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## Catalytic Thermal Decomposition of NO<sub>2</sub> by Iron(III) Nitrate Nonahydrate-Doped Poly(Vinylidene Difluoride)

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# Catalytic Thermal Decomposition of NO<sub>2</sub> by Iron(III) Nitrate Nonahydrate-Doped Poly(Vinylidene Difluoride)

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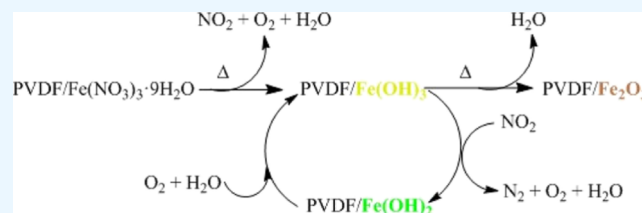


Article Recommendations



Supporting Information

**ABSTRACT:** The products of thermal decomposition of iron nitrate nonahydrate doped into poly(vinylidene difluoride) are examined using Mössbauer spectroscopy. Very little of the expected nitrogen dioxide product is observed, which is attributed to Fe<sup>3+</sup> catalysis of the decomposition of NO<sub>2</sub>. The active site of the catalysis is shown to be Fe(OH)<sub>3</sub> in the polymer matrix, which is, unexpectedly, reduced to Fe(OH)<sub>2</sub>. Thermodynamic calculations show that the reduction of Fe<sup>3+</sup> is exergonic at sufficiently high temperatures. A reaction sequence, including a catalytic cycle for decomposition of NO<sub>2</sub>, is proposed that accounts for the observed reaction products. The role of the polymer matrix is proposed to inhibit transport of gas-phase products, which allows them to interact with Fe(OH)<sub>3</sub> doped in the polymer.



## INTRODUCTION

Poly(vinylidene difluoride) (PVDF) has been studied for several decades because it has unique electrical properties.<sup>1–14</sup> PVDF is primarily found in three phases (although other minor phases have been reported). In the  $\alpha$ -phase, the polymer is nonpolar and chemically inert, so it has found use as a plastic support in chemically aggressive environments. The  $\beta$ -phase is the most electroactive being ferroelectric, piezoelectric, and pyroelectric. The  $\gamma$ -phase is piezoelectric and pyroelectric but does not support a permanent electric moment. The  $\alpha$ -phase is easily fabricated by deposition from low-polarity solvents or melt-casting.<sup>3,7,15</sup> The  $\beta$ -phase is the most difficult to obtain and is typically fabricated by electric field poling, that is, cooling a stretched sample under the influence of an electric field.<sup>12</sup> More recently, tuning of the phase behavior and properties of PVDF has been accomplished by doping with nanoparticles or metal-ion salts.<sup>7,16–31</sup> All of these efforts to exploit various properties of PVDF are under continuous study to find improved sensors,<sup>29,32,33</sup> modified optical properties,<sup>18,34,35</sup> lithium-ion battery membranes,<sup>36–38</sup> energy-harvesting devices,<sup>11,39–43</sup> electromagnetic shielding materials,<sup>26,28</sup> catalysts,<sup>22,24,30,44–48</sup> computer memory,<sup>10,49,50</sup> or antifouling membranes.<sup>51</sup>

The catalytic effect of PVDF on the thermal decomposition of transition-metal nitrate hydrates doped into the polymer was recently described.<sup>48</sup> When the transition-metal ion carried a 2+ charge, the surrounding PVDF matrix catalyzed the reaction of the nitrate ion into gas-phase nitrogen oxides, solid-phase binary metal oxides, and other products, lowering the decomposition temperature by over 100 °C in some cases. In contrast, for trivalent transition-metal ions, there was little evidence of catalysis, which was attributed to the slow ion migration required to form the multiatom metal oxides.

Moreover, with the trivalent metal ions, the generation of gas-phase nitrogen oxides was suppressed, with gas-phase IR signals at noise levels. It was hypothesized that the decomposition of NO<sub>x</sub> was catalyzed by the 3+ transition-metal oxides, in accordance with literature precedence.<sup>52–54</sup> There has been a continuing interest for many years in finding new catalysts to remove NO<sub>x</sub> gases,<sup>55–60</sup> so confirmation of this hypothesis is of great significance.

In this report, we use Mössbauer spectroscopy to better understand the compositional changes that occur during the thermal decomposition of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O doped into PVDF. Similar to previous studies,<sup>61</sup> it is determined that iron hydroxides are intermediates prior to the final formation of Fe<sub>2</sub>O<sub>3</sub> in the PVDF matrix. Further, it is these hydroxides that are responsible for the removal of NO<sub>2</sub>, not the final oxide. Thermodynamic calculations demonstrate that the reduction of Fe(OH)<sub>3</sub> to Fe(OH)<sub>2</sub> concurrent with NO<sub>2</sub> decomposition to N<sub>2</sub> and O<sub>2</sub> is exergonic. In competition with the Fe<sup>3+</sup> reduction, the generated O<sub>2</sub> can oxidize Fe<sup>2+</sup> back to Fe<sup>3+</sup>, so that the final product is always Fe<sub>2</sub>O<sub>3</sub>. Identification of the hydroxides as critical to the NO<sub>x</sub> decomposition may help develop better catalysts for removal of these gases.

