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Polydimethylsiloxane-magnetite nanoparticle complexes and dispersions in polysiloxane carrier fluids†

K. S. Wilson[1], J. D. Goff[1], J. S. Riffle[1]*, L. A. Harris[2] and T. G. St Pierre[2]

[1]Institute for Macromolecules and Interfaces, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA
[2]School of Physics, The University of Western Australia, Crawley, WA 6009, Australia

Dispersions of sterically stabilized magnetite nanoparticles in polydimethylsiloxane (PDMS) carrier fluids have been prepared for potential biomedical applications. Trivinylsiloxy-terminated PDMS was functionalized with mercaptoacetic acid or mercaptosuccinic acid to afford PDMS stabilizers containing either three or six carboxylic acid groups, respectively, at one chain-end. Magnetite nanoparticles were synthesized by a chemical co-precipitation reaction of $FeCl_2$ and $FeCl_3$ with hydroxide at pH 9–10. Subsequently, the PDMS stabilizers were adsorbed onto the magnetite nanoparticle surfaces via the carboxylate groups in an interfacial reaction at an acidic pH. The complexes were characterized with transmission electron microscopy to establish an average particle diameter of 7.4 ± SD 1.7 nm and approximately spherical shape. Complexes containing up to 67 wt% magnetite were prepared using these PDMS stabilizers, resulting in maximum saturation specific magnetizations of ~50 emu g^{-1}. The polymer-magnetite nanoparticle complexes could be dispersed in PDMS oligomers to afford polysiloxane ferrofluids. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: nanoparticles; magnetic polymers; dispersions; Polydimethylsiloxane; magnetite

INTRODUCTION

Magnetic fluids comprised of sterically-stabilized magnetite nanoparticles in polydimethylsiloxane (PDMS) oligomers have been prepared which may potentially be utilized for treating detached retinas.[1] At least three major obstacles must be overcome to achieve magnetic fluids suitable for biomedical applications. The magnetic nanoparticles must be stable against oxidation so that the oxygen-rich environment of the body will not affect their magnetization. Magnetic transition metals (e.g. iron, cobalt and nickel) oxidize readily, whereas iron oxides such as magnetite (Fe_3O_4) are much more stable against oxidation. Secondly, polymers that disperse the magnetic nanoparticles in the PDMS carrier fluid and prevent particle aggregation are needed. These polymers should contain two types of segments: a functionalized segment that adheres to the nanoparticle surface and a non-polar tail that extends into the PDMS fluid and prevents particle aggregation by steric repulsion. Finally, the magnetic fluids must be rigorously purified to avoid any toxicity.

Most of the literature on magnetite stabilization describes aqueous dispersions. Homopolymer stabilizers such as poly(methacrylic acid),[2] dextran,[3] poly(vinyl alcohol),[3] carboxylic acid-functional poly(ethylene oxide),[4] and sodium poly(oxyalkylene diphosphonate)s,[5] block copolymer stabilizers such as poly(ethylene oxide-b-methacrylic acid),[6] and graft copolymers such as poly(alkylene oxide-g-acrylic acid)[7] have been utilized to prepare aqueous magnetite dispersions. Magnetite dispersions in non-polar fluids[8–10] typically utilize oleic acid as a stabilizer. Non-polar magnetic PDMS fluids containing cobalt nanoparticles have been synthesized previously in our laboratories by thermolysis of dicobalt octacarbonyl in the presence of PDMS-b-(3-cyanopropyl)methylsiloxane-b-PDMS.[11] These fluids were stable in terms of dispersion quality, but the cobalt nanoparticle surfaces oxidized with time upon exposure to air. Magnetic silicone fluids containing magnetite have also been described in the patent literature using a polysiloxane surfactant[12] or a two-surfactant system in which the first was oleic acid and the second was a functionalized polysiloxane.[9] Unfortunately, very few details of the compositions and nature of these complexes were provided in the patents.

The focus of this research has been to synthesize and characterize stable, magnetic PDMS fluids, which could be utilized as biomaterials. The fluids were prepared by complexing magnetite nanoparticles having cationic surfaces with carboxylate-functional PDMS stabilizers, and then dispersing the PDMS-magnetite complexes in non-functionalized PDMS homopolymers. By combining the oxidative stability of magnetite and the biocompatibility of PDMS, it is anticipated that these fluids will be suitable for biomedical applications.

**Correspondence to*: J. S. Riffle, Institute for Macromolecules and Interfaces, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA.
E-mail: judyriffle@aol.com
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EXPERIMENTAL

Materials

Hexamethylcyclotrisiloxane (Gelest, D_3) was dried over calcium hydride and sublimed under vacuum into preweighed, flame-dried, roundbottom flasks, each containing a magnetic stirbar. The flasks were purged with nitrogen and re-weighed to determine the exact amount of D_3 in each flask. *n*-Butyllithium was generously donated by the Lithium Division of FMC as a solution in hexane (2.43 M) and was titrated with diphenylacetic acid prior to use.[13] Cyclohexane (EM Science, 99%) was stirred with concentrated sulfuric acid for 1 week, washed with deionized water until neutral, stirred over calcium hydride, distilled, stored over sodium under a nitrogen atmosphere, and distilled prior to use. Tetrahydrofuran (THF) (EM Science, 99.5%) was dried over calcium hydride, distilled, stored as a purple sodium/benzophenone dispersion under a nitrogen atmosphere, and distilled just prior to use. Trivinylchlorosilane (Gelest) was distilled under reduced pressure prior to use. Toluene (Burdick and Jackson, 99.9%) was distilled from calcium hydride and deoxygenated by sparging with dry nitrogen prior to use. Ethyl acetate (Mallinckrodt, 99.9%) was deoxygenated by sparging with dry nitrogen prior to use. Ammonium hydroxide (Alfa Aesar, 50% v/v aqueous) was used as received. Aqueous hydrochloric acid (25% by volume) was prepared, for example, by adding 5 ml concentrated hydrochloric acid (EM Science) to 15 ml deionized water in a graduated cylinder. Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) and ferrous chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$), both from Aldrich, were stored under nitrogen in a dessicator and used as received. Mercaptoacetic acid (97%), mercaptosuccinic acid (97%), and 2,2′-azobisisobutyronitrile (AIBN, 98%) were all used as received from Aldrich.

Synthesis of trivinylsiloxy-terminated PDMS

An exemplary procedure for preparing a 2100 g mol^{-1} PDMS oligomer with a trivinylsiloxy group at one end is provided. The reaction was conducted in a rigorously cleaned, flame-dried, nitrogen-purged roundbottom flask containing a magnetic stirbar and enclosed with a rubber septum bound with copper wire. Cyclohexane (42 ml) was added via a syringe to the flask containing the D_3 monomer (41.42 g, 0.187 mol) and the monomer was dissolved at room temperature. Next, *n*-butyllithium (7 ml, 18.8 mmol) was added via a syringe. This solution was stirred for approximately 1 hr followed by the addition of THF (58 ml), and the progress of the reaction was monitored by ^{1}H-NMR. At ~96% conversion of the monomer, the reaction was terminated with excess trivinylchlorosilane (4.4 ml, 28.2 mmol) and stirred overnight. The polymer solution was filtered and then concentrated by evaporating most of the solvent under reduced pressure. The concentrated polymer solution was precipitated into methanol, stirred for 90 min, and washed a second time with methanol for 30–90 min. The PDMS was separated from the methanol in a separatory funnel, diluted with chloroform, and washed three times with deionized water. Finally, chloroform and any other residual solvents were removed by drying under reduced pressure at 80°C for several hours. The products were clear, colorless liquids.

