Chem. Mater. **2006,** *18,* 5929−5936

Norbornene-Functionalized Diblock Copolymers via Ring-Opening Metathesis Polymerization for Magnetic Nanoparticle Stabilization

Kevin D. Belfield*,†,‡ and Li Zhang†

Department of Chemistry and CREOL, College of Optics and Photonics, University of Central Florida, P.O. Box 162366, Orlando, Florida 32816-2366

Received August 24, 2006. Revised Manuscript Received October 11, 2006

There are a number of strategies in molecular nanoscience to prepare stabilized magnetic nanocomposites, including the use of polymeric surfactants. 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. Cyanoester groups were incorporated into the norbornene polymers to chelate and stabilize iron oxide magnetic nanoparticles. These polynorbornene-based copolymers were characterized by GPC, along with ^{1}H NMR, FTIR, DSC, and TGA. Nanostructured maghemite (γ-Fe_2O_3) magnetic ferrofluids were prepared using diblock copolymers as stabilizers in toluene or cyclohexanone, via thermal decomposition of $Fe(CO)_5$ and subsequent oxidation of the iron nanoparticles. Transmission electron microscopic images showed a highly crystalline structure of monodispersed γ-Fe_2O_3 nanoparticles, with average particle sizes varying from 5 to 7 nm.

Introduction

Nanoparticle materials have become the focus of increasing interest in recent years. With particle diameters in the range of 1−10 nm, these materials can exhibit novel electronic, optical, magnetic, and chemical properties due to their extremely small dimensions.[1] Controlled synthesis and assembly of small magnetic nanoparticles have potential applications in ultra-high-density magnetic recording,[2−3] advanced nanocomposite permanent magnets,[4] magnetic ferrofluids, and medical imaging.[5] Growing attention is paid to ferrous magnetic nanoparticles, such as maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4). Due to high magnetization, high magnetic susceptibility, and low toxicity, these iron oxide nanoparticles are promising candidates in magnetic resonance imaging and drug delivery.[6−7]

The tendency of magnetic nanoparticles to aggregate and form clusters is a major obstacle in assembling magnetic nanoparticle composites.[1] When surfactants are used, stabilized magnetic dispersions in a particular fluid are promoted by the adsorption or reaction of steric or electrostatic stabilizers, which prevent the coagulation of the metal particles.[8] Polymeric materials are one of the most suitable nonmagnetic media to disperse magnetic nanoparticles, forming self-assembled polymer nanocomposites in ferrofluids. On one hand, the polymer matrix acts as a stabilizer or controls the particle size; on the other hand, it determines the physicochemical properties of the material or allows surface functionalization.[9] In such polymeric nanocomposites, the polymer is often only weakly bound to the metal particles. However, with freedom in molecular design, block copolymers can be functionalized with a strongly binding headgroup (anchoring block), binding more securely and densely on the metal surface.[10] Our efforts have focused on studies of copolymer systems containing both anchoring (binding headgroup) and steric stabilizing blocks (Figure 1). Thus, the “iron-loving” binding headgroup of block copolymers (siderophore) can chelate and interact with iron or iron oxide nanoparticle surfaces and the steric stabilizing block will prevent metal nanoparticle aggregation.

It is important to choose a polymerization method that tolerates iron-chelating groups and can lead to controlled molecular weight. Ring-opening metathesis polymerization (ROMP) is a variant of the olefin metathesis reaction. The reaction uses strained cyclic olefins to produce stereoregular and monodisperse polymers and copolymers.[11] It has attracted growing interest because of its capability of producing a wide range of functionalized polymers with control over polymer molecular weight and structure by well-defined living ROMP catalysts that are unable to be prepared by other polymeri-

---

* To whom correspondence should be addressed. E-mail: kbelfiel@mail.ucf.edu.

† Department of Chemistry.

‡ CREOL.

(1) Lee, D. K.; Kang, Y. S.; Lee, C. S. *J. Phys. Chem. B* **2002**, *106*, 7267.
(2) Weller, D.; Moster, A. *IEEE Trans. Magn.* **1999**, *35*, 4423.
(3) Weller, D.; Moser, A.; Folks, L.; Best, M. E.; Lee, W.; Toney, M. F. *IEEE Trans. Magn.* **2000**, *36*, 10.
(4) Kneller, E. F.; Hawig, R. *IEEE Trans. Magn.* **1991**, *27*, 3588.
(5) Ziolo, R. F.; Giannelis, E. P.; Winstein, B. A.; O’Horo, M. P.; Ganguly, B. N.; Mehrota, V.; Russel, M. W.; Huffman, D. R. *Science* **1992**, *257*, 219.
(6) Hinds, K. A.; Hill, J. M.; Shapiro, E. M.; Laukkanen, M. O.; Silva, A. C.; Varney, T. R.; Balaban, R. S.; Koretsky, A. P.; Dunbar, C. E. *Blood* **2003**, *102*, 867.
(7) Chatterjee, J.; Haik, Y.; Chen, C. J. *J. Magn. Magn. Mater.* **2003**, *257*, 113.
(8) Dailey, J. P.; Phillips, J. P.; Li, C.; Riffle, J. S. *J. Magn. Magn. Mater.* **1999**, *194*, 140.
(9) Petri, A.; Chastellain, M.; Hofmann, H.; Rao, D. V. *Eur. Cells Mater.* **2002**, *3* (Suppl. 2), 183.
(10) Burke, N. A. D.; Stover, H. D. H.; Dawson, F. P. *Chem. Mater.* **2002**, *14*, 4752.
(11) Toreki, R. *Organometallic Hyper Textbook: Ring Opening Metathesis Polymerization (ROMP)*; Interactive Learning Paradigms, Inc.: Lexington, KY, 2004, http://www.ilpi.com/organomet/romp.html.