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## EXPERIMENTAL SECTION

PVDF ( $M_w \sim 534,000 \text{ g}\cdot\text{mol}^{-1}$ ) and  $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  were purchased from Sigma-Aldrich, and acetone and *N,N*-dimethylformamide (DMF) were purchased from Fisher Scientific. Thin-film samples were fabricated on precleaned glass substrates using a dip coating method. For that, 10% (w/v) PVDF solutions were prepared using a solvent composed of a mixture of 9:1 (v/v) acetone: DMF. This solution was sonicated in a water bath for 3 h at 40 °C. The amount of  $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  required to form 4 mol % of  $\text{Fe}^{3+}$  in PVDF (relative to the repeat units) was added to the prepared PVDF solution and sonicated for another 2 min without heat.

Thin films were formed using an MTI dip-coater (model TL0.01) under an  $\text{N}_2$  environment to control the humidity and at a withdrawal rate of  $124 \text{ mm}\cdot\text{min}^{-1}$ . The prepared samples were annealed 2 min in an oven at 60 °C to evaporate the excess solvent. The samples were peeled off the substrate and cut to  $2.5 \times 2.5 \text{ cm}$  dimension. Then,  $\sim 40$  thin films were packed in an aluminum pan to give a high enough quantity of  $^{57}\text{Fe}$  for spectroscopic analysis in the natural abundance samples. The composite samples were about  $20 \mu\text{m}$  thick and contained about  $17 \mu\text{g}$  of  $^{57}\text{Fe}$ . These samples were heated to critical temperatures using a furnace (MTI Corporation EQ-CVF-1300T) with a  $5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$  rate under an  $\text{N}_2$  atmosphere. The heated samples were immediately cooled down to room temperature by removing them from the oven. Another set of samples were prepared in the same fashion with 5 h annealing time at the chosen temperature.

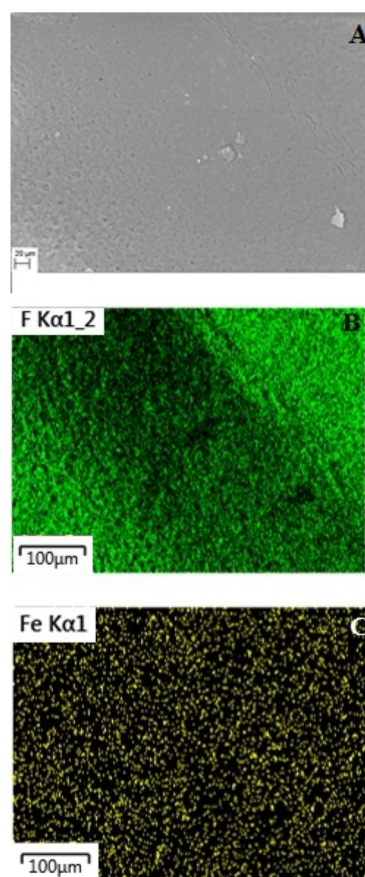
The characterization of  $\text{Fe}^{3+}$ /PVDF thin films and pure  $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  samples were carried out using a Mössbauer spectrometer (SEE Co. Resonant Gamma-Ray Spectrometer model W304) with a  $^{57}\text{Co}$  source at room temperature. Metallic  $\alpha$ -Fe foil ( $30 \mu\text{m}$ ) was used as a reference for calibration of the velocity scale. The velocity window  $\pm 4 \text{ mm}\cdot\text{s}^{-1}$  was selected for the thin-film samples as it fully captured all transmittance peaks. Mössbauer spectra of the pure salt at selected temperatures were also collected for comparison. Spectral parameters were obtained by fitting data using the MossA 1.01g software package<sup>62</sup> to give isomer shifts ( $\delta$ ), full width at half-maxima ( $\Gamma$ ), and quadrupole splittings ( $\Delta E_Q$ ). All XRD data were measured using a Rigaku-Miniflex 600 diffractometer using a  $\text{Cu K}\alpha$  source with 0.154 nm wavelength, an accelerating voltage of 40 KV, and a tube current of 15 mA. A Perkin-Elmer Spectrum 100 infrared spectrometer in the attenuated total reflectance mode was used to collect vibrational spectra with a  $4 \text{ cm}^{-1}$  resolution. Scanning electron microscopy (SEM) images were obtained using a Zeiss Sigma VP field emission scanning electron microscope in the backscatter mode with an Oxford Instruments X-max 50  $\text{mm}^2$  energy dispersive X-ray spectroscopy (EDS/EDX) detector.