Thiol-ene addition of mercaptoacetic acid to the trivinylsiloxy end group

These reactions were conducted in either ethyl acetate or toluene with from one to three moles of mercaptoacetic acid relative to the equivalents of vinyl groups.

The 2350, 4270, and 7290 g mol^{-1} trivinylsiloxy-terminated polymers were functionalized in ethyl acetate according to the following representative procedure. A 2350 g mol^{-1} PDMS (20 g, 8.5 mmol) was weighed into a roundbottom flask equipped with a magnetic stirbar. Ethyl acetate (13 ml) was charged via a syringe and the solution was bubbled with dry nitrogen. AIBN (67.7 mg, 0.41 mmol) was added and the flask was purged with nitrogen. Mercaptoacetic acid (2.1 ml, 30.3 mmol) was added via a syringe and the reaction flask was placed in an oil bath at 55°C. The reactions were monitored via ^{1}H-NMR by following the disappearance of the peaks corresponding to the vinyl protons. The reactions were complete after approximately 20 hr. The solvent was removed under vacuum, and the concentrated polymer solution was precipitated into water. The polymer was dissolved in chloroform and washed with water three times. Sodium chloride was added to break up emulsions formed during the washing process. The solutions were concentrated, filtered to remove salts, and the remaining solvent was removed under reduced pressure at 60°C.

A 1270 g mol^{-1} trivinylsiloxy-terminated PDMS was functionalized by a thiol-ene addition reaction in toluene. The 1270 g mol^{-1} PDMS (20.0 g, 16 mmol) was added to a clean, nitrogen-purged roundbottom flask equipped with a magnetic stirbar. Toluene (200 ml) was added via a syringe, and the polymer solution was bubbled with dry nitrogen to remove oxygen. AIBN (0.125 g, 0.76 mmol) and mercaptoacetic acid (10.6 ml, 0.153 mol) were added to the flask, and the mixture was reacted at 80°C for 45 min. The polymer was purified by removing the toluene under reduced pressure at 30°C. The polymer was dissolved in methanol and stirred for 30 min. (Note: The low molecular weight polymers with carboxylic acid functional groups were soluble in methanol, whereas most PDMS oligomers are insoluble in methanol.) Water was added and the polymer coagulated. The polymer was collected and the dissolution/coagulation process was repeated. The polymer was collected, dissolved in methanol, and dried over magnesium sulfate. The solution was filtered once by vacuum filtration and filtered twice through syringes equipped with 0.1 μm Whatman Anotop 25 mm filters. The polymer was dried under reduced pressure at 35°C.

Thiol-ene addition of mercaptosuccinic acid to the trivinylsiloxy end group

These reactions were conducted in ethyl acetate since mercaptosuccinic acid is insoluble in toluene. In a representative example, mercaptosuccinic acid (2.07 g, 13.8 mmol) was weighed into a roundbottom flask containing a magnetic stirbar and ethyl acetate (29 ml) was added. Next, trivinylsiloxy-terminated PDMS (2350 g mol^{-1}, 10 g, 4.3 mmol) was weighed into the flask. AIBN (70 mg, 0.4 mmol) was weighed separately and added to the solution. The flask was sealed with a rubber septum bound with copper wire and purged with dry nitrogen. The reaction was stirred in an oil bath maintained at 55°C for 15 hr and conversion of the vinyl

groups was monitored by ^{1}H-NMR. The polymers were purified as described previously for the thiol-ene addition reactions conducted in ethyl acetate.

Studies to confirm that the acidic conditions utilized in synthesizing the PDMS stabilizers did not affect their molecular weight distributions

Two reaction conditions were modeled using 1270 g mol^{-1} PDMS. PDMS (0.5 g), ethyl acetate (5 ml), and mercaptoacetic acid (0.28 ml) were added to a roundbottom flask and stirred at 65°C for 3.5 hr. In the second set of conditions, PDMS (0.5 g), toluene (5 ml), and mercaptoacetic acid (0.28 ml) were added to a roundbottom flask and stirred at 80°C for 45 min.

Preparation of PDMS-magnetite nanoparticle complexes

A representative example for preparing a PDMS-magnetite complex charged with 30 wt% magnetite is described. The magnetite (theoretically 0.86 g) was prepared by a chemical co-precipitation reaction. The iron chloride salts, $FeCl_3{\cdot}6H_2O$ (2.0 g, 7.4 mmol) and $FeCl_2{\cdot}4H_2O$ (0.736 g, 3.7 mmol), were each dissolved separately in 20 ml of deoxygenated water and then combined in a two-necked, nitrogen-purged roundbottom flask, equipped with a rubber septum and mechanical stirrer. The aqueous solution was vigorously stirred while adding ammonium hydroxide (~20 ml) until the reaction mixture reached pH 9–10. Black, magnetite nanoparticles precipitated immediately upon adding the base. After 15–30 min, a solution containing the carboxylate terminated PDMS stabilizer (2.0 g) in dichloromethane (60 ml) was added to the aqueous magnetite dispersion. The two phases were vigorously stirred for 15–30 min. While stirring, aqueous hydrochloric acid was added dropwise until the dispersion became acidic (pH ~3) as determined with pH paper. The PDMS-magnetite nanoparticle complexes were separated from the emulsion by evaporating the dichloromethane under reduced pressure using a rotary evaporator. If any non-complexed magnetite was present, this remained in the aqueous phase while the PDMS-magnetite nanoparticle complexes congealed into a hydrophobic phase. The solid-rubbery, black, PDMS-magnetite nanoparticle complex was washed with water once and methanol twice, then collected with a permanent magnet. The complex was dissolved in chloroform and centrifuged until no significant amount of magnetite precipitated from the dispersion. The chloroform was removed under vacuum and the complex was washed three times with methanol, several times with water, and dried under reduced pressure at ~40°C.

Preparation of magnetic PDMS fluid dispersions

An aliquot of 15,000 g mol^{-1} PDMS (2.5 g) was dissolved in chloroform (20 ml) in a roundbottom flask. The PDMS was synthesized by living polymerization of D_3 using *sec*-butyllithium as the initiator and was terminated with trimethylchlorosilane. A PDMS-magnetite nanoparticle complex (5.0 g) containing a 1400 g mol^{-1} PDMS stabilizer and displaying a saturation magnetization of 48 emu g^{-1} was added to the PDMS solution. The solution was ultrasonicated in 2-sec intervals for a total of approximately 20 sec. The chloroform was removed under reduced pressure in a rotary evaporator. The dispersion was washed with methanol three times (to remove any non-complexed PDMS surfactant) and then washed with water four times by mixing thoroughly with a spatula and collecting the dispersion with a magnet. The product was dried under vacuum at 45°C.

Measurements and instrumentation

^{1}H-NMR and ^{29}Si-NMR spectra were obtained on a Varian Unity 400 NMR instrument operating at 400 and 80 MHz, respectively, using chloroform-*d* as the solvent. Quantitative ^{29}Si-NMR analyses were obtained using inverse gated decoupling, approximately 500 scans, and chromium(III) acetylacetonate as a relaxation reagent. Polymer molecular weights and polydispersities were determined using a Waters 2690 GPC instrument equipped with Styragel columns HR-1, HR-2, HR-3 and HR-4, a viscosity detector (Viscotek model T60A) and an external refractive index concentration detector. Samples were analyzed using chloroform as the solvent at a flow rate of 1 ml min^{-1}. Transmission electron microscopy (TEM) images of PDMS-magnetite complexes and dispersions were obtained using a Philips 420T transmission electron microscope with an accelerating voltage of 100 kV. The magnetite complexes and dispersions were diluted with toluene until a light brown color was achieved. A few drops of each were deposited onto carbon-coated copper grids (SPI Supplies, West Chester, PA) and the grids were allowed to air-dry. The presence of both iron and oxygen in the particles was confirmed by acquiring ''elemental maps'' using a Gatan image filter (GIF) attached to a JEOL 3000F FEGTEM.