10.1021/cm062004u CCC: $33.50

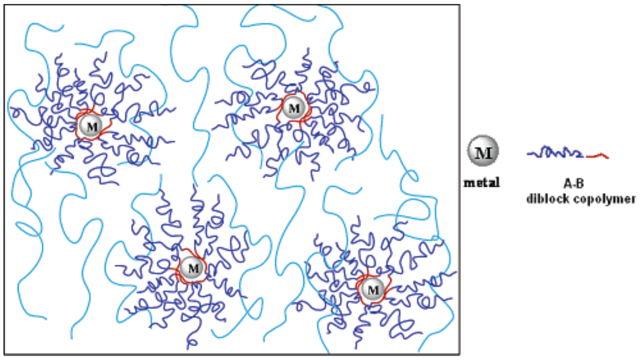
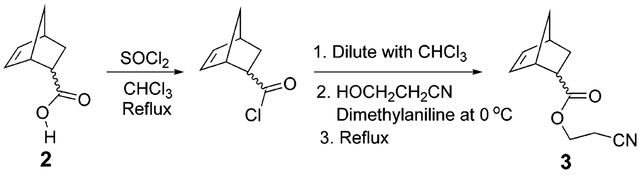


Figure 1. Illustration of block copolymer stabilization of metallic nanoparticles.

zation methods.[12−14] Ruthenium catalysts, such as Grubbs' catalyst and Schrock's Mo ROMP catalysts, have found wide use in the synthesis of block copolymers,[15] affording control over many aspects of the polymer assembly, including molecular weight, molecular weight distribution, alkene backbone configuration, and in some cases, tacticity.[16] 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.[17]

Block copolymer nanoparticles have been formed by the assembly of polymers synthesized by a variety of procedures, such as anionic polymerization and atom transfer radical polymerization.[18,19] A major drawback for many applications is still the lack of well-defined morphology and size of nanoparticles. It was found[20−23] that ROMP provides a particularly attractive route to the formation of polymeric nanostructures of controlled dimensions, and recently for magnetic nanoparticle stabilization.[24,25] Norbornene-based monomers are characterized with high ring strain. 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.[26] Poly(norbornene) is an amorphous polymer with high thermal stability, optical transparency, and low dielectric constant with potential applications. Our previous study[27] demonstrated 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 nanoparticle anchoring group **3**. Via living ROMP, well-defined diblock copolymers **4** with relatively low polydispersity and narrow molecular distribution were prepared. The molar ratio of anchoring block (binding headgroup) and steric block (more hydrophobic) were altered to study its effects on the polymer thermal stability and ferrofluid stability. An ultimate block ratio was found that affords good control of the magnetic nanoparticle size and morphology.

Scheme 1



Experimental Section

Materials. Bicyclo[2.2.1]hept-5-ene 2-carboxylic acid **2** (98%, mixture of *endo* and *exo*), norbornylene (99%), trimethylamine *N*-oxide (98%), tris(hydroxymethyl)phosphine, and bis(tricyclohexylphosphine)-benzylideneruthenium dichloride **1** $\{RuCl_2(CHPh)[P(C_6H_{11})_3]_2\}$ (Grubbs' catalyst) were purchased from Aldrich and used as received. 3-Hydroxypropionitrile (98%, Acros) and $Fe(CO)_5$ (99.5%, Strem) were also used as-received. CH_2Cl_2 and $CHCl_3$ were dried over CaH_2 and $CaCl_2$, respectively, and distilled before use.

Instruments and Methods. Thermogravimetric analysis (TGA) was performed with a TA Instruments model 2050 thermogravimetric analyzer. The temperature range used was from room temperature to 800 or 1000 °C at a rate of 20 °C /min. All the samples were dried under vacuum for 2 days before measurement. Differential scanning calorimetry (DSC) was conducted with a TA Instruments 2920 differential scanning calorimeter. The temperature range was from −10 to 250 °C at a rate of 10 °C /min. ^1H NMR and ^{13}C NMR spectra were acquired on a Varian Mercury Gemini spectrometer at 300 and 75 MHz, respectively. $CDCl_3$ was used as the solvent for both monomer and diblock copolymers. X-ray diffraction (XRD) (Multiplex Rigaku, $\lambda = 0.154$ nm) was used for all the powder X-ray diffraction pattern spectra. Transmission electron microscopy (TEM) was accomplished using 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 2414 refractive index detector, Waters 2996 photodiode array, and Waters 1525 binary HPLC pump (THF as the mobile phase, flow rate at 0.3 mL/min).

Synthesis of Bicyclo[2.2.1]hept-5-ene 2-carboxylic Acid 2-Cyanoethyl Ester 3. The synthetic strategy[28,29] is illustrated in Scheme 1. Specifically, a mixture of *endo*- and *exo*-bicyclo[2.2.1]-hept-5-en-2-carboxylic acid **2** (18.0 g, 130 mmol) and thionyl

---

(12) Katayama, H.; Fukuse, Y.; Nobuto, Y.; Akamatsu, K.; Ozawa, F. *Macromolecules* **2003**, *36*, 7020.

(13) Maughon, B. R.; Grubbs, R. H. *Macromolecules* **1997**, *30*, 3459.

(14) Schrock, R. R. *Ring-Opening Polymerization: Mechanisms, Catalysis, Structure, and Utility*; Brunelle, D. J., Ed.; Hanser Publishers: Munich, 1993; Chapter 4: Ring-Opening Metathesis Polymerization, p 129.