## RESULTS AND DISCUSSION

$\text{Fe}^{3+}$ /PVDF composite thin films were fabricated by doping PVDF with  $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  in solution and casting the films using dip coating. The prepared room-temperature thin films were yellow in color indicating a weak ligand coordination sphere around the  $\text{Fe}^{3+}$  in the thin films. The IR data of the fabricated thin films<sup>48</sup> (Figure S1) kept at 25 °C show peaks related to C–H stretching at  $\sim 3000 \text{ cm}^{-1}$  and the presence of residual solvents including  $\text{H}_2\text{O}$  (OH stretching at  $\sim 3400 \text{ cm}^{-1}$ ) and DMF (C=O stretching at  $1660 \text{ cm}^{-1}$ ). Further,

these thin films are primarily in the polar  $\beta$ -phase with a trace amount of nonpolar  $\alpha$ -phase as indicated by the intense peak at  $1275 \text{ cm}^{-1}$  ( $\beta$ -phase marker) and  $840 \text{ cm}^{-1}$  (a combination peak of  $\beta$ - and  $\gamma$ -phases) and a less intense peak at  $764 \text{ cm}^{-1}$  ( $\alpha$ -phase marker).<sup>3,9,63</sup> The charge from the  $\text{Fe}^{3+}$  dopant aligns the bond dipole moments of the polymer chain to give a  $\beta$ -phase crystalline fraction as high as 0.69, as calculated using Beer's law with the peaks at 840 and  $764 \text{ cm}^{-1}$  from the IR data.<sup>63</sup> Further, the XRD data from these films are consistent with the FTIR data, showing a high fraction of polar phases in thin-film samples kept at room temperature.<sup>48</sup> The XRD data does not have any peaks related to the initial crystalline iron salt, indicating that the dopants are fully dissolved in the composite thin films.<sup>48</sup>

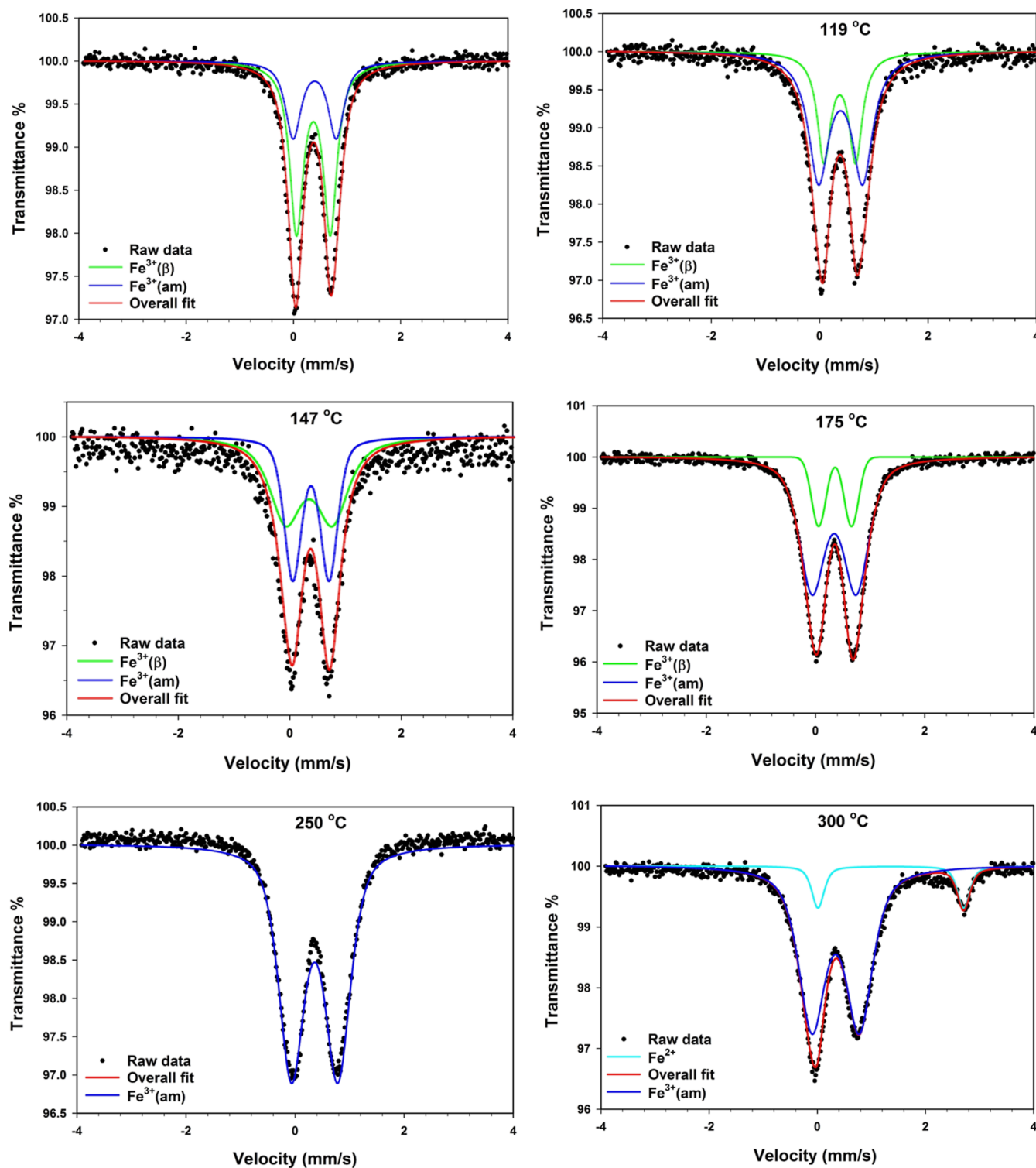
To further demonstrate that the iron ions are uniformly distributed, SEM/EDS measurements were made, as shown in Figure 1. The SEM image shows that the PVDF film is



