# Magnetic properties of ceramics from the pyrolysis of metallocene-based polymers doped with palladium

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processing is Solution a facile method to generate magnetic thin films. Polyferrocenylethylmethylsilane (PFEMS) was doped with palladium (II) acetylacetonate using two methods: sublimation of Pd(acac)<sub>2</sub> to form Pd nanoparticles in the PFEMS films and direct mixing of Pd with the PFEMS polymer precursor prior to film deposition. These polymer composites all exhibit paramagnetic behavior, with increasing magnetic susceptibility for increasing Pd content. Pyrolysis of the precursors yields ferromagnetic ceramics at room temperature. The effect of the pyrolysis temperature and atmosphere on the magnetic properties, chemical composition, and crystalline structure of the ceramics was explored. For ceramics containing Pd, FePd alloys are observed to form pyrolyzed under argon at 1000 °C. The formation of these alloys results in enhanced coercivity, remanent magnetization, and saturation magnetization of the ceramics. © 2011 American Institute of Physics. [doi:10.1063/1.3558987]

# I. INTRODUCTION

Organometallic polymers containing transition metals in the backbone have attracted considerable attention<sup>1–4</sup> since the discovery of ferrocene nearly 60 years ago.<sup>5</sup> These materials have properties distinct from their organic and inorganic components<sup>6</sup> and have many applications, including catalysts,<sup>7</sup> sensors,<sup>8</sup> and ceramic precursors.<sup>9</sup> Their solution processing characteristics allow for the possible fabrication of complex and nanostructured shapes<sup>10,11</sup> with a variety of magnetic properties.<sup>12</sup>

One organometallic system that has received a large amount of interest over recent years is the metallocene-based polyferrocenylsilane (PFS).<sup>11,13</sup> PFS is an iron- and siliconcontaining polymer, which, when pyrolyzed, yields magnetizable ceramics due to the presence of iron-containing clusters.<sup>14,15</sup> The size and type of these clusters can be controlled by adjusting the pyrolysis conditions. At lower pyrolysis temperatures (around 600 °C) the formation of ceramics containing small superparamagnetic iron nanoclusters in an amorphous carbon/silicon carbide matrix<sup>16</sup> is observed. Increasing the temperature of pyrolysis to around 1000 °C leads to an increase in the cluster size and the generation of ferromagnetic ceramics containing  $\alpha$ -Fe crystallites.<sup>16</sup> Cross-linking of polymeric precursors allows for higher ceramic yields, magnetic properties that are tunable, and the ability to produce molded ceramics due to high shape retention.<sup>10,12,17</sup> For example, MacLachlan et al.<sup>12</sup> have shown that a cross-linked network of spirocyclic [1]silaferrocenophane can be used to form ceramics, whose properties can be tuned between superparamagnetic and ferromagnetic states, by controlling the pyrolysis conditions. These polymers can be shaped on the macroscopic scale or patterned on the

micron scale prior to pyrolysis, with the ceramic products retaining the patterned shape with high fidelity. Higher ceramization yields and increased iron content are also obtained from hyperbranched polyferrocenylsilanes.<sup>18</sup> These produce mesoporous ferromagnetic materials with a negligible hysteresis loss when pyrolyzed at high temperatures under argon due to the formation of iron silicides. These materials have potential applications for data storage and electromagnetic shielding.<sup>19</sup> PFS has also been used as a precursor to form microspheres with low polydispersity,<sup>10</sup> allowing for the synthesis of microspheres with tailorable redox, semiconductive, and magnetic properties.<sup>20</sup>

Another application of metal-containing polymers is their use as precursors for the synthesis of bimetallic nanoparticles. This has been demonstrated for iron-platinum (FePt) nanoparticles<sup>21</sup> formed from the pyrolysis of bimetallic metallopolyyne precursors. Pyrolysis of PFS precursors with pendant cobalt clusters and polycarbosilanes with pendant nickel clusters have been shown to yield cobalt-iron<sup>22</sup> and nickel or nickel silicide nanoparticles, respectively.<sup>23</sup>

Variation in the pyrolysis conditions results in changes to the nanoparticle size, distribution, and composition. The CoFe nanoparticle containing thin films were shown to exhibit superparamagnetic properties, with ferromagnetic behavior being observed for pyrolysis at higher temperatures. This is attributed to a stabilization of the nanoparticle magnetization on the time scale of the hysteresis measurement due to the increased size of the nanoparticles that form at higher temperatures. Pyrolysis of the nickel-containing polycarbosilanes yielded ceramics embedded with nickel particles or nickel silicides depending on the pyrolysis conditions, with both superparamagnetic and ferromagnetic behavior being observed. While this shows that bimetallic precursors can be used to synthesize nanoparticles with desirable properties, these precursors can be hard to synthesize

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as they require the controlled incorporation of different metals into the macromolecular architecture and ancillary ligands that do not interfere in the nanoparticle formation.