(15) Ahmed, S. R.; Bullock, S. E.; Cresce, A. V.; Kofinas, P. *Polymer* **2003**, *44*, 4943.

(16) Gibson, V. C.; Okada, T. *Macromolecules* **2000**, *33*, 655.

(17) Adlhart, C.; Hinderling, C.; Baumann, H.; Chen, P. *J. Am. Chem. Soc.* **2000**, *122*, 8204.

(18) Liu, S. Y.; Weaver, J. V. M.; Save, M.; Armes, S. P. *Langmuir* **2002**, *18*, 8350.

(19) Pyun, J.; Jia, S.; Kowalewski, T.; Patterson, G. D.; Matyjaszewski, K. *Macromolecules* **2003**, *36*, 5094.

(20) Carrillo, A.; Kane, R. S. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 3352.

(21) Bazan, G. C.; Schrock, R. R.; Cho, H. N.; Gibson, V. C. *Macromolecules* **1991**, *24*, 4495.

(22) Schrock, R. R. *Tetrahedron* **1999**, *55*, 8141.

(23) Kanaoka, S.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 4707.

(24) Sohn, B. H.; Cohen, R. E. *Chem. Mater.* **1997**, *9*, 264.

(25) Sohn, B. H.; Cohen, R. E.; Papaefthymiou, G. C. *J. Magn. Magn. Mater.* **1998**, *182*, 216.

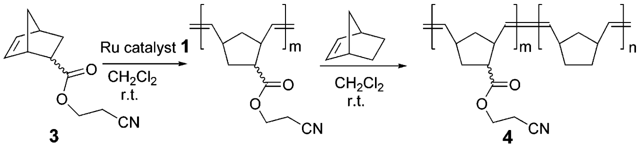
(26) Imgmoglu, Y. *Metathesis Polymerization of Olefins and Polymerization of Alkynes*; Kluwer Academic Publishers: Dordrecht, 1998; pp 189−199.

(27) Belfield, K. D.; Wang, Y. *Polym. Prepr.* **2003**, *44* (1), 1124.

(28) Bueno, M. P.; Cativiela, C.; Mayoral, J. A.; Avenoza, A.; Charro, P.; Roy, M. A.; Andres, J. M. *Can. J. Chem.* **1988**, *66*, 2826.

(29) Stille, J. R.; Santarsiero, B. D.; Grubbs, R. H. *J. Org. Chem.* **1990**, *55*, 843.

Scheme 2



chloride (25.8, 217 mmol) in dry $CHCl_3$ were refluxed under nitrogen for 3 h. Next, the solvent was removed under reduced pressure with a rotary evaporator and the residue was distilled at 0.75 Torr (40 °C) to generate the acid chloride in 80% yield. The acid chloride (10.0 g, 64 mmol) was then diluted with 20 mL of dry $CHCl_3$ and added over 60 min to a mixture of *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 completed, it was heated to reflux with stirring for another 12 h. When the reaction was completed, 65 mL of 6 N H_2SO_4 was used to quench the reaction at 0 °C. The organic and aqueous layers were separated. The aqueous layer was extracted with ethyl ether three times, and the organic extracts were combined. H_2SO_4 (50 mL, 6 N) was used to wash the extract, followed by washing with 2 × 60 mL of H_2O and K_2CO_3 (10% aqueous solution, 2 × 60 mL) to neutralize residual H_2SO_4. Finally, saturated $NaCl_{(aq)}$ (30 mL) was added to "salt out" the organic product. The solvent was evaporated after the mixture was dried over anhydrous Na_2SO_4. Reduced pressure fractional distillation was performed at 0.75 Torr (114−117 °C), affording 10.1 g of colorless oil (*endo* and *exo* mixture) in 83% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 6.20−6.22 (dd, $J = 3.0$, 5.6 Hz, 1H, *endo*-olefinic CH), 6.14−6.17 (dd, $J = 2.8$, 5.6 Hz, 1H, *exo*-olefinic CH), 6.10−6.13 (dd, $J = 2.9$, 5.3 Hz, 1H, *exo*-olefinic CH), 5.95−5.98 (dd, $J = 2.8$, 5.6 Hz, 1H, *endo*-olefinic CH), 4.17−4.32 (m, 2H), 3.25 (s, 1H, *endo*), 3.07 (s, 1H, *exo*), 2.98−3.04 (m, 1H, *endo*), 2.93 (s, 1H), 2.67−2.76 (m, 2H), 2.26−2.31 (m, 1H *exo*), 1.90−1.98 (m, 1H), 1.50−1.53 (d, $J = 8.3$ Hz, 1H, *exo*), 1.38−1.49 (br, 2H), 1.29−1.32 (d, $J = 8.1$ Hz, 1H, *endo*). ^{13}C NMR (75 MHz, $CDCl_3$): δ (*endo*) 174.3, 138.3, 132.3, 117.2, 58.8, 50.0, 46.1, 43.5, 42.9, 29.6, 18.5; δ (*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 $C_{11}H_{13}O_2N$ (191.09): C, 69.09; H, 6.85; N, 7.32. Found: C, 69.06; H, 6.85; N, 7.34. GC-MS (EI, 70 eV): *m/z* 191.02 (M^+, Calcd 191.09), fragmentation *m/z* 121 ($-OCH_2CH_2CN$, 9.1), *m/z* 93 ($-COOCH_2CH_2CN$, 9.2), *m/z* 91 ($C_7H_7^+$, 13.6), *m/z* 66 ($C_5H_6^+$, 100).