The particle size distributions were obtained by measuring the largest dimension of individual particles within a defined region of a micrograph. Areas containing aggregates were avoided in the analysis. Vibrating sample magnetometry (VSM) was performed using a Lakeshore model 7300 magnetometer. The applied field was ramped from +8000 to −8000 Gauss and the saturation magnetizations of the samples were recorded. Elemental analysis was performed by Desert Analytics Laboratory (Tucson, AZ) by treating the samples with hot concentrated nitric acid followed by concentrated perchloric acid until complete dissolution was achieved. The sample solution was analyzed by inductively coupled plasma (ICP) to determine the percent iron. The percent iron was calculated from sample response relative to standards and blanks. Viscosities of the magnetic dispersions were determined using a Brookfield rheometer model DVIII and the reported viscosities were obtained at 25°C. Carboxylic acid functional PDMS stabilizers were titrated in isopropanol with methanolic potassium hydroxide utilizing phenolphthalein as an indicator.

RESULTS AND DISCUSSION

Synthesis of PDMS dispersion stabilizers with multiple carboxylic acid groups at one end only

Living anionic ring-opening polymerization of D_3 has been well documented.[14–17] This technique was utilized herein to synthesize a series of PDMS oligomers having one trivinylsiloxy end group in a range of controlled molecular weights.

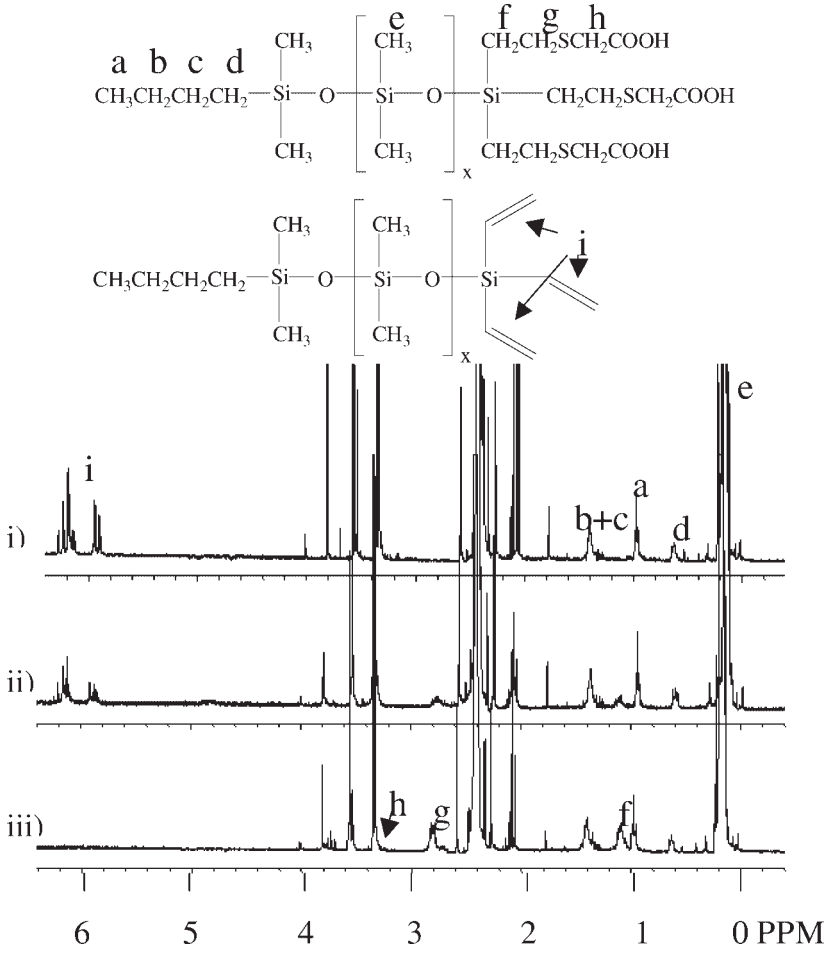


Figure 1. ^{1}H-NMR spectra monitoring the thiol-ene addition of mercaptoacetic acid to a 2000 g mol^{-1} trivinylsiloxy-terminated PDMS at: (i) 0 min; (ii) 15 min; (iii) 45 min.

The polymerizations were monitored with ^{1}H-NMR by following the disappearance of the D_3 methyl peak at 0.2 ppm and concurrent appearance of the methyl protons on the polymer repeat units at 0.05 ppm. The polymers were terminated with trivinylchlorosilane prior to 100% conversion to avoid any backbiting reactions that may occur upon depletion of the monomer. NMR analysis was also utilized to determine number average molecular weight (M_n) by comparing the integrations of the initiator *n*-butyl peaks at 1.25, 0.9, and 0.5 ppm to the integration of the methyl peaks of the PDMS repeat unit at 0.05 ppm (Fig. 1). Quantitative termination of the living chain end with the trivinylchlorosilane was verified by comparing the integrations of the butyl peaks to the integrations of the vinyl peaks at ~6.0 ppm. Similarly, ^{29}Si-NMR was employed to calculate M_n and verify complete termination with the trivinylsiloxy group (Fig. 2). Four peaks were observed in the ^{29}Si-NMR spectra and were attributed to the two terminal silicon atoms, $BuMe_2SiO-$ (8 ppm) and $(H_2C{=}CH-)_3SiO-$ (−27 ppm), and the silicon atoms of the polysiloxane repeat units, $-SiMe_2O-$ (−22 ppm). The peak at −19 ppm corresponded to the silicon atom of the polysiloxane chain adjacent to the terminal functionalized silicon atom (trivinylsiloxy or acid-functionalized). Gel permeation chromotography (GPC) chromatograms showed sharp, unimodal peaks indicating narrow molecular weight distributions characteristic of polymers synthesized by living polymerizations. Absolute molecular weights were obtained from GPC by using polystyrene standards with a universal calibration. A summary of molecular weights calculated from ^{1}H-NMR, ^{29}Si-NMR and GPC for the series of trivinylsiloxy-terminated polymers is provided in Table 1.