The objective of this work is to form FePd-containing ceramics in an easy, quick, one-step process through incorporation of Pd into iron-containing polymers. Metal alloy nanoparticles and films are normally prepared using a number of physical and chemical methods;<sup>24-27</sup> for example, FePd nanoparticles can be formed via electron-beam evaporation,<sup>28</sup> and FePd thin films can be formed through sputtering under ultrahigh-vacuum conditions.<sup>29</sup> However, all these techniques require specialist equipment and can be costly and time consuming. Here we demonstrate the formation of ceramic films containing FePd nanoparticles from polyferrocenylethylmethylsilane (PFEMS) using physiochemical methods of evaporation and reduction and thermal breakdown. The incorporation of Pd into polymer precursors is desirable due to the unique properties of Pd and the magnetic properties of FePd alloys.<sup>30</sup> These are of paramount technological relevance due to the large saturation magnetization and magnetocrystalline anisotropy (hard magnetic behavior), persistent even in FePd nanoparticles larger than 8 nm,<sup>31,32</sup> rendering them suitable for ultrahigh-density magnetic storage.<sup>32</sup>

#### **II. EXPERIMENTAL DETAILS**

The PFEMS homopolymer was prepared by living anionic ring opening polymerization of ethylmethylsila[1]ferrocenophane as previously described.<sup>34</sup> Figure 1 shows the molecular structure of the PFEMS. The molecular weight and polydispersity index of the material used in this study were 22.5 kg mol<sup>-1</sup> and 1.01, respectively, as determined by gel permeation chromatography (GPC). GPC was carried out on a Viscotek GPCmax chromatograph equipped with a triple detector array. A flow rate of 1.0 ml min<sup>-1</sup> was used with tetrahydrofuran as the eluent. Palladium(II) acetylacetonate [Pd(acac)<sub>2</sub>] 99% purity was obtained from Sigma-Aldrich and used without modification.

The addition of Pd to the PFEMS was carried out using two different methods: as nanoparticles through sublimation of Pd(acac)<sub>2</sub> or through direct mixing of the Pd(acac)<sub>2</sub> into the PFEMS prior to pyrolysis of the films. The ceramics formed and the pyrolysis conditions under which they were formed are shown in Table I. Three sets of films were made: pure PFEMS films (precursor 1), PFEMS films containing Pd nanoparticles (precursor 2), and PFEMS films containing Pd(acac)<sub>2</sub> (precursor 3). Pure PFEMS films were formed by drop coating PFEMS-toluene solutions onto naturally oxidized Si(100) wafer substrates. The dry films were annealed in a vacuum oven at 60 °C for 24 h. For PFEMS films con-



FIG. 1. Molecular structure of the PFEMS polymer.

TABLE I. Pyrolysis scheme for the different ceramics.

Ceramic name	Precursor	Pyrolysis temperature (°C)	Pyrolysis atmosphere	
1aN	1	600	$N_2$	
1bN	1	1000	$N_2$	
1bA	1	1000	Ar	
2aN	2	600	$N_2$	
2bN	2	1000	$N_2$	
2bA	2	1000	Ar	
3aN	3	600	$N_2$	
3bN	3	1000	$N_2$	
3bA	3	1000	Ar	

taining Pd(acac)<sub>2</sub>, the Pd(acac)<sub>2</sub> was mixed into the PFEMStoluene solutions prior to drop coating with a weight for weight (w/w) ratio of 1:4 Pd(acac)<sub>2</sub>:PFEMS. The Pd nanoparticle deposition was carried out by sublimation of Pd(acac)<sub>2</sub> as previously described.<sup>35</sup> The PFEMS films were placed in a crystallization dish, with ~13 mg of Pd(acac)<sub>2</sub>. The crystallization dish was filled with nitrogen, sealed, and placed in a box oven, which was preheated to 170 °C, for 1 h. Transmission electron microscope (TEM) images before and after this exposure are shown in Fig. 2, indicating the incorporation of Pd nanoparticles into the films.