General Procedure for Preparation of Polymer 4 by ROMP of Bicyclo[2.2.1]hept-5-ene 2-carboxylic Acid 2-Cyanoethyl Ester and Bicyclo[2.2.1]hept-2-ene (2). ROMP of the cyanoethyl ester monomer 3 with initiator 1 was accomplished according to a literature method[30,31] and shown in Scheme 2. Generally, a catalyst solution (6.4×10^{-3} M) was prepared by dissolving Grubbs' catalyst in dry CH_2Cl_2. The cyanoethyl ester monomer was diluted in dry CH_2Cl_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 into the "living" reaction mixture, and the solution was stirred for another 24 h at room temperature. The color of the solution changed from pink to dark brown. The polymerization was terminated by the addition of 500 equiv of ethyl vinyl ether. After termination, the solution was stirred for an additional 30 min. The reaction mixture was then poured into excess methanol with stirring, and the precipitates went through a further purification process,[32] resulting in a gray to white flaky solid (88%−93% yield). ^1H 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).

Table 1. Target Block Ratio (*m*:*n*) of Five Diblock Copolymers ($[NORCOOCH_2CH_2CN]_m[NOR]_n$), Related Molar Feed Ratio of Monomers and Catalyst, and Reaction Yield

entries	$[NORCOOCH_2CH_2CN]/[I]$	[NOR]/[I]	block ratio (target)	yield (%)
1	200	20	200:20	88
2	100	20	100:20	92
3	100	100	100:100	91
4	100	200	100:200	90
5	100	700	100:700	93

Preparation of Stabilized Magnetic Nanoparticle Dispersions. In preparation of stabilized monodisperse iron oxide nanocrystals within block copolymer matrixes, known methods[33] were modified as follows: the diblock copolymer was dissolved in cyclohexanone, 1,4-dioxane, or toluene and heated to 100 °C, followed by addition of $Fe(CO)_5$ to the polymer solution and reflux 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 to room temperature, trimethylamine *N*-oxide was added to oxidize the iron nanoparticles. Upon reflux for another 4 h under N_2, the solution finally changed color to black and was cooled to room temperature. Stabilized γ-Fe_2O_3 dispersions were observed. Polymer-stabilized γ-Fe_2O_3 nanoparticles were obtained by addition of ethanol to the magnetic nanoparticle dispersions to yield a black powder precipitate and then separation by centrifugation.

Results and Discussion

Monomer Preparation. Synthesis of **3** is illustrated in Scheme 1. The first step of the synthesis was to generate the acid chloride intermediate by treatment of **2** with thionyl chloride. The esterification reaction of the acid chloride with 3-hydroxypropanenitrile was straightforward and high yielding. After fraction distillation, the monomer was dried under vacuum for 24 h. Compared with the starting material **2**, the $-OH$ group was absent in the product ^1H NMR spectrum and two $-CH_2$ proton peaks appeared at 2.75 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 showed three new peaks at 18.5, 58.8, and 117.2 ppm, due to the cyanoethyl ester group.

ROMP To Form Diblock Copolymers 4. Five diblock copolymers with different molar ratios between the anchoring and steric blocks were synthesized according to the feed listed in Table 1. Under mild conditions (room temperature), Grubbs catalyst **1** was used for ROMP according to the procedure described in the Experimental Section (Scheme 2). Grubbs' catalyst is an air- and water-sensitive metal complex. For effective initiation, the reactions were performed in a dry N_2 or Ar-protected environment. The glassware was dried overnight and CH_2Cl_2 was distilled over calcium hydride just before use. To ensure the reaction was "living", the rate of propagation ideally should be ap-

---

[30] Wu, Z.; Benedicto, A. D.; Grubbs, R. H. *Macromolecules* **1993**, *26*, 4975.

[31] Liaw, D. J.; Huang, C. C.; Wu, P. L. *Polymer* **2001**, *42*, 9371.

[32] Maynard, H. D.; Grubbs. R. H. *Tetrahedron Lett.* **1999**, *40*, 4137.

[33] Hyeon, T.; Lee, S. S.; Park, J.; Chung, Y.; Bin, N. H. B. *J. Am. Chem. Soc.* **2001**, *123*, 12798.