**Figure 1.** (A) SEM image of a PVDF film doped with  $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ . (B) F elemental distribution (green). (C)  $\text{Fe}^{3+}$  distribution (yellow).

generally smooth with an unremarkable surface morphology. The elemental analysis found from the EDS measurement shows that the surface is primarily dominated by F atoms, while the  $\text{Fe}^{3+}$  ions are located throughout the entire sample area. There is no evidence of aggregation of iron ions. Integration of the F and  $\text{Fe}^{3+}$  signals shows that the Fe/F mole ratio is 0.021 or 0.042  $\text{Fe}^{3+}$  ions per polymer repeat unit, consistent with the preparation conditions.

$\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  decomposes thermally to give  $\text{NO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{Fe}_2\text{O}_3$ .<sup>48</sup> The Mössbauer spectra of  $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$



**Figure 2.** Mössbauer spectra of Fe<sup>3+</sup>/PVDF thin films heated to the indicated temperature and then quenched to room temperature. The measured data are shown as closed circles, the total fits to the data are red lines, and the components to the total fits are blue, green, or cyan lines.

heated to several temperatures are shown in Figure S2. At room temperature, the spectrum can be fitted with two components: a broad peak with isomer shift  $\delta_1 = 0.44 \pm 0.04$  mm·s<sup>-1</sup> (line width 4.27 mm·s<sup>-1</sup>) and a narrow peak with isomer shift  $\delta_2 = 0.34 \pm 0.01$  mm·s<sup>-1</sup> (line width 0.95 mm·s<sup>-1</sup>). Any quadrupole splitting that may be present is not resolved. The isomer shifts are consistent with Fe<sup>3+</sup>, and the small quadrupole coupling is consistent with an octahedral

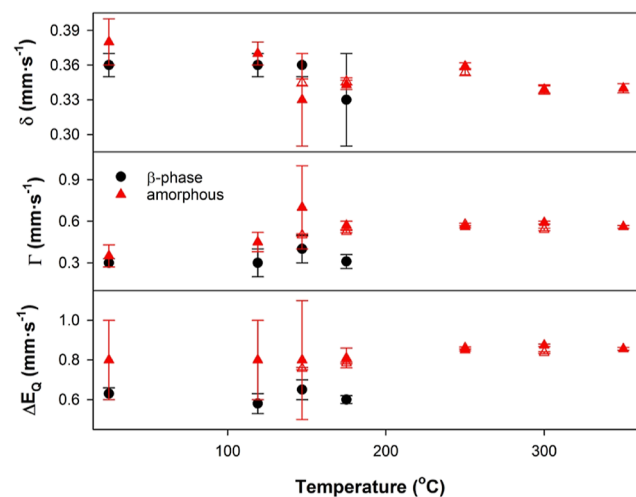
coordination in a symmetric (<sup>6</sup>A<sub>1g</sub>) high-spin ( $t_{2g}^3e_g^2$ ) electronic state. The electric field gradient from the Fe<sup>3+</sup> electronic state and octahedral coordination is 0, and the contribution from the surrounding environment would be small. Figure S3 shows the powder X-ray diffractogram of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, which is consistent with a monoclinic crystal structure. Upon heating to 250 or 300 °C, thermal decomposition of the salt occurs, as shown in Figure S2.