Pyrolysis was carried out in a tube furnace under nitrogen at 600 °C and 1000 °C and under argon at 1000 °C for 3 h with a heating rate of  $15 °C min^{-1}$ . Substrates were weighed before and after film deposition, and samples were weighed before and after pyrolysis.



FIG. 2. TEM micrographs of a PFEMS film (a) before and (b) after Pd nanoparticle deposition via sublimation of  $Pd(acac)_2$ . Scale bar is 200 nm.

Magnetization curves of the precursors and resulting ceramics were measured at room temperature (RT) and 5 K using a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer.

Energy dispersive x-ray (EDX) elemental analysis was performed using an FEI Philips XL30 sFEG with an EDX detector. Measurements were carried out at 20, 15, and 12 kV at a working distance of 5 mm. Three different areas were measured for each sample and averaged to take into account composition variations across the films.

X-ray diffraction (XRD) was performed using Philips PW1820 and PW3020 x-ray generators with a CuK $\alpha$  ( $\lambda = 1.54178$  Å) radiation source. The samples were mounted on an amorphous silicon wafer. The angle was varied from 2° to 75° in steps of 0.05° with 2.5 s per step.

Image analysis was carried out using a Leo variablepressure scanning electron microscope (SEM) and a Philips Technai 20 TEM.

### **III. RESULTS**

Pyrolysis of the PFEMS without the addition of Pd under nitrogen, 1aN and 1bN, resulted in a red-colored ceramic. Figure 3 shows examples of the film structure for ceramics pyrolyzed under argon. Similar morphologies were seen for all ceramics.

EDX analysis was used to investigate the chemical composition of the PFEMS polymer and the ceramics. Four elements were detected by EDX in the polymer film prior to pyrolysis: carbon, silicon, iron, and oxygen. For ceramics 1aN and 1bN three elements were found: O, Si, and Fe. Si and Fe come from the polymer precursor. Oxygen has been found in the ceramics, even though pyrolysis was conducted in a sealed quartz tube under nitrogen. No carbon was detected in samples pyrolyzed under nitrogen but was seen for samples pyrolyzed under argon (Table II).

The literature shows that oxygen is often found in ceramics prepared using the precursor method.<sup>18</sup> Oxygenic compounds may stem from moisture absorbed by the polymers prior to pyrolysis and/or from postoxidation of the samples during handling and storage. They may also arise from impurities in the nitrogen used to purge the furnace prior to and during pyrolysis. Table II shows the composition of each film in terms of the weight percent of each element at a beam energy of 20 keV.

The EDX data for the ceramics pyrolyzed under argon are shown in Table II. The data are representative of those seen for the other ceramics. Analysis of ceramics 2bA and 3bA indicates the presence of Pd. For ceramic 2bA, Pd nano-



FIG. 3. SEM micrographs of ceramics (a) 1bA, (b) 2bA, and (c) 3bA. Scale bar is 1  $\mu$ m.

TABLE II. Composition of ceramics pyrolyzed under argon, estimated using EDX analysis. Values indicate the weight percentage of each element, measured with a beam energy of 20 keV. For sample 3bA, weight percentages of each element measured at 15 and 12 keV are shown in the parentheses and square brackets, respectively.

Element	1bA	2bA	3bA
С	28.61	23.70	22.26 (13.83) [8.34]
0	39.46	34.47	34.64 (34.83) [33.63]
Si	11.96	13.91	9.52 (11.44) [13.00]
Fe	19.97	18.88	21.22 (27.84) [33.86]
Pd	-	9.004	12.36 (12.06) [11.18]

particles were incorporated into the films through sublimation of  $Pd(acac)_2$ . TEM images before and after this exposure are presented in Fig. 2 and show the addition of Pd nanoparticles with an average diameter of 6 nm.

When probing the ceramics with electron beams of different energies, the probing depth of the sample is altered, with lower beam energies having a smaller penetration depth.<sup>36</sup> For films pyrolyzed under argon, a dramatic decrease in the carbon content is seen as the beam energy is decreased. Data for sample 3bA are shown in Table II. This suggests that there is less carbon at the surface than in the bulk. The decrease in the carbon content may be due to oxidation of the surface, perhaps due to the adsorption of oxygen on the film prior to loading.