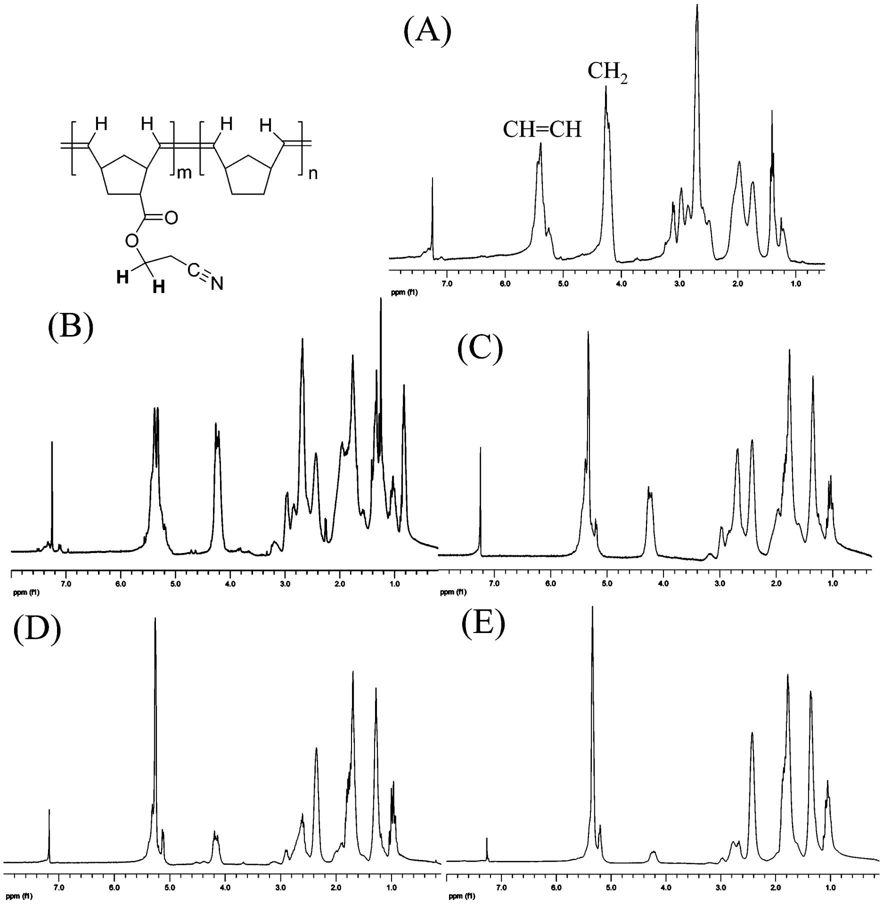


Figure 2. ^{1}H NMR spectra of (A) 7:1 diblock copolymer, (B) 3:1 diblock copolymer, (C) 1:1 diblock copolymer, (D) 1:3 diblock copolymer, and (E) 1:10 diblock copolymer.

Table 2. Block Ratio and Molecular Weight of Diblock Copolymers

block ratio (target)	*m*:*n* (target)	M_n[a] (theo)	*m*:*n*[b] (NMR)	M_n[c] (GPC)	block ratio[d] (calculated)	PDI[c] (M_w/M_n)
200:20	10:1	40080	7:1	39530	193:28	1.28
200:40	5:1	41960	3:1	55470	250:82	1.59
100:100	1:1	28500	1:1	27720	97:98	1.52
100:200	1:2	37900	1:3	35770	76:227	1.27
100:700	1:7	84900	1:10	71230	63:630	1.37

[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, the polymer block ratio was calculated.

proximately the same order of magnitude as the rate of initiation.[11] 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].[34] In the case of entry 1 (Table 1), in the first stage of polymerization, the molar amount of norbornene cyanoethyl ester monomer [$NORCOOCH_2CH_2CN$] was 200 times that of the initiator. Theoretically, the degree of polymerization (*m*) for the first block should be 200, which is expressed as [$NORCOOCH_2CH_2CN$]$_{200}$. According to [NOR]/[I] = 20, the target diblock copolymer was obtained as [$NORCOOCH_2CH_2CN$]$_{200}$-[NOR]$_{20}$.

Monomer consumption was monitored using TLC (cyclohexane:ethyl acetate = 3:1 as the mobile phase) and ^{1}H NMR. 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 olefinic proton signals at 5.18−5.55 ppm. The reaction took longer as the amount of cyanoethyl ester monomer was increased in the first step of ROMP. After all the first block monomer was consumed, norbornene was added to form the second block in the living polymer mixture. It took the same time to complete the second stage of polymerization.

One of the biggest challenges in the preparation of this series of diblock copolymers was removing the highly colored ruthenium catalyst from the polymer. The residual ruthenium can cause problems such as olefin isomerization during heating the product, decomposition over time, and the increased toxicity of the final materials.[32] After precipitation of the polymer mixture into vigorously stirred, cold methanol, in most cases brown crude polymers were obtained that contained Ru, even after repeated precipitation. A few literature reports used short columns of silica gel to remove some impurities after ROMP.[30,35] According to the solubility of the diblock copolymers prepared here, CH_2Cl_2:THF = 4:1 was chosen as the mobile phase for elution of the polymer solution through a short silica gel column. It turned out that a much longer time was needed to elute out the polymers when part of the catalyst was still remaining.

---

(34) Lynn, D. M.; Kanaoka, S.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 784.

(35) Bielawski, C. W.; Benitez, D.; Morita, T.; Grubbs, R. H. *Macromolecules* **2001**, *34*, 8610.

