 66) associated with the chelating of nitrile and carbonyl groups with iron oxide, respectively.
**Figure 65.** FTIR spectrum of static casting polymer thin film.

**Figure 66.** FTIR spectrum of polymer film containing iron oxide nanoclusters.
CONCLUSIONS AND FUTURE WORK

We successfully synthesized an ethynitrile derivative of norbornene carboxylic acid and obtained a series of low polydispersity diblock copolymers functionalized with both anchoring and steric blocks via living ROMP. A series of diblock copolymers with relatively narrow molecular weight distribution were prepared by varying the ratios of the two blocks. The molar ratios between the two blocks of the diblock copolymers were estimated from 1H NMR analysis. The actual number of two blocks was calculated from GPC results. TGA results indicated that the diblock copolymers have good thermal stability, decomposing above 300 °C. Increasing the cyano block of the diblock copolymers decreased the thermal stability (lowered initial decomposition temperature). Measured Tgs of this series of diblock copolymers correlated well with the calculated values from the Fox equation, another demonstration of the block ratios.

Maghemite magnetic nanoparticle ferrofluids were prepared through the decomposition of an iron complex, Fe(CO)$_5$. Comparing magnetic fluids prepared from a commercial triblock copolymer Pluronic$^R$ F127 with that prepared from synthesized norbornene diblock copolymers, possessing both anchoring ([NORCOOCH$_2$CH$_2$CN]) and steric ([NOR]) blocks, the norbornene diblock copolymers were able to better control nanoparticle size and morphology. Ferrofluids generated in norbornene diblock copolymers had monodisperse nanoparticle morphology with less aggregation and average particle size of 5–7 nm. TEM images showed that γ-Fe$_2$O$_3$ nanoparticles were dispersed better by cyano-rich diblock copolymers than norbornene-rich diblock copolymers, which confirmed that the nitrile group is effective for the stabilization of iron oxide magnetic nanoparticles. Future studies can focus on exploring alternative iron-loving groups for magnetic nanoparticle stabilization, such as the conversion of the nitrile (CN) group in
the block copolymers to acetamide (CONH₂), which is a more hydrophilic and in principle, a stronger iron chelating group. Furthermore, copolymers with amphiphilic blocks, [NORCOOCH₂CONH₂] and [NOR] may form micelles in the ferrofluids, a known method to stabilize nanoparticles.

The γ-Fe₂O₃ nanoparticles can be well stabilized in different solvents with diblock copolymers, such as 1,4-dioxane, toluene and cyclohexanone. The lattice structure of γ-Fe₂O₃ nanoparticles was clearly observed when prepared in the higher boiling point solvent cyclohexanone. The structure of the magnetic nanoparticles was characterized by EDX, XRD and EELS. Under magnetic force, obvious movements were observed from both ferrofluids and dry γ-Fe₂O₃ nanoparticles, indicating strong magnetic properties of the particles.

An iron oxide nanoparticle-containing polymer film was prepared by static casting. FTIR analysis results demonstrated that iron oxide chelated with the nitrile (CN) group. The next step would be trying to compare the mechanical strength of the polymer film with and without nanoparticles.

Another type of magnetic nanoparticle, face-centered cubic (FCC) and face-centered tetragonal (FCT) FePt, with a particle diameter of about 3-4 nm was successfully synthesized. The stabilization of FCC FePt nanoparticles with Pluronic® F127 was achieved using a standard polyol reduction of iron acetylacetonate and platinum acetylacetonate method. We compared the effects of different techniques of FePt synthesis on the particle size and morphology. Chemically ordered FCT FePt particles were obtained after annealing at 600 °C in Ar. Further research will be conducted by using norbornene diblock copolymers in preparing FePt dispersions to see if pendant cyanoethyl ester groups also are effective in their stabilization, particle size and morphology control.
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