The Pd content of ceramics 2bA and 3bA does not change with probe depth, while the Fe content increases with decreasing probe depth. This suggests that Fe is more abundant at the surface of the films. Similar behavior is observed for all Pd-containing ceramics and is consistent with previous studies.<sup>15</sup>

XRD analysis was carried out to investigate the bulk composition and crystal structure of the ceramic products. The XRD patterns are shown in Fig. 4. All samples had a strong reflection peak at 69.13° arising from the Si(100) wafer used as substrates. This peak was used to align the



FIG. 4. XRD data. (a) PFEMS precursor and ceramic films. (b) PFEMS precursor and ceramic films containing Pd nanoparticles. (c) PFEMS precursor and ceramic films containing Pd(acac)<sub>2</sub>. (d) Ceramic films pyrolyzed under argon at 1000 °C.

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TABLE III. Nanocrystals in the ceramics as identified by XRD analysis.

Crystal	1aN <sup>a</sup>	1bN <sup>a</sup>	1bA <sup>a</sup>	2aN	2bN	2bA	3aN	3bN	3bA	File
α–Fe			43.4 (2.05)							31-0619
Fe <sub>3</sub> O <sub>4</sub>	35.62 (2.52)	35.53 (2.53)	35.65 (2.52)	35.51 (2.53)	35.61 (2.52)	35.62 (2.52)	35.63 (2.52)	35.63 (2.52)	35.55 (2.53)	19-0629
α−Fe <sub>2</sub> O <sub>3</sub>		32.93 (2.72)	33.08 (2.71)		33.16 (2.70)	33.08 (2.71)	33.08 (2.71)	33.08 (2.71)	33.08 (2.71)	33-0664
		35.53 (2.53)	35.65 (2.52)		35.61 (2.52)	35.62 (2.52)	35.63 (2.52)	35.63 (2.52)	35.55 (2.53)	
						54.08 (1.7)			54.13 (1.69)	
γ-Fe <sub>2</sub> O <sub>3</sub>	35.62 (2.52)	35.53 (2.53)	35.65 (2.52)	35.51 (2.53)	35.61 (2.52)	35.62 (2.52)	35.63 (2.52)	35.63 (2.52)	35.55 (2.53)	39-1346
			57.24 (1.61)							
$SiO_2$	30.33 (2.95)	30.49 (2.93)	30.28 (2.95)			30.28 (2.95)		30.13 (2.97)	30.08 (2.71)	72-2310
	29.14 (3.06)			29.03 (3.08)						72-1601
С			26.64 (3.35)			26.65 (3.35)	26.83 (3.32)		26.52 (3.39)	75-2078
SiC					35.61 (2.52)	35.62 (2.52)	35.63 (2.52)	35.63 (2.52)	35.55 (2.53)	75-1541
					38.25 (2.35)	38.56 (2.33)	38.60 (2.33)	38.39 (2.34)	38.46 (2.34)	
Pd	—	—	—					40.5 (2.23)		7440-05-3
FePd	—	—	—		40.16 (2.25)	40.06 (2.25)			40.01 (2.25)	[25,39]
	_	—	—		46.68 (1.95)	46.74 (1.94)			46.60 (1.95)	
PdSi		_	_	29.03 (3.08)						07-0127
Pd <sub>2</sub> Si	—	—	—		38.25 (2.35)	38.56 (2.35)	38.60 (2.33)	38.39 (2.34)	38.46 (2.34)	06-0559
	_	_	_		41.53 (2.17)			42.31 (2.14)	41.94 (2.15)	
	_	_	_		42.22 (2.14)				48.24 (1.89)	
	_	_	_		48.76 (1.87)					

<sup>a</sup>Dashes indicates the absence of Pd in ceramics pyrolyzed from precursor 1.

individual scans and to determine the accurate position of the other peaks; it is not shown in Fig. 4 for clarity. XRD characterization of samples 1bA, 2bA, and 3bA was carried out on a different generator to that used for the other samples. Harmonic spectral peaks are observed from the Si(400) peak when using this generator due to the absence of a filter. These three spectra are plotted together along with the spectra of the silicon substrate for clarity.