When the thermal products are quenched, the Mössbauer spectra again show two Fe<sup>3+</sup> sites at (250 °C:  $\delta_1 = 0.326 \pm 0.004 \text{ mm}\cdot\text{s}^{-1}$ ,  $\Delta E_{Q1} = 0.89 \pm 0.08$ ,  $\delta_2 = 0.346 \pm 0.007 \text{ mm}\cdot\text{s}^{-1}$ ,  $\Delta E_{Q2} = 0.54 \pm 0.03$ , 300 °C:  $\delta_1 = 0.330 \pm 0.002 \text{ mm}\cdot\text{s}^{-1}$ ,  $\Delta E_{Q1} = 0.87 \pm 0.02$ ,  $\delta_2 = 0.357 \pm 0.003 \text{ mm}\cdot\text{s}^{-1}$ ,  $\Delta E_{Q2} = 0.55 \pm 0.01$ ). These are consistent with Fe(OH)<sub>3</sub> or FeOOH as previously reported,<sup>62–64</sup> although in an amorphous environment rather than crystalline. When the thermal products are annealed for 5 h, a third component is formed that is identified as crystalline Fe<sub>2</sub>O<sub>3</sub> (250 °C:  $\delta = 0.32 \pm 0.02 \text{ mm}\cdot\text{s}^{-1}$ ,  $\Delta E_Q = 0$ , hyperfine splitting =  $50.3 \pm 0.1 \text{ mm}\cdot\text{s}^{-1}$ , 300 °C:  $\delta_1 = 0.34 \pm 0.01 \text{ mm}\cdot\text{s}^{-1}$ ,  $\Delta E_Q =$ , hyperfine splitting =  $50.6 \pm 0.1 \text{ mm}\cdot\text{s}^{-1}$ ).<sup>64</sup> The XRD data (Figure S3) show that the samples heated to 250 or 300 °C but not annealed are largely amorphous, but annealing leads to formation of crystalline Fe<sub>2</sub>O<sub>3</sub>, consistent with the Mössbauer spectra.<sup>64</sup>

When the Fe<sup>3+</sup>-doped PVDF films were heated, the only changes in the IR spectra noted (Figure S1) were loss of residual solvent and conversion of the PVDF crystallinity from primarily  $\beta$ -phase to primarily  $\alpha$ -phase. The solvent loss was mostly complete when the films were heated to 175 °C, although there were small peaks associated with OH groups up to 300 °C. The formation of  $\alpha$ -phase PVDF only occurred when the films were heated above the melting point of  $\beta$ -phase PVDF (which was about 147 °C for these doped PVDF films, slightly depressed from 160 °C for pure  $\beta$ -PVDF<sup>7</sup>). XRD shows similar behavior.<sup>48</sup> Neither technique provides insight into the changes in the iron ion dopant. However, as previously reported, the gas-phase products show no evidence of NO<sub>2</sub>,<sup>48</sup> indicating a different thermal decomposition pathway when Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O is doped in PVDF.

The Mössbauer spectra of Fe<sup>3+</sup>/PVDF thin films heated to selected temperatures and then quenched to room temperature are shown in Figure 2 (wider velocity range spectra were measured to look for other peaks, but none were found). The spectrum of the sample kept at room temperature is an asymmetric doublet with a narrow line width, indicating the iron ions are likely isolated but occupy two slightly different microenvironments. Deconvolution of the spectrum gives  $\delta_1 = 0.38 \pm 0.02 \text{ mm}\cdot\text{s}^{-1}$ ,  $\Gamma_1 = 0.35 \pm 0.08 \text{ mm}\cdot\text{s}^{-1}$ ,  $\Delta E_{Q1} = 0.8 \pm 0.2 \text{ mm}\cdot\text{s}^{-1}$  and  $\delta_2 = 0.36 \pm 0.01 \text{ mm}\cdot\text{s}^{-1}$ ,  $\Gamma_2 = 0.30 \pm 0.03 \text{ mm}\cdot\text{s}^{-1}$ ,  $\Delta E_{Q2} = 0.63 \pm 0.03 \text{ mm}\cdot\text{s}^{-1}$ . The isomer shifts are consistent with Fe<sup>3+</sup>,<sup>65–67</sup> as expected from the fabrication conditions. The larger quadrupole coupling for site 1 is assigned to Fe<sup>3+</sup> located in amorphous regions, and site 2 is assigned to Fe<sup>3+</sup> located in  $\beta$ -phase regions of the thin film. Since the  $\alpha$ -phase is nonpolar, the electric field gradient is expected to be small with a near-zero quadrupole coupling. When the thin films are heated to temperatures below the PVDF melting point, there are small changes in the Mössbauer spectra indicative of some mobility of Fe<sup>3+</sup> ions between the different environments. However, when the PVDF melts and then is recooled, the  $\beta$ -phase is lost, and the resulting Mössbauer spectra only show features associated with site 1:  $\delta \sim 0.35 \text{ mm}\cdot\text{s}^{-1}$  and  $\Delta E_Q \sim 0.85 \text{ mm}\cdot\text{s}^{-1}$ . The fit parameters for the Fe<sup>3+</sup> species as a function of temperature are shown in Figure 2. The values found for the Fe<sup>3+</sup> isomer shifts and quadrupole couplings found after heating the PVDF-doped composites to temperatures above 175 °C are consistent with the formation of Fe(OH)<sub>3</sub> or FeOOH, as with the decomposition of the pure material. This assignment is supported by the IR spectra (Figure S1) as well, where there are small absorbance features in the OH stretching region of