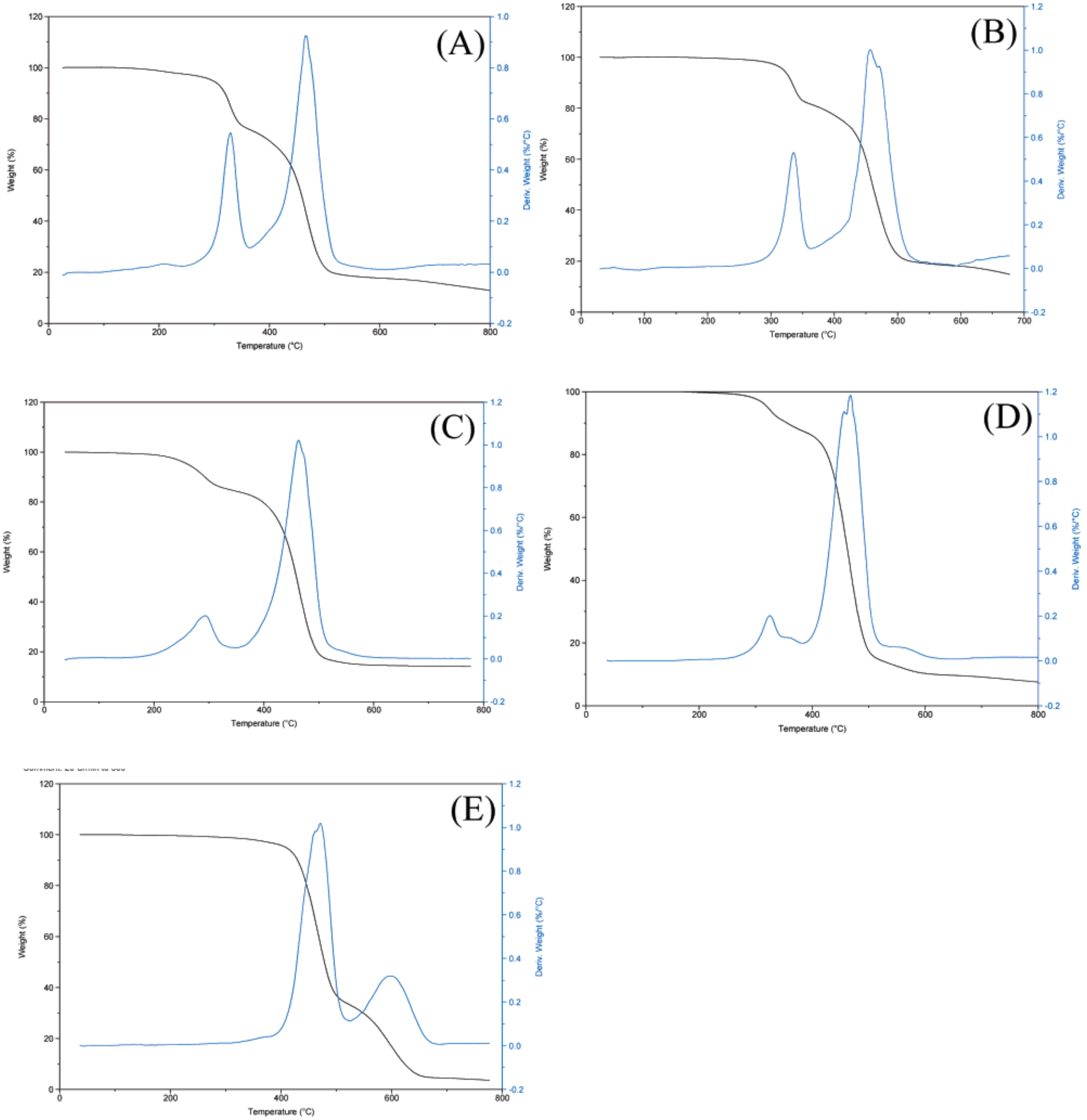


Figure 3. TGA analysis of (A) 7:1 diblock copolymer, (B) 3:1 diblock copolymer, (C) 1:1 diblock copolymer, (D) 1:3 diblock copolymer, and (E) 1:10 diblock copolymer.

An alternative technique for the removal of ruthenium from olefin metathesis reaction products[30] for the ring-closing metathesis (RCM) products (small molecules) was then tried and proved useful for ROMP products (polymers). It has been reported that tris(hydroxymethyl)phosphine can readily coordinate to the ruthenium, resulting in a water-soluble complex.[35−37] When the crude product containing ruthenium was added to a solution of the phosphine and triethylamine in CH_2Cl_2, the color of the solution changed from black-brown to pale yellow within several minutes, indicating that phosphine had been coordinated to the ruthenium.[38] It was also known that the phosphine is polar and is able to graft onto silica gel.[39] With running of the polymer solution, which was treated with the phosphine solution, through a short silica gel column or stirring of the polymer solution with silica gel, the ruthenium catalyst was removed.

Characterization of Diblock Copolymers 4. ^{1}H NMR spectra of five diblock copolymers after purification are shown in Figure 2. 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

---

(36) Ellis, J. W.; Harrison, K. N.; Hoye, P. A.; Orpen, A. G.; Pringle, P. G.; Smith, M. B. *Inorg. Chem.* **1992**, *31*, 3026.

(37) Higham, L.; Powell, A. K.; Whittlesey, M. K.; Wocadlo, S.; Wood, P. T. *Chem. Commun.* **1998**, 1107.

(38) Driessen-Holscher, B.; Heinen, J. *J. Organomet. Chem.* **1998**, *570*, 141.

(39) Shido, T.; Okazaki, T.; Ichikawa, M. *J. Catal.* **1995**, *157*, 436.

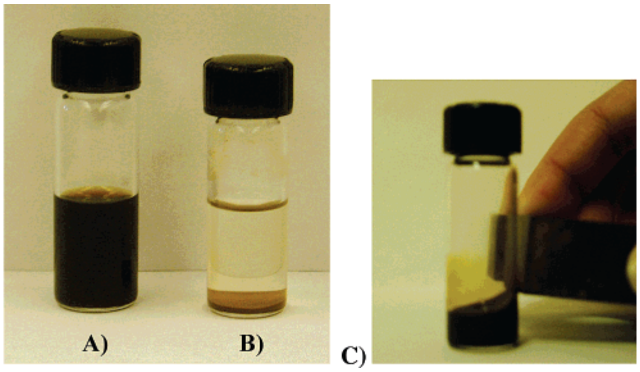


Figure 4. Comparison of (A) γ-Fe_2O_3 nanoparticles stabilized by diblock copolymer in solvent and (B) nanoparticles dispersed in pure solvent without diblock copolymer. The polymer−nanoparticle solution (A) had 1.25 wt % of diblock copolymer and 0.23 wt % iron oxide nanoparticles. (C) γ-Fe_2O_3 nanoparticles magnetic fluids stabilized by diblock copolymer under magnetic force.

protons in the range 5.18−5.55 ppm. From ^{1}H NMR spectral analysis, the ratio between *m* and *n* was estimated according to the ratio of two blocks' vinyl proton integration. For example, in Figure 2a, 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 pendent 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's vinyl proton integration was 0.13 (1.05−0.92), resulting in m:n = 0.92:0.13 = 7:1. When the same methodology was used, the actual *m* to *n* values for all five diblock copolymers were determined (Table 2).