The PFEMS polymer precursor 1 is amorphous, exhibiting no sharp reflection peaks, but a diffuse halo in the  $2\theta$ angle region centered around 13° between 10° and 18°. The diffuse halo is also seen for the Pd-containing precursor films 2 and 3 along with additional peaks, which come from the Pd. Comparison of precursor films 1 and 3 shows that the Pd(acac)<sub>2</sub> has strong peaks at  $2\theta = 11.85^{\circ}$  (d = 7.47 Å), 12.66° (6.99 Å), 16.39° (5.41 Å), 17.90° (4.96 Å), 26.08° (3.42 Å), and 28.45° (3.14 Å). These correspond very closely to those found for powdered Pd(acac)<sub>2</sub> by Cominos *et al.*<sup>37</sup>

The ceramic products of 1, 2, and 3 show diffraction patterns with numerous Bragg reflections, indicating that the ceramics contain a number of crystalline species. Using the Scherrer equation,<sup>38</sup> the size of the crystals is estimated to be between 18 and 45 nm. This is smaller than the size of the crystals seen in the SEM images (Fig. 3), which are on the order of 100–200 nm in size, suggesting that the ceramic crystalline structures, as seen by SEM, are not pure in composition and clusters of different species coexist.

Data files from the crystallographic database were used to identify the peaks observed in the XRD spectra (Fig. 4). The results are summarized in Table III.

All the ceramics show reflection peaks at around  $2\theta = 35.6^{\circ}$  (d = 2.52 Å), corresponding to ferrimagnetic Fe<sub>3</sub>O<sub>4</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. Sample 1bA exhibits an additional

higher-order reflection peak of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> at 57.24° (1.61 Å). This was not detected for the other ceramic samples, probably due to imperfect packing of the crystals. The reflection peaks associated with antiferromagnetic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> at 33.15° (2.70 Å) and 35.61° (2.52 Å) are seen for all ceramics apart from 1aN and 2aN. The second-order reflection observed in the XRD spectra from  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> suggests that Fe<sub>2</sub>O<sub>3</sub> exists mainly in the  $\alpha$  form. The peaks associated with reflections of  $\alpha$ -Fe metal are only seen in the spectra for 1bA, where a very weak peak is observed. Thus, the majority of iron species exist in oxide form. The stronger peaks are seen for the ceramics pyrolyzed at 1000 °C under argon (1bA, 2bA, and 3bA).

For ceramics pyrolyzed under nitrogen, carbon is only seen in the spectra of 3aN. It is present in all samples pyrolyzed under argon. This strongly suggests impurities in the nitrogen atmosphere used for pyrolysis lead to oxidative degradation. The reflection peaks of  $SiO_2$  and SiC are weak and broad. This is probably due to the majority of silicon and carbon species being in the amorphous state.

Pd is seen to exist as pure Pd (3aN), PdSi (2aN), and Pd<sub>2</sub>Si. The peaks of Pd<sub>2</sub>Si are observed at  $38.26^{\circ}$  (2.35 Å) for all Pd-containing samples apart from 2aN. Ceramics 2bN and 3bA also show higher-order reflections of Pd<sub>2</sub>Si at 41.53° (2.17 Å), 42.22° (2.14 Å), and 48.76° (1.87 Å). The peaks are more prominent in ceramics pyrolyzed under argon.

Pd and FePd alloys exhibit similar reflection peaks. Bryden *et al.*<sup>25</sup> have shown that pure Pd exhibits a peak at  $\sim 40^{\circ}$ . They synthesized FePd alloys and showed that as the volume fraction of Fe in the alloys increases, secondary reflections at  $\sim 46^{\circ}$  start to appear and grow stronger. A small shift in the position of FePd peaks relative to Pd peaks<sup>39</sup> has also been previously reported. Ceramic 3bN exhibits a small peak at



FIG. 5. SQUID magnetization curves at RT. (a) Precursor 1 and ceramics, (b) precursor 2 and ceramics, and (c) precursor 3 and ceramics. (d), (e), (f) Magnification of (a), (b), and (c) respectively. [ $\bullet$ ], precursor films; [ $\blacksquare$ ], ceramics pyrolyzed at 600 °C under nitrogen; [ $\blacktriangle$ ], ceramics pyrolyzed at 1000 °C under nitrogen; [ $\diamond$ ], ceramics pyrolyzed at 1000 °C under argon.