The trivinylsiloxy-terminated polymers were functionalized with a controlled number of terminal carboxylic acid groups utilizing thiol-ene addition reactions (Scheme 1). Free radical additions of thiols across vinylsilanes proceed well since such vinyl groups do not polymerize significantly by free radical addition. Thiol-ene reactions have previously been utilized by Chojnowski and coworkers to add mercaptoacetic acid across the vinyl groups of poly(dimethylsiloxane-b-methylvinylsiloxane) and poly((dimethylsiloxane-co-methylvinylsiloxane)-b-dimethylsiloxane) copolymers.[18] Those reactions were conducted in toluene at 80°C and 98% of the vinyl groups were converted to the *β*-addition product. Thiol-ene reactions have also been employed to incorporate *t*-butyl[19] and pyridinyl[20] groups into polysiloxanes through pendent vinyl groups. In the research presented herein, carboxylic acid groups were added to one end of the polymer, resulting in PDMS surfactants with non-polar PDMS tails and

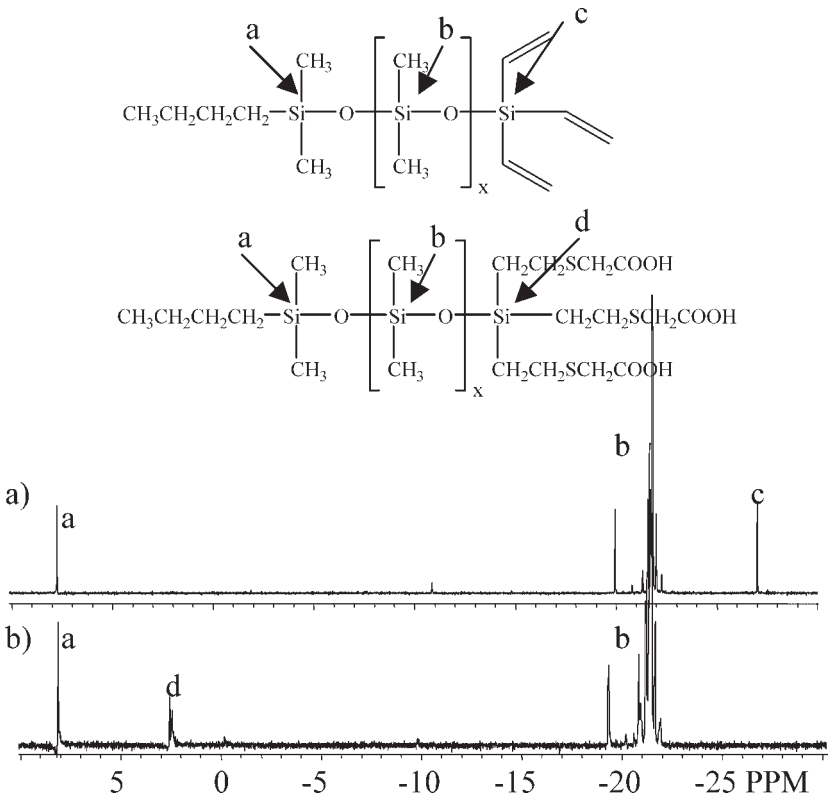


Figure 2. ^{29}Si-NMR spectra showing: (a) 2200 g mol^{-1} trivinylsiloxy-terminated PDMS; (b) 2600 g mol^{-1} trimercaptoacetic acid-terminated PDMS.

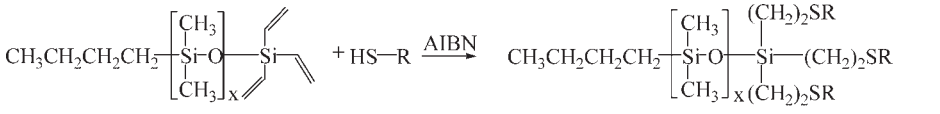
Table 1. Number average molecular weights and polydispersities obtained from ^{1}H-NMR, ^{29}Si-NMR and GPC for trivinylsiloxy-terminated PDMS oligomers

Target M_n (g mol^{-1})	M_n by ^{1}H-NMR (g mol^{-1})	M_n by ^{29}Si-NMR (g mol^{-1})	M_n by GPC (g mol^{-1})	M_w/M_n
1220	1180	1140	2170	1.06
2280	2350	2510	3080	1.04
4430	4270	4600	5770	1.03
7290	7290	7930	9150	1.01

functionalized head groups containing either three (mercaptoacetic acid addition) or six (mercaptosuccinic acid addition) carboxylic acid groups.

The thiol-ene additions were monitored with ^{1}H-NMR by following the disappearance of the vinyl peaks at ~6.0 ppm (Fig. 1). Table 2 summarizes the series of polymers that were prepared. The average numbers of carboxylic acid groups per butyl end group were confirmed by titrating the polymers in isopropanol with a methanolic solution of potassium hydroxide and employing molecular weights derived from ^{1}H-NMR. The degrees of functionalization agreed reasonably well with the targeted amounts of one (mercaptoacetic acid) or two (mercaptosuccinic acid) carboxylic acids per vinyl end group on the precursors.

The carboxylic acid-functional polymers were analyzed by GPC to optimize the required reaction conditions for obtaining thiol-ene addition versus any unwanted vinylsilane polymerization. It was noted that polymers functionalized in reactions containing approximately 1 to 1.1 moles of mercaptan per vinyl sometimes exhibited shoulders (or even bimodal peaks) on the main peak in the GPC traces. For example, an addition reaction conducted in ethyl acetate that utilized approximately 1.1 equivalents of acid per vinyl resulted in a polymer with a bimodal GPC chromatogram (see Fig. 3b). One peak corresponded to the expected molecular weight of a single PDMS chain and the second peak (at lower elution volumes) appeared to represent two chains that had coupled. It is proposed that the coupling was



R = -CH_2COOH (mercaptoacetic acid),

-CH(COOH)CH_2COOH (mercaptosuccinic acid)

Scheme 1. Thiol-ene addition of mercaptocarboxylic acids to trivinylsiloxy-terminated PDMS.

Table 2. Characterization of the carboxylic acid-containing PDMS surfactants

M_n by ^{1}H-NMR (g polymer/mole butyl end group)	M_n by ^{29}Si-NMR (g polymer/ mole butyl end group)	Targeted #COOH per butyl end group	#COOH per butyl end group (titration)
1400	1350	3	2.3
2620	2710	3	3.0
4540	4600	3	2.8
7560	8400	3	2.7
2800	—	6	5.7
4720	—	6	5.5
7740	—	6	5.5

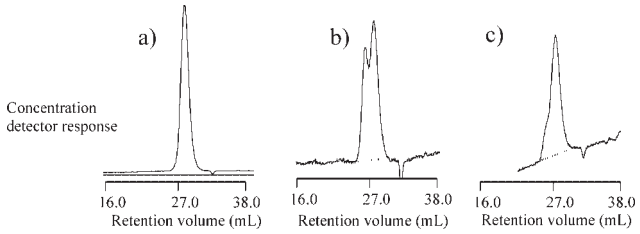
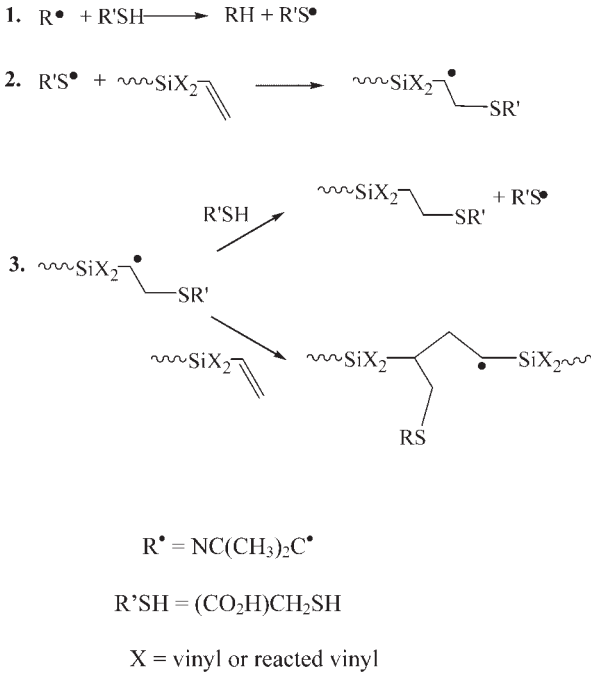