the spectra of the heated materials at temperatures far above those at which the C=O band from the residual DMF has disappeared. However, the intermediate hydroxides are located in the amorphous or  $\alpha$ -phase regions of the PVDF upon cooling. The  $\alpha$ -phase is nonpolar, and the amorphous regions are expected to have low polarity as well, so the electronic microenvironments surrounding the Fe<sup>3+</sup> are similar throughout the entire polymer film, leading to  $\delta$  and  $\Delta E_Q$  values similar to the room-temperature spectra. As shown in Figure 3,

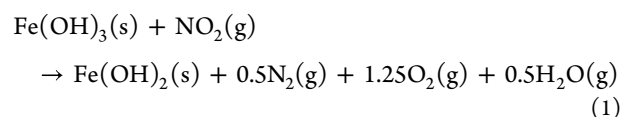


**Figure 3.** Isomer shifts,  $\delta$  (top), full width at half-maxima,  $\Gamma$  (middle), and quadrupole couplings,  $\Delta E_Q$  (bottom), of the Fe<sup>3+</sup> sites as a function of temperature. Black circles are assigned to sites in the  $\beta$ -phase region of PVDF, and red triangles are assigned to sites in the amorphous regions of the polymer.

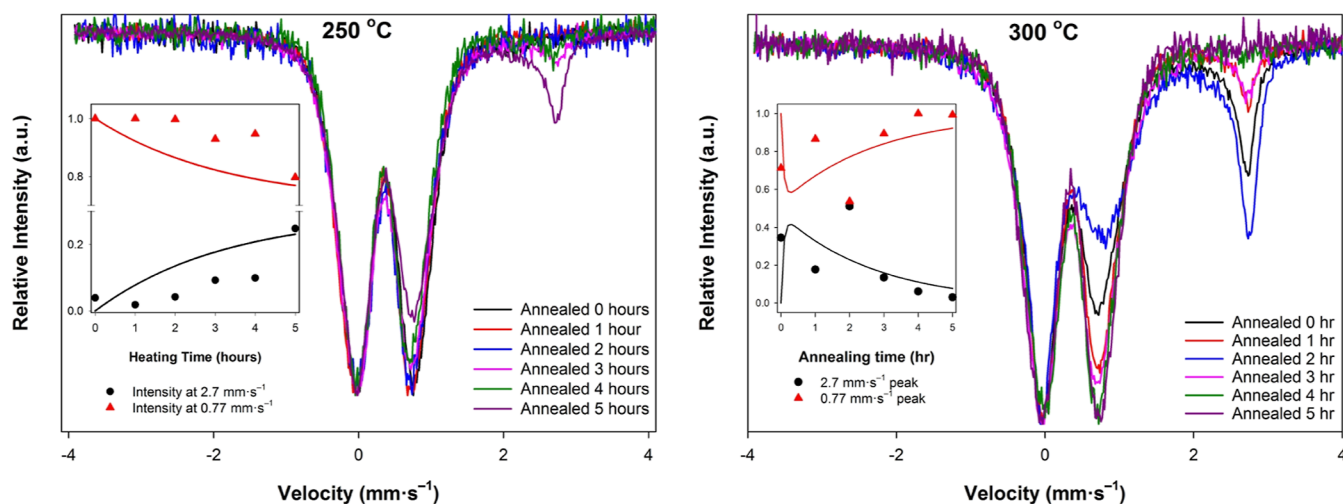
the biggest effect of the PVDF environment on the Mössbauer spectrum is the reduction of the quadrupole splitting for Fe<sup>3+</sup> ions located in  $\beta$ -phase regions. Since the  $\beta$ -phase is expected to have a large constant local electric field, it makes sense that the electric field gradient, which determines the magnitude of the quadrupole coupling, around the Fe<sup>3+</sup> will be reduced.

When the films are heated to 300 °C, a new peak is found at  $\sim 3.2 \text{ mm}\cdot\text{s}^{-1}$ . Deconvolution of the high-temperature spectrum shows that the new peak has  $\delta = 1.359 \pm 0.009 \text{ mm}\cdot\text{s}^{-1}$ ,  $\Gamma = 0.28 \pm 0.02 \text{ mm}\cdot\text{s}^{-1}$ , and  $\Delta E_Q = 2.69 \pm 0.02 \text{ mm}\cdot\text{s}^{-1}$ , which are assigned to Fe(OH)<sub>2</sub>.<sup>65</sup> To investigate the origin of the Fe(OH)<sub>2</sub> component, the time dependence of the thermal reaction was measured at 250 °C and 300 °C, as shown in Figure 4. At 250 °C, the feature at  $2.7 \text{ mm}\cdot\text{s}^{-1}$  grows with annealing time, indicating no Fe(OH)<sub>2</sub> initially to a significant peak after 2 h. In contrast, at 300 °C, the Fe(OH)<sub>2</sub> content is present when the sample is immediately quenched and then generally diminishes with annealing.