40.5° (2.23 Å), corresponding to a reflection peak of Pd; no higher-order reflections are seen. Ceramics 2bA and 3bA have a reflection peak at 40.01° (2.25 Å), which is lower than that seen in 3bN, and have higher-order reflections at 46.6° (1.95 Å), suggesting that the reflections come from FePd. This peak increases in magnitude from sample 2bA to 3bA, which is indicative of an increase in iron content in the FePd alloys.<sup>25</sup>

SQUID magnetometry was used to investigate the magnetic behavior of the films at RT. The ceramic films fabricated from polymer precursors with the addition of Pd nanoparticles and Pd(acac)<sub>2</sub> and pyrolyzed at different temperatures and under different atmospheres were seen to display different magnetic properties.

The magnetization curves are shown in Fig. 5. The precursor films 1, 2, and 3 display paramagnetic behavior at RT. The PFEMS precursor film (precursor 1) had a susceptibility of  $11.28\pm0.08 \times 10^{-6}$  emu/g. The addition of Pd in nanoparticle form (precursor 2) to the PFEMS increased the susceptibility fourfold. Films made from precursor 3, where the Pd(acac)<sub>2</sub> had been mixed directly with the polymer, had a susceptibility that was increased nearly tenfold from precursor 1 (Table IV).

The pyrolyzed films were all found to display ferromagnetic behavior (Fig. 5). The saturation magnetization, remanent magnetization, and coercivity for the samples are given in Table IV and are displayed in Fig. 6. Films pyrolyzed from precursor 1 had the lowest coercivity, which then increased as Pd was added first in nanoparticle form (samples pyrolyzed from precursor 2) and then directly as Pd(acac)<sub>2</sub> (samples pyrolyzed from precursor 3). The highest coercivity was seen for samples pyrolyzed under argon. Increasing the pyrolysis temperature to 1000 °C resulted in an increase of the coercivity for all the ceramics. The coercivity of samples 1bN and 2bN were comparable, while sample 3bN had a coercivity four times greater. For samples pyrolyzed under argon the coercivity of ceramics 1bA and 2bA was the same, with a small increase for 3bA.

The remanent magnetization measured for the ceramic films from the SQUID magnetization curves at RT are shown in Fig. 6(b). The remanence increased with increasing pyrolysis temperature and from films pyrolyzed under  $N_2$  to those pyrolyzed under Ar (Table IV). An increase in the remanence was observed on addition of Pd, with films pyrolyzed from precursor 3 displaying the largest remanent magnetization.

The remanent magnetization for precursor 1 pyrolyzed at 600 °C was  $0.031\pm0.005$  emu/g. This increased sixfold for Pd-containing films. There was only a small difference between the remanence of the Pd-containing ceramics 2aN and 3aN formed using the two different Pd deposition methods. For films pyrolyzed at 1000 °C under N<sub>2</sub>, the remanent magnetization for 1bN and 2bN was comparable and strongly increased for 3bN. For films pyrolyzed under argon

TABLE IV. Magnetic properties of the precursors and ceramics.

Comple	Susceptibility	Saturation magnetization	Remanent magnetization	Coercivity	
Sample	$\chi_{\rho} (\times 10^{-5} \text{emu/g})$	$M_s$ (emu/g)	$M_r$ (emu/g)	$H_c$ (Oe)	
Precursor 1	$11.28\pm0.08$	_	_	_	
Precursor 2	$40.04 \pm 0.4$	_	_	_	
Precursor 3	$101.6 \pm 0.3$	_	_	_	
1aN		$4.3 \pm 0.1$	$0.031 \pm 0.005$	$9.7\pm0.5$	
2aN	_	$6.96 \pm 0.2$	$0.17 \pm 0.01$	$64 \pm 2$	
3aN		$5.68 \pm 0.2$	$0.20 \pm 0.01$	$80\pm5$	
1bN		$7.16 \pm 0.07$	$1.16 \pm 0.01$	$77\pm5$	
2bN		$6.95 \pm 0.3$	$1.26 \pm 0.02$	$87 \pm 2$	
3bN		$9.12 \pm 0.1$	$3.99 \pm 0.02$	$338\pm20$	
1bA		$8.18 \pm 0.2$	$3.48 \pm 0.01$	$257\pm5$	
2bA	_	$12.2 \pm 0.2$	$5.74 \pm 0.01$	$256\pm10$	
3bA	—	$12.0 \pm 0.2$	$5.30\pm0.01$	298 ± 10	



FIG. 6. (a) Coercivity, (b) remanent magnetization, and (c) saturation magnetization measured from the SQUID data for samples measured at RT.

from precursor 1 the remanence increased threefold as compared to those pyrolyzed under  $N_2$ . The remanence for films 2bA and 3bA also strongly increased.