Figure 3. GPC chromatograms of a 4270 g mol^{-1} PDMS: (a) trivinylsiloxy-terminated; (b) after the thiol-ene addition of mercaptoacetic acid with 1.1 mole of mercaptoacetic acid per equivalent of vinyl; and (c) after the thiol-ene addition of mercaptosuccinic acid with 1 mole of mercaptosuccinic acid per equivalent of vinyl. The bimodal nature of "b" and high molecular weight shoulder on "c" suggest that some chain coupling occurs under these conditions.

caused by a free radical reaction between vinyl end groups on two PDMS chains (Scheme 2). Step 2 of the reaction scheme depicts addition of the mercaptoacetic acid thiol radical across the vinyl group, as expected. In step 3, the newly formed radical species can either abstract a hydrogen radical from a second molecule of mercaptoacetic acid or add across a vinyl group on another PDMS chain. According to this proposed mechanism, the coupling reaction should become more prominent toward the end of the reaction when there is less mercaptoacetic acid available for hydrogen abstraction. Consistent with this premise, a 1270 g mol^{-1} trivinylsiloxy-terminated PDMS was functionalized by utilizing 3.0 equivalents of mercaptoacetic acid per vinyl, and this material displayed a unimodal GPC trace. It should be noted, however, that all of the carboxylate-functional PDMS oligomers functioned well as dispersion stabilizers for magnetite. Thus, the small amounts of coupling in some of these materials did not significantly inhibit dispersion stabilization.

It is well known that siloxane bonds (Si–O) are susceptible to cleavage by acids and bases, and that this can cause redistributions of polysiloxane molecular weights.[21,22] During the thiol-ene addition reactions, the PDMS oligomers were exposed to mercaptoacetic or mercaptosuccinic acid at temperatures between 55 to 80°C for 45 min to several hours. Thus, controlled studies were conducted to establish that



Scheme 2. Proposed free radical mechanism involving PDMS-vinylsilyl chain coupling.

these acidic conditions did not affect PDMS molecular weight distributions. In each of the two conditions studied, three moles of mercaptoacetic acid were used for every equivalent of vinyl. AIBN was not added to the solutions because the goal was to simulate the conditions of the thiol-ene addition reactions without executing the free radical addition reaction. One PDMS sample was exposed to mercaptoacetic acid in ethyl acetate at 65°C for 3.5 hr and the other in toluene at 80°C for 45 min. The polymers were analyzed by GPC after exposing them to the acidic conditions, and the results were compared to the 1270 g mol^{-1} trivinylsiloxy-terminated PDMS control (Fig. 4). Since these were low molecular weight chains, the GPC was able to separate oligomers that differed by only one or two siloxane repeat units, which resulted in four overlapping peaks in the GPC chromatograms. No significant differences were detected between the control ($M_n = 2330$, $M_w/M_n = 1.04$), the PDMS exposed to acidic conditions in toluene ($M_n = 2340$, $M_w/M_n = 1.06$), and the PDMS exposed to acidic conditions in ethyl acetate ($M_n = 2240$, $M_w/M_n = 1.06$). These results suggested that

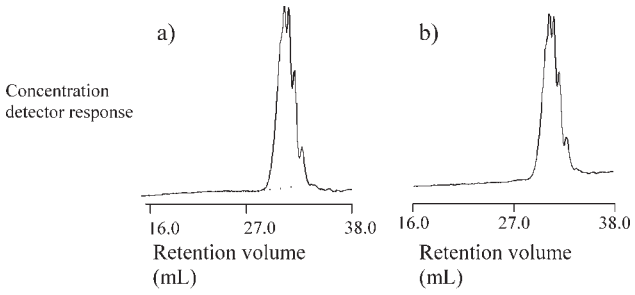


Figure 4. GPC chromatograms showing: (a) 1270 g mol^{-1} trivinylsiloxy-terminated PDMS; (b) 1270 g mol^{-1} trivinylsiloxy-terminated PDMS after exposure to acidic conditions at 80°C for 45 min.

Table 3. Characterization of PDMS-magnetite complexes

Stabilizer[a] (g mol^{-1})	wt% magnetite charged	wt% Fe (elemental analysis)	wt% Fe_3O_4	Specific saturation magnetization (emu g^{-1} complex)
1400 PDMS$(COOH)_3$	30	45	63	45.7
	50	48	67	49.2
	60	48	67	51.6
2620 PDMS$(COOH)_3$	30	32	45	35.8
	50	35	49	37.3
	60	40	56	38.6
4540 PDMS$(COOH)_3$	30	27	37	25.0
	50	33	46	31.1
	60	37	51	34.1
7560 PDMS$(COOH)_3$	30	17	24	15.3
	50	21	29	20.1
2800 PDMS$(COOH)_6$	30	30	42	27.9
	50	37	51	38.5
	60	38	52	34.5
4720 PDMS$(COOH)_6$	30	27	37	27.7
	50	32	44	36.2
7740 PDMS$(COOH)_6$	30	14	20	13.9
	50	16	22	15.6

[a] PDMS$(COOH)_3$ denotes stabilizers functionalized with mercaptoacetic acid and PDMS$(COOH)_6$ denotes stabilizers functionalized with mercaptosuccinic acid.

both sets of conditions were sufficiently mild to avoid significant cleavage of the PDMS chains.

PDMS-magnetite nanoparticle complexes

A series of PDMS surfactants having approximately three or six terminal carboxylic acid groups were synthesized to establish relationships between PDMS composition (molecular weight and number of carboxylic acid groups) and the amount of PDMS surfactant that could be bound to the magnetite nanoparticles. One objective was to calculate the magnetite surface area occupied per PDMS chain and to determine how the type of polar head group (mercaptoacetic acid or mercaptosuccinic acid) related to the surface area coverage.

PDMS-magnetite nanoparticle complexes were prepared with the PDMS surfactants and the amount of magnetite nanoparticles charged to the reactions was varied between 30, 50 and 60 wt%. First, the magnetite nanoparticles were synthesized in aqueous chemical co-precipitation reactions at pH 9–10 following a previously reported method.[4] Upon adding the hydroxide base, the initially clear yellow solutions immediately turned black, indicating the precipitation of magnetite nanoparticles. Next, a solution of the carboxylic acid-functionalized PDMS in dichloromethane was added to the aqueous magnetite dispersion to adsorb the polymer onto the particle surfaces. The aqueous magnetite dispersion would completely separate from the organic phase if stirring was discontinued, suggesting that the carboxylic acid groups did not bind to the magnetite at the basic pH.

In the last step of the reaction, the pH was adjusted to be slightly acidic. The change in pH resulted in transfer of the magnetite particles from the aqueous phase to the organic phase. In reactions where the magnetite complexation was highly effective, the final aqueous phases were clear and colorless with no observable traces of magnetite. The pH of the dispersion (pH 3–6) was below the isoelectric point of magnetite (≈pH 6.8),[23] where the magnetite surface had a net positive charge and above the pK_a of mercaptoacetic and mercaptosuccinic acid (≈3) so that the carboxylic acid groups were mostly dissociated. It is proposed that at the acidic pH values, dissociated PDMS carboxylic acid groups (carboxylate groups) at the dichloromethane-water interface adsorbed onto the cationic surface of the magnetite.

At a basic pH, the carboxylate groups were unable to bind to the anionic magnetite surface. Similar results were previously found by our research group in a study that utilized carboxylic acid-functionalized poly(ethylene oxide) to stabilize magnetite nanoparticles in aqueous dispersions.[4] It was found that dispersions of the poly(ethylene oxide)-magnetite nanoparticle complexes were stable at pH 2–7 but were unstable at pH values greater than or equal to 8. These results also suggested that the carboxylate groups were bound to magnetite at neutral to acidic pH values, but not at a basic pH. In the current study, the surfaces of the magnetite nanoparticles were effectively coated with PDMS at a neutral to slightly acidic pH, and these particles were dispersible in the dichloromethane phase but not in water.