The observations can be explained by the reduction of Fe(OH)<sub>3</sub> by NO<sub>2</sub>

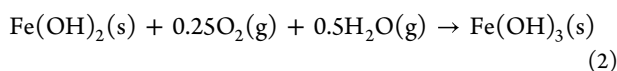


This reaction becomes exergonic for temperatures greater than 271 °C (calculated using the Shomate equation and data from the NIST Chemistry web book<sup>68</sup>). This reaction accounts for the absence of NO<sub>2</sub> in the gas-phase IR spectra reported

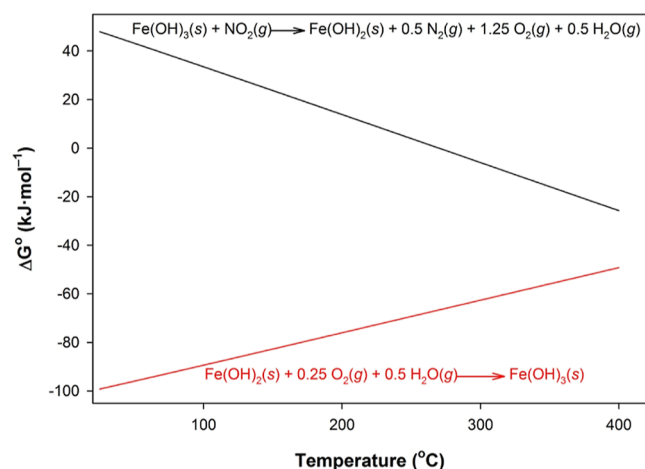


**Figure 4.** Temporal evolution of the Mössbauer spectra of Fe<sup>3+</sup>/PVDF samples at 250 °C and 300 °C. The spectra are normalized to the peak near 0 mm·s<sup>-1</sup>. The insets show the intensities of the peaks at 2.7 mm·s<sup>-1</sup> (black circles) and 0.77 mm·s<sup>-1</sup> (red triangles). The lines are modeled using the kinetic equations discussed in the text.

earlier.<sup>48</sup> The reoxidation of Fe(OH)<sub>2</sub> by dioxygen is exergonic throughout the entire temperature range investigated



The temperature dependence of  $\Delta G^\circ$  for eqs 1 and 2 are shown in Figure 5. Reaction (1) becomes more favorable as



**Figure 5.**  $\Delta G^\circ$  calculated for the indicated reactions using the Shomate equation.

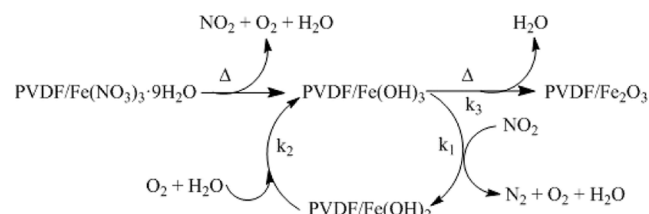
the temperature increases. At 250 °C, the reduction of the Fe<sup>3+</sup> species is slightly endergonic. The reoxidation of Fe(OH)<sub>2</sub> is thermodynamically very favorable, but access to other gas-phase reactants, O<sub>2</sub> and H<sub>2</sub>O, is limited in the thin films, so that the reduced iron can remain stable for several hours.

Scheme 1 summarizes the thermal reactions of the Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O-doped PVDF thin films. The rate equations for the catalytic cycle are given in the Supporting Information and can be solved by linearizing the rate constants as

$$k'_1 = k_1[\text{NO}_2] + k_3 \quad (3)$$

$$k'_2 = k_2[\text{O}_2]^{1/4}[\text{H}_2\text{O}]^{1/2} \quad (4)$$

### Scheme 1. Reaction Sequence in the Thermal Decomposition of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O Doped Into PVDF