The change in saturation for the different ceramics is shown in Fig. 6(c). A strong enhancement in saturation magnetization was seen for films containing Pd and pyrolyzed under argon. Ceramics 2bA and 3bA had saturation magnetizations of  $12.2\pm0.2 \text{ emu/g}$  and  $12.0\pm0.2 \text{ emu/g}$ , respectively. This is nearly three times higher than the saturation magnetization of ceramic 1aN of  $4.3\pm0.1 \text{ emu/g}$ .

## **IV. DISCUSSION**

We have shown that the pure PFEMS polymer and Pddoped polymer precursors are paramagnetic, with susceptibilities ranging from 11 to  $102 \times 10^{-6}$  emu/g. This appears to be the first time that such data on the paramagnetic behavior of PFEMS have been reported. This behavior may arise from small amounts of oxidation of the Fe(II) centers to the Fe(III) state. Pd is a strong paramagnet with a susceptibility of 567.4 × 10<sup>-6</sup> emu/g at RT. The increase in susceptibility of the precursor on addition of Pd is most likely a result of the Pd acting as additional localized dipoles in the precursor. When pyrolyzed under nitrogen, the pure PFEMS film forms a ceramic predominantly containing Fe oxides, in particular Fe<sub>3</sub>O<sub>4</sub> or  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. Both these oxides are ferrimagnetic materials. Only the main XRD peaks are seen here (Fig. 4), which are similar and therefore hard to distinguish from one another. While the x-ray results do not show unambiguous stoichiometry, in some cases the EDX results can be used to deduce whether Fe<sub>3</sub>O<sub>4</sub> or  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is most prevalent in the sample. Analysis of the data for samples 1aN and 2aN suggests that the peak at 35.62° most likely comes from Fe<sub>3</sub>O<sub>4</sub> due to the amount of oxygen available to form Fe oxides. However, the presence of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> cannot be ruled out, and it is likely that a mixture of the two oxides is present in the ceramics.

The EDX analysis of the ceramics indicates that oxidation of the samples occurs either during or after pyrolysis. Analysis of sample 1bA shows that elemental iron formed during pyrolysis, suggesting that Fe forms initially and is then oxidized, forming core-shell particles. The lack of carbon in the ceramics pyrolyzed under nitrogen suggests that for these samples, oxidation occurs both during and after pyrolysis, perhaps as a result of a contaminated atmosphere. For the ceramics pyrolyzed under argon, the results indicate that oxidation of the Fe predominantly occurs postpyrolysis. It should be noted that the ceramics were not encapsulated, and once removed from the furnace, they immediately came into contact with the air in the room.

The presence of the antiferromagnetic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite) phase is confirmed by x-ray analysis in the majority of the samples and by magnetometry results. An exchange bias effect<sup>40</sup> is observed in pure PFEMS (1bN and 1bA) and in Pd nanoparticle doped ceramics (2bN and 2bA) pyrolyzed at 1000 °C upon field cooling of the samples with a 1 T applied field to 5 K. This is below the Morin transition temperature of 250 K.<sup>41</sup> The resulting exchange bias fields were -90 Oe for 1bA and 2bA, -60 Oe for 1bN, and -40 Oe for 2bN. These results indicate the presence of core-shell clusters of ferromagnetic Fe (1bA) and ferrimagnetic Fe oxides surrounded by a shell of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, similar to those seen by Crisan et al.<sup>42</sup> No such effect was observed for the ceramics arising from PFEMS and Pd(acac)<sub>2</sub> (3bN and 3bA). The exchange bias effect that arises from the pinning of the ferromagnetic domain by the adjuncted antiferromagnetic surface not only results in a shift of the hysteresis, known as the exchange bias field, but can also significantly alter the coercivity of the ferromagnet/ferrimagnet by acting as a pinning site of the domains upon reversal of the magnetization. The absence of this effect in the ceramics pyrolyzed from the  $Pd(acac)_2$  precursor indicates the absence of physical contact between hematite and the FePd clusters.