Following purification, the PDMS-magnetite nanoparticle complexes were solid, rubbery, or viscous liquid materials depending on the molecular weight of the stabilizer and magnetite concentration. The complexes were studied by elemental analysis to determine the concentration of magnetite and by VSM to determine the mass specific saturation magnetizations (Table 3). The complexes were also analyzed by TEM to verify particle size and shape (Fig. 5). The average magnetite particle size for one sample was calculated to be 7.4 ± 1.7 nm and was determined by averaging the diameters of hundreds of particles, excluding particle clusters where individual particles could not be identified (Fig. 6). The magnetite particles were approximately spherical in shape and their general size and shape did not vary between samples.

These analyses verified that the molecular weight of the PDMS stabilizer had a large influence on the compositions of the PDMS-magnetite nanoparticle complexes. For example, complexes made with 7560 or 1400 g mol^{-1} PDMS containing

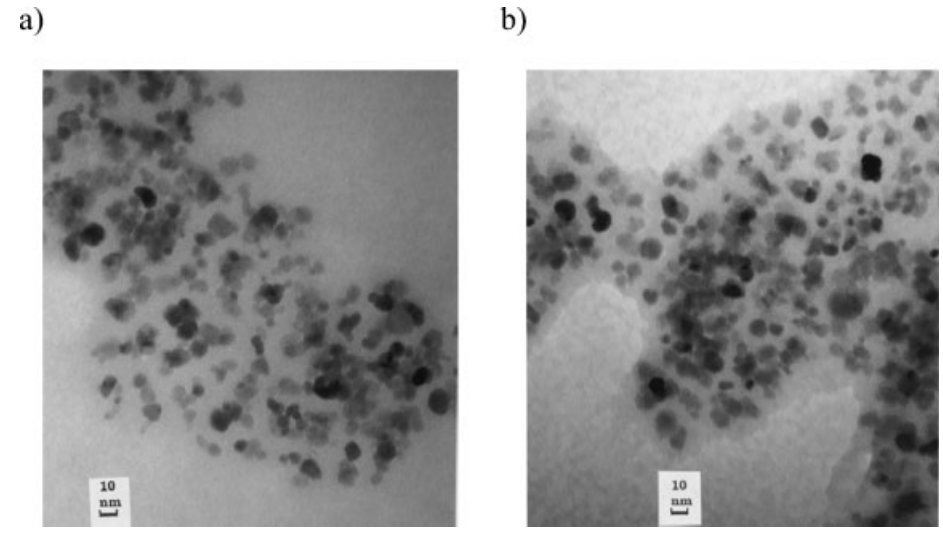


Figure 5. TEM images: (a) PDMS-magnetite complex containing 50 wt% magnetite and a 3500 g mol^{-1} PDMS(COOH)$_3$ stabilizer; (b) the same complex dispersed in a 2000 g mol^{-1} PDMS carrier fluid.

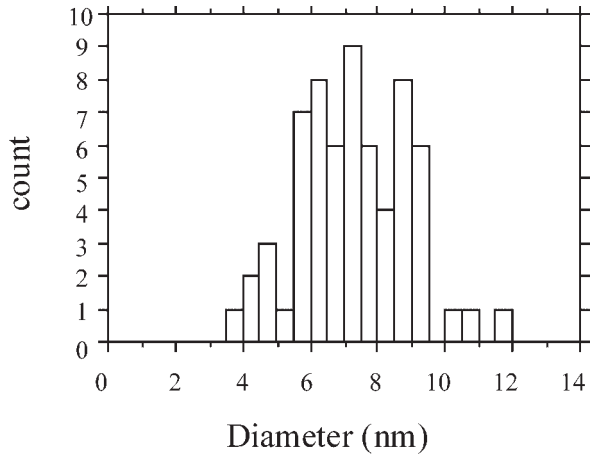


Figure 6. Histogram depicting the distribution of magnetite particle diameters.

three carboxylic acid groups per chain and wherein the reactions had been charged with 30 wt% magnetite contained 24 and 63 wt% magnetite, respectively. This difference in magnetite concentration resulted from the fact that the lower molecular weight stabilizers contained more carboxylic acid groups per gram of polymer than the higher molecular weight stabilizers. Surprisingly, however, the data also showed that there was little difference in the amount of magnetite complexed by the mercaptoacetic acid and mercaptosuccinic acid-functionalized polymers of a given molecular weight.

To obtain a more quantitative understanding of these results, the compositions from elemental analyses and the particle sizes from TEM were utilized to estimate the amount of magnetite surface covered per PDMS chain (Fig. 7). The total number of PDMS carboxylate groups relative to the numbers of active binding sites on the magnetite were also compared for each complex (Table 4). For example, in the complex that contained the 1400 g mol^{-1} PDMS stabilizer with three carboxylic acid groups at the head of the chains, and 63 wt% magnetite as determined by elemental analysis, a 100-gram sample of this complex containing 63 grams of magnetite and 37 grams of PDMS was considered. An example is provided for calculating the number of PDMS carboxylate groups and the total number of magnetite binding sites in a 100-gram sample of this complex, and for calculating the magnetite surface area coverage per PDMS chain. The average volume per magnetite particle (212 nm^3)

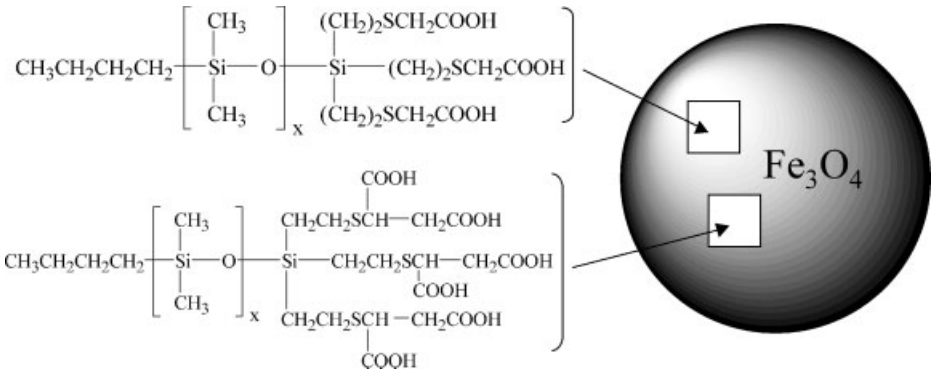


Figure 7. Schematic representation of the magnetite surface area covered by a PDMS chain functionalized with either mercaptoacetic acid or mercaptosuccinic acid.