Molecular weights were determined by GPC using a universal calibration curve obtained from polystyrene standards. The actual molecular weight values were in close agreement with the calculated theoretical molecular weights $M_{\mathrm{n,theo}}$ (Table 2). $M_{\mathrm{n,theo}}$ was calculated in accordance with the target block ratios. For instance, the molecular weights of the first and the second repeat unit were 191 and 94, respectively; if the target block ratio was 200:20, then $M_{\mathrm{n,theo}} = (191 \times 200) + (94 \times 20) = 40080$.

The monomer concentration had an effect on the rate of propagation in the first stage in the ROMP. The specific functional group of the norbornene monomer affected the polydispersity index (PDI) of ROMP polymers. It was reported that the homopolymer of norbornene had a PDI of 2.0 when initiated with Grubbs' catalyst **1** in ROMP[40] due to the higher rate of propagation of norbornene than that of initiation.[15] With known monomer concentration, after complete polymerization of monomer **3**, unfunctionalized norbornene was added as the second polymer block. It was found that synthesized diblock copolymers had lower PDI (Table 2) than the norbornene homopolymer.

The thermal stability of the diblock copolymers was evaluated by TGA. The results are shown in Figure 3. Different ratios between the two blocks had pronounced and predictable effects on the thermal stability of the copolymers. It was found that the pendent cyanoethyl ester chains decomposed before the norbornene backbone. The first peak on the TGA indicated the decomposition of cyanoethyl ester side chain, and the second peak resulted from decomposition of the polymer backbone. When the amount of the cyanoethyl ester group in the copolymer was decreased, 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 decomposition temperatures at 320 and 470 °C while the norbornene-rich copolymer (1:10) had a thermal decomposition at 450 and 600 °C, respectively.

The homopolymer of norbornene had a T_{g} of 40 °C and the homopolymer of norbornene with pendent cyanoethyl ester side chains had a T_{g} of 50 °C. The DSC analysis revealed that diblock copolymers 7:1, 3:1, 1:1, 1:3, and 1:10 had T_{g}'s at 50, 47, 45, 44, and 42 °C, respectively, which match well with the calculated T_{g} values (49, 48, 46, 44, and 41 °C, respectively) from the Fox equation,

$$\frac{1}{T_g} = \frac{W_{\mathrm{a}}}{T_{\mathrm{g,a}}} + \frac{W_{\mathrm{b}}}{T_{\mathrm{g,b}}} \tag{1}$$

where $T_{\mathrm{g,a}}$ and $T_{\mathrm{g\ b}}$ 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.

Generation of Magnetic Nanoparticle Dispersions. Iron oxide nanoparticles, including γ-Fe_2O_3 and Fe_3O_4, have been synthesized by using microemulsion, sonication, and other methods. However, particle size uniformity and crystallinity of these nanoparticles are comparatively poor. Hyeon et al.[33] recently reported a novel nonhydrolytic synthetic method of fabricating highly crystalline and monodisperse γ-Fe_2O_3 nanocrystalline particles. Stabilized γ-Fe_2O_3 nanoparticle ferrofluids were generated within norbornene diblock copolymer systems via a slight modification of this procedure (Figure 4). Figure 4b shows that the nanoparticle precipitated out when dispersed in solvent alone. In contrast, stabilized ferrofluids were formed in the presence of norbornene diblock copolymers as surfactant stabilizers (Figure 4a). In a simple qualitative demonstration, γ-Fe_2O_3 nanocomposite stabilized ferrofluids, generated with the diblock copolymers, were placed under magnetic force. Obvious movement (Figure 4c) was observed even with a weak magnetic force, an indication of high magnetism of the synthesized γ-Fe_2O_3 nanoparticles.

High-resolution TEM images (Figures 5) show good control of nanoparticle morphology and size using the functionalized norbornene diblock copolymers with anchoring and steric blocks. The spherical magnetic nanoparticles, with average diameter of 5−7 nm, were found in all the ferrofluids prepared. Generally, nanoparticles stabilized by cyano (CN) rich diblock copolymers exhibited less aggregation than that with norbornene-rich diblock copolymers. For example, γ-Fe_2O_3 nanoparticles were better dispersed by 7:1,

---

(40) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100.