The magnetic properties of Fe oxides were found to be highly dependent on crystallinity, particle size, sample shape, and purity.<sup>43</sup> The saturation and remanent magnetization of nanocomposites of Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> have been widely studied<sup>42–45</sup> and were found to be significantly lower than the values reported for bulk material.<sup>46,47</sup> The difference is attributed to the small particle size effect<sup>48</sup> and the inclusion of magnetic nanocomposites within the matrix of other materials, which reduces the mass magnetization. For  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles of 20nm with an amorphous SiO<sub>2</sub> coating, the saturation magnetization, remanent magnetization, and coercivity were reported as 4 emu/g, 1.07 emu/g, and 252.92 Oe, respectively.<sup>43</sup> These correspond to the values seen here for ceramics pyrolyzed from precursor 1, which did not contain any Pd, and to those reported in the literature for ceramics pyrolyzed from similar Fe-containing polymers,<sup>16,17</sup> confirming that the observed magnetic behavior is, indeed, a result of the presence of Fe oxides.

Two methods were used to dope the PFEMS films with Pd prior to pyrolysis: evaporation and reduction of Pd(acac)<sub>2</sub> to form nanoparticles and thermal degradation of Pd(acac)<sub>2</sub> mixed directly into the PFEMS. The results show that while both methods produce Pd-containing ceramics with enhanced magnetic properties, as compared to the ceramics formed from pure PFEMS, direct mixing of the PFEMS into the precursor was the most successful method. Ceramics pyrolyzed at a temperature of 1000 °C showed the greatest increase in the magnetic properties. Argon is the most efficient of the two pyrolysis atmospheres and results in the creation of ceramics containing FePd alloys.

Binary alloys of FePd have attracted considerable technological interest due to their high magnetocrystalline anisotropy, rendering them suitable for next-generation harddisk drives. In contrast to FePt alloys, they seem to retain a ferromagnetic ground state even at small cluster sizes.<sup>31,32</sup> As with Fe oxide nanoparticles, the magnetic properties of FePd alloys depend on a number of parameters, including the size of the crystal and the composition.<sup>47</sup> Fe<sub>50</sub>Pd<sub>50</sub> particles at RT have been reported to have a coercivity ranging from 200 Oe for 6 nm particles<sup>31</sup> to 1251 Oe for 40 nm particles.<sup>49</sup> The coercive fields seen here for FePd-containing ceramics are ~340 Oe. This is higher than the coercive fields reported for Fe oxides, indicating that the enhanced magnetic behavior is a result of the presence of FePd alloys.

Metal alloy nanoparticles and films are prepared using a number of physical and chemical methods,<sup>24-26</sup> including sputter deposition under ultrahigh vacuum, electrodeposition, and chemical vapor deposition. All of these methods require specialist equipment and can be costly and time consuming. By incorporating the Pd into iron-containing polymers, FePd-containing ceramics can be produced cheaply and quickly in an one-step process. The polymer precursors can be molded or shaped prior to calcination, enabling the formation of structured and shaped ceramics.<sup>17</sup> Complex patterns can be templated using the self-assembly of block copolymers.<sup>50</sup> This self-assembly has been used to pattern organometallic polymers<sup>34</sup> with structures on the order of 10–20 nm.<sup>51</sup> Liu et al.<sup>52</sup> have recently shown that iron-containing polymer films can be structured on the nanoscale using an imprint method, with feature sizes of 50-100 nm. This feature size is similar to the grain sizes currently used in hard-disk drive technology. This structure is retained on pyrolysis to form the ceramic. Structuring of our Pd-containing ceramics in a similar manner could be used to form regular arrays of pillars with desirable properties for data storage, providing an alternative to current data storage technologies.

### **V. CONCLUSIONS**

In summary, we have shown that PFEMS can be successfully doped with Pd, either as nanoparticles or by directly mixing  $Pd(acac)_2$  to the polymer. These polymers exhibit paramagnetic behavior, with increasing magnetic susceptibility with Pd content. On pyrolysis of these polymer precursors, ferromagnetic ceramics are formed. The magnetic behavior is dependent on the temperature and atmosphere used for pyrolysis. For ceramics containing Pd pyrolyzed under argon at 1000 °C, FePd alloys were observed. The formation of these alloys results in enhanced coercivity, remanent magnetization, and saturation magnetization of the ceramics. On the basis of these results we suggest that an imprint method recently developed by Liu et al.<sup>52</sup> could be used for the fabrication of FePd-containing ceramics for use in high-density magnetic data storage technologies.

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