Table 4. Relationships between the number of COOH groups in the polymer and the number of active magnetite binding sites in the complexes

PDMS surfactant[a]	Magnetite in the complex[b] (g)	PDMS in the complex[b] (g)	Number of polymer COOH groups	Number of active magnetite binding sites	Magnetite surface area (nm^2) per PDMS chain
1400-$(COOH)_3$	63	37	4.77E + 22	5.21E + 22	0.63
	67	33	4.26E + 22	5.54E + 22	0.75
	67	33	4.26E + 22	5.54E + 22	0.75
2620-$(COOH)_3$	45	55	3.81E + 22	3.72E + 22	0.56
	49	51	3.53E + 22	4.05E + 22	0.66
	56	44	3.05E + 22	4.64E + 22	0.88
4540-$(COOH)_3$	37	63	2.50E + 22	3.06E + 22	0.71
	46	54	2.15E + 22	3.81E + 22	1.02
	51	49	1.95E + 22	4.22E + 22	1.25
7560-$(COOH)_3$	24	76	1.83E + 22	1.99E + 22	0.63
	29	71	1.71E + 22	2.40E + 22	0.81
2800-$(COOH)_6$	42	58	7.47E + 22	3.48E + 22	0.54
	51	49	6.31E + 22	4.22E + 22	0.77
	52	48	6.19E + 22	4.30E + 22	0.80
4720-$(COOH)_6$	37	63	4.82E + 22	3.06E + 22	0.73
	44	56	4.28E + 22	3.64E + 22	0.98
7740-$(COOH)_6$	20	80	3.76E + 22	1.65E + 22	0.51
	22	78	3.66E + 22	1.82E + 22	0.57

[a] $(COOH)_3$ denotes stabilizers functionalized with mercaptoacetic acid and $(COOH)_6$ denotes stabilizers functionalized with mercaptosuccinic acid.
[b] Calculations assume 100 g of complex and the relative amounts of magnetite and PDMS were obtained by elemental analysis.

and surface area per particle (172 nm^2) were estimated from the average particle diameter determined by TEM (7.4 nm), the density of magnetite (5.1×10^{-21} g nm^{-3}) was taken from the literature,[24] and the number of active magnetite binding sites (5.2 per nm^2) was also taken from the literature.[25]

$$\begin{aligned}&\#\text{ carboxylates in 100 grams of the complex} = 37\text{ g PDMS}\\&\times (1\text{ mole}/1400\text{ g}) \times (3\text{ COOH/mole PDMS})\\&\times (6.022 \times 10^{23}\text{ chains/mole}) = 4.77 \times 10^{22}\end{aligned}$$

$$\begin{aligned}&\#\text{ magnetite binding sites in 100 grams of the complex}\\&= 63\text{ g magnetite} \times (1\text{ nm}^3/5.1 \times 10^{-21}\text{g})\\&\times (1\text{ particle}/212\text{ nm}^3) \times (172\text{ nm}^2/1\text{ particle})\\&\times (5.2\text{ binding sites/nm}^2) = 5.21 \times 10^{22}\end{aligned}$$

$$\begin{aligned}&\text{magnetite surface area per PDMS chain}\\&= \text{total magnetite surface area} \div \text{molecules of PDMS}\\&= 1.00 \times 10^{22}\text{nm}^2 \div 1.59 \times 10^{22}\text{ PDMS chians}\\&= 0.63\text{ nm}^2\text{ per chain}\end{aligned}$$

The average surface area coverage per PDMS chain for the mercaptoacetic acid and mercaptosuccinic acid-functionalized polymers was 0.79 ± 0.2 and 0.70 ± 0.2 nm^2, respectively. These results suggested that there was no significant difference in magnetite surface area coverage between the two types of functionalized PDMS surfactants, despite the fact that the mercaptosuccinic acid-functionalized PDMS contained twice the number of carboxylate groups. For example, Fig. 8 shows a comparison of the data obtained for complexes prepared using 2620 g mol^{-1} PDMS-$(COOH)_3$ (with mercaptoacetic acid) and 2800 g mol^{-1} PDMS-$(COOH)_6$ (with mercaptosuccinic acid). Calculations on the complexes with the mercaptoacetic acid-functionalized PDMS suggested comparable numbers of magnetite binding sites and carboxylate groups, with small excesses of binding sites. Thus, almost all of the carboxylate groups could have been bound to the cationic magnetite surface. Because these calculations suggest that there were excess binding sites, this suggests that full magnetite surface coverage may not be required for the particles to be stabilized in an organic solvent. However, analogous calculations on complexes with mercaptosuccinic acid-functionalized PDMS stabilizers suggested a large excess of carboxylate groups relative to binding sites. This indicated that many of the carboxylate groups were not bound to magnetite. To reiterate, the PDMS-$(COOH)_6$ and PDMS-$(COOH)_3$ polymer stabilizers complex approximately the same amounts of magnetite but the PDMS-$(COOH)_6$ stabilizers bind in such a way that many of the carboxylate groups remain unbound.

To support these calculations, the mercaptocarboxylate groups and magnetite surface were modeled with Chem3D Pro software utilizing an MM2 energy model. The objective was to obtain a qualitative understanding of the behavior of the PDMS carboxylate groups in the presence of a cationic magnetite crystal surface (Fig. 9). Iron oxide surfaces have

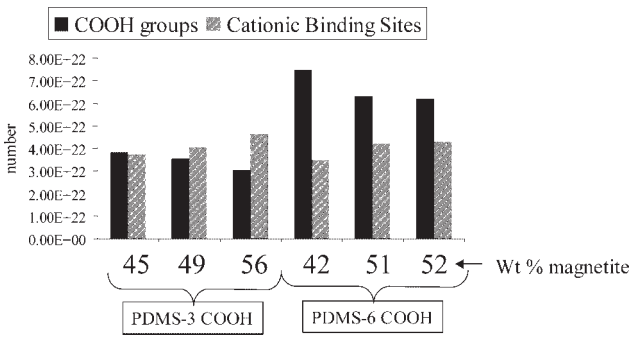


Figure 8. A comparison of the number of COOH groups and magnetite binding sites in PDMS-magnetite complexes prepared using 2620 g mol^{-1} PDMS-$(COOH)_3$ and 2800 g mol^{-1} PDMS-$(COOH)_6$.