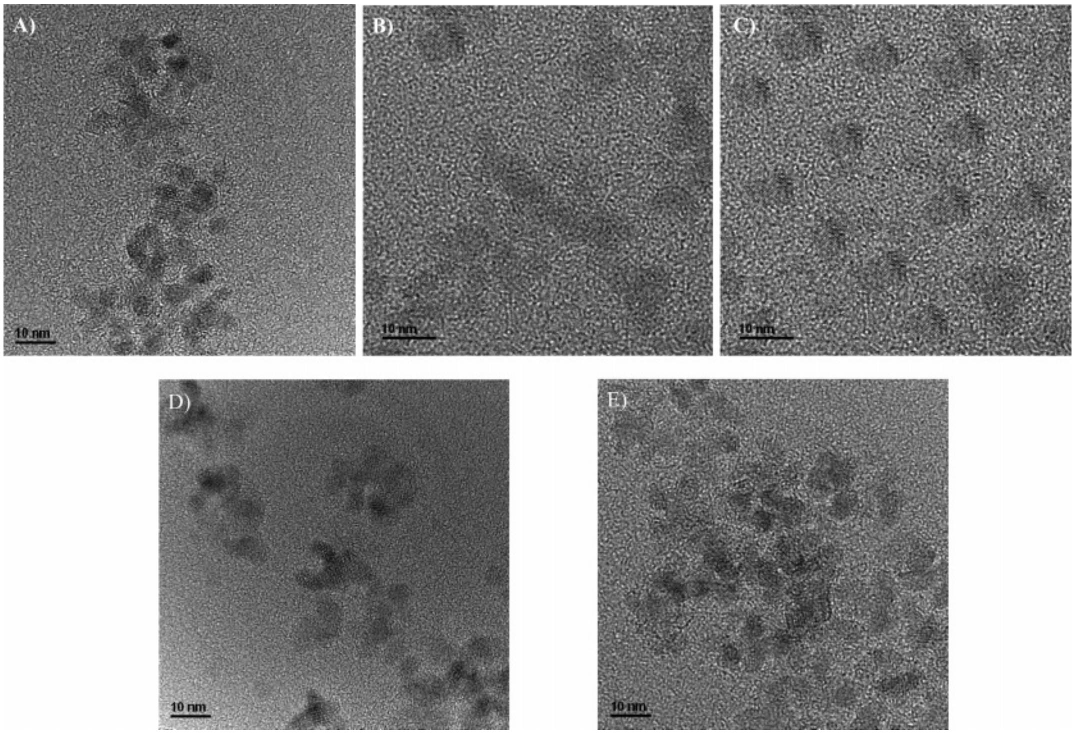


Figure 5. High-resolution TEM image of maghemite (γ-Fe_2O_3) nanoparticle dispersions stabilized by (A) 7:1 diblock copolymer, (B) 3:1 diblock copolymer (less aggregation), (C) 1:1 diblock copolymer, (D) 1:3 diblock copolymer, and (E) 1:10 diblock copolymer (more aggregation), in cyclohexanone.

3:1, and 1:1 diblock copolymers (Figures 5a−5c) than when 1:3 and 1:10 diblock copolymers (Figures 5d and 5e) were used that possess fewer anchoring groups (−CN). The first number in the ratio refers to the CN-containing block while the second number is the unsubstituted norbornene block. However, this does not necessarily mean that the richer the polymer is in −CN groups, the better the dispersions. An ultimate ratio between copolymer two blocks was found to create nanoparticles of relatively uniform size and good dispersion. When magnetic fluids formed using 7:1, 3:1, and 1:1 cyano-rich diblock copolymers were compared, it was found that the 1:1 diblock copolymer (Figure 4c) provided the best stabilization of magnetic nanoparticles.

The effect of solvent on nanoparticle formation was also evaluated by generating the iron-based nanoparticles in situ in various solvents, such as 1,4-dioxane, toluene, and cyclohexanone. It was found that γ-Fe_2O_3 nanoparticles synthesized in the higher boiling point solvent, cyclohexanone, afforded nanoparticles with a nice crystal lattice structure. This is likely due to the fact that after each reflux step the reaction mixture was cooled to room temperature; the higher the temperature of the mixture, the longer the time for nanoparticle crystal formation.

The X-ray powder diffraction pattern (Figure 6) and electron diffraction pattern of the block copolymer-stabilized magnetic nanoparticles exhibited a high-crystalline structure of maghemite (γ-Fe_2O_3), consistent with that reported in the literture.[33,41]

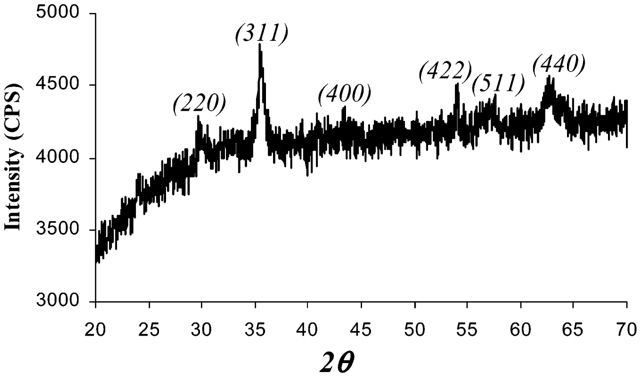


Figure 6. X-ray diffraction (XRD) pattern of synthesized γ-Fe_2O_3 magnetic nanoparticles.

Conclusions

A cyanoethyl derivative of norbornene carboxylic acid was synthesized to prepare a series of relatively low polydispersity (narrow molecular weight distribution), well-defined diblock copolymers, functionalized with varied ratios of anchoring and steric blocks, via living ROMP. The molar ratios between the two blocks of the diblock copolymers were estimated from ^{1}H NMR, and the actual number of two blocks was calculated from GPC results. TGA results indicated that the diblock copolymers possessed good thermal stability, decomposing above 300 °C. Increasing the cyano block of the diblock copolymers decreased the thermal stability (lowered initial decomposition temperature). Measured T_g's of this series of diblock copolymers correlated well with the calculated values from the Fox equation. Maghemite magnetic nanoparticle ferrofluids were prepared in a norbornene diblock copolymer system, which were able to control nanoparticle size and morphology. Stabilized

---

(41) Euliss, L. E.; Grancharov, S. G.; O'Brien, S.; Deming, T. J.; Stucky, G. D.; Murray, C. B.; Held, G. A. *Nano Lett.* **2003**, *3*, 1489.

magnetic nanoparticle ferrofluids were prepared with a relatively monodisperse nanoparticle morphology and an average particle size of 5−7 nm. TEM images showed γ-Fe_2O_3 nanoparticles with clear lattice structure were dispersed better by cyano-rich diblock copolymers than norbornene-rich diblock copolymers, confirming the stabilization ability of the nitrile group.

Acknowledgment. The authors wish to thank the National Science Foundation (ECS-0103587) for support of this work. We thank Dr. Michael Hampton and Ms. Mirna Resan for assistance securing the XRD data and Dr. Helge Heinrich for assistance with TEM.

CM062004U