with the rate constants  $k_1$ ,  $k_2$ , and  $k_3$  shown for the reactions in Scheme 1. The model assumes that gas-phase dioxygen, water, and nitrogen dioxide are in sufficient excess so that the values of  $k'_1$  and  $k'_2$  are essentially constant. In addition, the initial conditions needed to solve of the coupled kinetic equations were that the intermediate and product species (PVDF/Fe(OH)<sub>2</sub> and PVDF/Fe<sub>2</sub>O<sub>3</sub>) are absent at  $t = 0$ . The Mössbauer spectra can be used to determine the relative amounts of Fe<sup>2+</sup> and Fe<sup>3+</sup> species independently. The peak at  $\sim 0.3$  mm·s<sup>-1</sup> has components from all absorbing species and hence is used as an internal reference. Then, the intensity of the peak at 2.7 mm·s<sup>-1</sup> measures the relative amount of Fe<sup>2+</sup>, and the intensity of the feature at 0.77 mm·s<sup>-1</sup> represents the relative amount of Fe<sup>3+</sup> species, approximated as Fe(OH)<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> in Scheme 1. The relative intensities of each species are calculated using the eqs S1, S2, and S3 in the Supporting Information and are shown as the solid lines in the insets of Figure 3. At 250 °C, the model parameters are  $k'_1 = 0.1$ ,  $k'_2 = 0.2$ , and  $k_3 = 0.01$ , and at 300 °C,  $k'_1 = 7.1$ ,  $k'_2 = 7.2$ , and  $k_3 = 0.7$ . These values are only representative since there are not enough data points to evaluate a unique fit. The model is not ideal but captures the magnitudes of the compositional changes and qualitatively accounts for the increase and then decrease in concentration the intermediate Fe[OH]<sub>2</sub>. The magnitudes of the pseudo-first-order rate constants are consistent with the qualitative observations: the rate constants within the Fe<sup>2+</sup>/Fe<sup>3+</sup> catalytic cycle are comparable to each other, allowing for cycling, but greater than the rate constant leading to the final decomposition to the oxide product. In addition, the rate constants at the lower temperature are much smaller than those at the higher temperature, as would be

expected by elementary considerations. The limitations of the model arise from two assumptions. First, the concentrations of the gas-phase components ( $\text{NO}_2$ ,  $\text{O}_2$ , and  $\text{H}_2\text{O}$ ) are assumed to be constant relative to the concentration of the iron species. Second, the model assumes that at a given temperature, the initial concentrations of  $\text{Fe}(\text{OH})_2$  and  $\text{Fe}_2\text{O}_3$  are zero. However, as the samples are brought to the desired temperature, reaction is occurring during heating. Despite the limitations of the model, however, the general behavior of the reaction is recovered.

Since no  $\text{Fe}^{2+}$  species are observed in the thermal decomposition of the pure salt, it is apparent that the PVDF environment is critical for the decomposition of  $\text{NO}_2$ . Since the thermal reaction occurs above the melting point of any of the PVDF phases, the crystallinity and associated properties are not germane. There may be some weak bonding between the F atoms and the  $\text{Fe}^{3+}$  ions, but there is no direct evidence of this type of coordination. Finally, the PVDF melt likely retards the transport of the gas-phase products from the nitrate decomposition. Thus, any  $\text{NO}_2$  formed that is not at the surface of the melt must diffuse through the viscous polymer allowing an encounter with  $\text{Fe}(\text{OH})_3$  sites to activate the reduction of the iron ion.

## CONCLUSIONS

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ -doped PVDF was studied using IR, XRD, and Mössbauer spectroscopy. At room temperature, the cast films show a high fraction of the ferroelectric  $\beta$ -phase in the crystalline fraction of the polymer host. Moreover, the Mössbauer spectrum shows two  $\text{Fe}^{3+}$  sites, which are assigned to iron ions located in the  $\beta$ -phase and amorphous regions of the polymer. Heating the films to temperatures below the polymer melting point shows little change in the Mössbauer spectra, but when heated above the polymer melting point, all of the  $\beta$ -phase PVDF is lost and the polymer crystallizes in the  $\alpha$ -phase. Further heating leads to decomposition of the iron nitrate dopant. Examination of the Mössbauer spectra of thermal decomposition products of the composite material has identified an unexpected  $\text{Fe}^{2+}$  intermediate. The initial thermolysis of the nitrate ion gives dioxygen, water, and, presumably, nitrogen dioxide as gas-phase products and the remaining iron as likely in the form of  $\text{Fe}(\text{OH})_3$  or  $\text{FeOOH}$ . The reduction reaction is induced by decomposition of  $\text{NO}_2$  into  $\text{O}_2$  and  $\text{N}_2$ , which is supported by thermodynamic calculations. The  $\text{Fe}^{2+}$  species, assigned to  $\text{Fe}(\text{OH})_2$ , is reoxidized to  $\text{Fe}^{3+}$  by  $\text{O}_2$  so that the final product for the iron species is  $\text{Fe}_2\text{O}_3$ . A catalytic cycle is proposed showing how the iron sites doped in the polymer promote the loss of  $\text{NO}_2$  initially generated by the  $\text{NO}_3^-$  decomposition. The polymer is a critical component of the catalytic cycle retarding the diffusion of the gas-phase products away from the iron-ion sites. Addition of an external source of  $\text{NO}_2$  to determine if the composite material can catalyze the decomposition of this pollutant will be the work of future studies.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c04970>.

FTIR spectra, Mössbauer spectra, and XRD diffractograms of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  heated to various temperatures and kinetic equations (PDF)

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### Notes

The authors declare no competing financial interest.

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