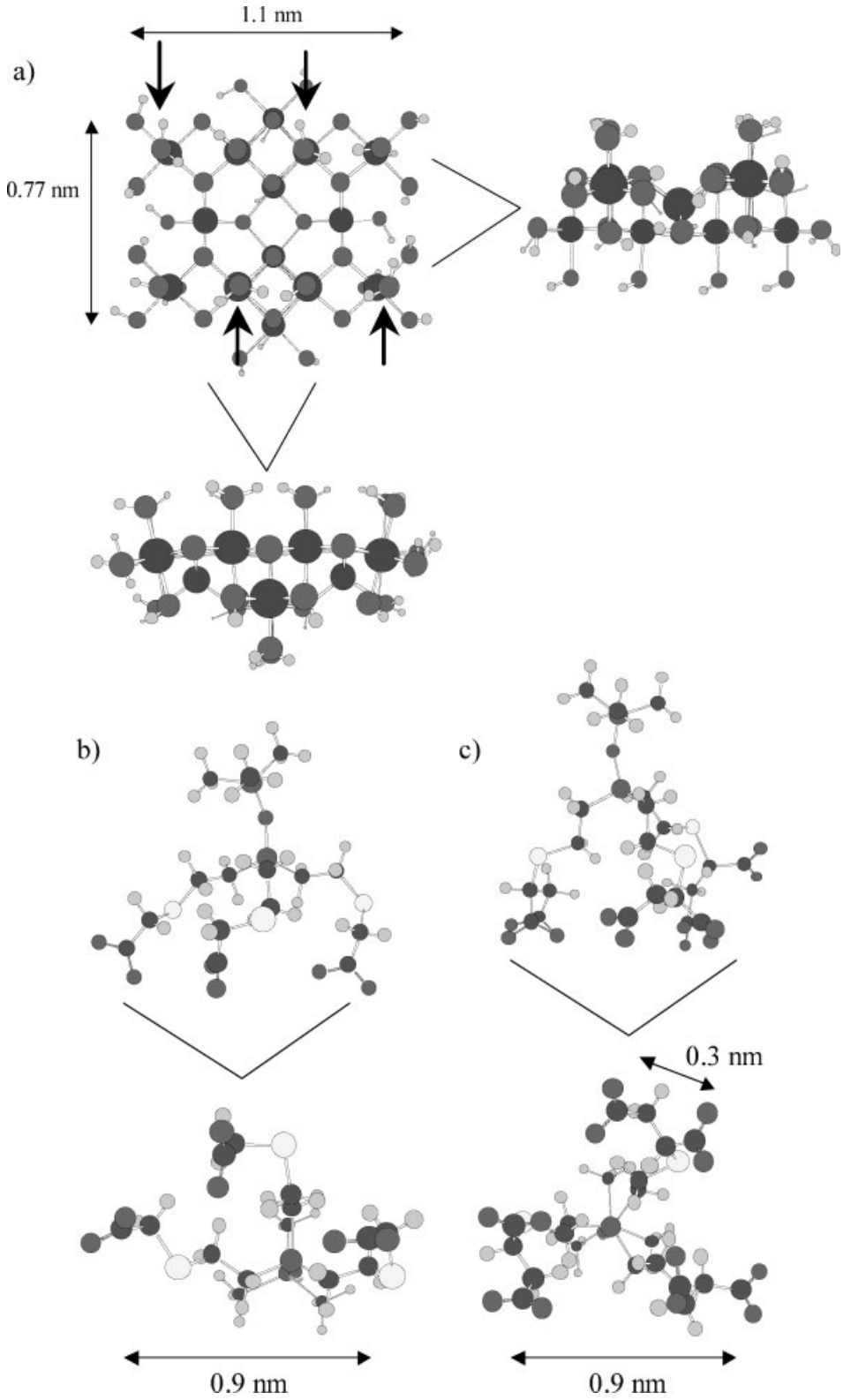


Figure 9. Molecular models generated using MM2 energy models and Chem3D Pro software: (a) magnetite surface (top and side views); (b) PDMS mercaptoacetate end groups; (c) PDMS mercaptosuccinate end groups after energy minimization near a magnetite surface. Cationic surface sites are denoted with black arrows.

been modeled previously to understand the effects of different crystal planes on surface hydration.[26] In the current study, the magnetite surface was designed with approximately 5 cationic binding sites per nm^2 to keep the model consistent with the literature value of 5.2 sites per nm^2 (derived from titration),[25] and cationic sites were modeled as protonated hydroxyl groups. As a simplification, the PDMS carboxylates were modeled using a trimethylsilyl moiety to replace the long PDMS chain. The energies of the PDMS carboxylates were minimized in the presence of the

magnetite surface while keeping the surface unchanged. This minimization allowed for an understanding of the electrostatic interactions between the carboxylate groups and the cationic magnetite surface, but did not provide insight into the binding mechanism. According to the models, the surface area coverage of the mercaptoacetate and mercaptosuccinate groups was in agreement with the coverage derived from TEM and elemental analysis. The models in Fig. 9 predicted that there was 0.9 nm between certain carboxylate groups while the calculations indicated surface areas in the range of 0.7 nm^2. The models showed that there was not a significant difference between the magnetite surface areas covered by the mercaptoacetate and mercaptosuccinate groups under the given conditions. Interestingly, for the surface charge density that was modeled, the average distance between two cationic binding sites on the magnetite surface was 0.6 nm, while the distance between two carboxylate groups on a mercaptosuccinate moiety was 0.3–0.4 nm. This suggested that it was unlikely for both of the mercaptosuccinate carboxylate groups to bind to magnetite. The model prediction that both mercaptosuccinate carboxylate groups cannot bind to magnetite was consistent with the surface area calculations that denoted an excess of mercaptosuccinate carboxylate groups relative to magnetite binding sites.

Magnetic PDMS ferrofluids

Stable, superparamagnetic PDMS fluids were prepared by ultrasonicating the PDMS-magnetite nanoparticle complexes in solutions of PDMS carrier fluids in chloroform, followed by solvent removal and purification of the dispersions. A representative fluid containing 66.6 wt% of a PDMS-nanomagnetite complex [1400 g mol^{-1} PDMS-$(COOH)_3$] and 33.3 wt% of a 15,000 g mol^{-1} PDMS carrier fluid displayed a saturated specific magnetization of 30.7 emu g^{-1}. Lower molecular weight carrier fluids were also investigated. For example, a magnetic fluid containing 75 wt% of a PDMS-magnetite nanoparticle complex [2620 g mol^{-1} PDMS-$(COOH)_3$] and 25 wt% of a 2100 g mol^{-1} PDMS exhibited a saturation magnetization of 23.7 emu g^{-1}. As expected due to the small size of the magnetite particles, neither of these fluids displayed magnetic hysteresis. The fluids respond to applied magnetic field gradients by moving toward the direction of highest field.

The fluids were analyzed by TEM to verify that the morphology of the magnetite particles had not been altered during the ultrasonication procedure. In the TEM image (Fig. 5), the PDMS carrier fluid, visible as a gray material that enveloped the magnetite particles, was observed. Despite dilution of the magnetite complex with the PDMS carrier fluid, the interparticle distances observed in the TEM images of the PDMS-magnetite complex and the complex dispersed in the carrier fluid appeared to be similar. These distances were not assumed to be a measure of the true interparticle distance in the magnetic fluid since the process of solution casting the PDMS film on the carbon-coated TEM grid was expected to affect the distribution of the nanoparticles in the fluid.

The fluid viscosities are of particular interest because the fluids may potentially be used for treating retinal detachments. Thus, detailed investigations of fluid viscosities relative to fluid structure will be conducted at a later time. It is expected that viscosities will be functions of the concentrations of magnetite in the complexes, the concentrations of PDMS-nanomagnetite complexes in the carrier fluids, the molecular weights of the carrier fluids, and the quality of the dispersions in terms of any aggregation.

In addition, both mercaptoacetic acid ($LD_{50} = 250$ mg kg^{-1}) and mercaptosuccinic acid ($LD_{50} = 800$ mg kg^{-1}) are highly toxic materials. In this study, the polymers, complexes, and dispersions were purified to remove these toxic materials. However, purification of the magnetic fluids must be scrutinized in the future before they can be used for treating retinal detachment.

CONCLUSIONS

Methods were developed for preparing PDMS containing approximately three or six terminal carboxylic acid groups at one end only to afford dispersion stabilizers for magnetite nanoparticles in PDMS carrier fluids. PDMS-magnetite nanoparticle complexes were formed by interfacial adsorption of the carboxylic acid functional PDMS stabilizers onto magnetite nanoparticles in slightly acidic media. The studies suggest that the binding process involved adsorption of PDMS carboxylate groups onto positively charged magnetite surfaces.

The compositions of the polymer-magnetite complexes suggested that mercaptoacetic acid and mercaptosuccinic acid functional PDMS stabilizers covered approximately the same magnetite surface area per chain. This was surprising since the mercaptosuccinic acid functionalized polymers contained twice the number of carboxylic acid groups relative to the mercaptosuccinic acid terminated materials. Comparisons between the numbers of carboxylic acid groups in the complexes with literature values for the number of cationic binding sites on magnetite suggest that essentially all of the acid groups on the mercaptoacetic acid functional stabilizers may bind to the surface, whereas many acid groups on the mercaptosuccinic acid functional stabilizers may remain unbound. This may afford an opportunity for subsequent reactions of unbound carboxylate groups to biomolecules.

The PDMS-magnetite complexes could be dispersed in PDMS carrier fluids, resulting in magnetic PDMS fluids that have the potential to be used in future biomedical applications. Careful analyses of such dispersions will be carried out to better understand the characteristics of such dispersions.

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