Sensors

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Magnetochromatic Polydiacetylene by Incorporation of Fe_3O_4 Nanoparticles**

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Conjugated polymers have been explored for a broad spectrum of applications, particularly in optoelectronic and sensing materials, because the π-electron delocalization in the backbones provides them with intriguing electronic and optical properties.[1] For example, polydiacetylene (PDA) exhibits an intense chromatic transition, typically from blue to red, in response to various external stimuli, such as temperature, pH, ion, solvent, and ligand interaction.[1–11] This colorimetric change can be easily perceived by the naked eye, making PDA an ideal candidate for sensing applications. The color changes of PDAs are caused by the shortening of the effective PDA conjugation length as a result of changes in the conformation of the polymer backbone under stimuli. To improve their practical applications, increasing interest has been extensively attracted to explore PDAs with new sensing functionalities. For example, electron- and light-induced PDA/carbon nanotube fibers and PDA/azobenzene nanomaterials were recently discovered by the groups of Peng[12–14] and Zou,[15,16] respectively. The common and critical strategy is to form nanocomposites by introducing the second phases with specifically designed structures and functionalities. However, to the best of our knowledge, no magnetism-induced chromatism has ever been realized in PDA. However, magnetochromatic PDA materials could be advantageous for many applications ranging from small devices to aircraft as they are low-cost in fabrication, simple in structure, high-efficiency in sensitivity, and convenient and safe in operation.

A possible approach to fabricate magnetochromatic PDA systems is to introduce other nanomaterials that may induce PDA conformational changes upon exposure to a magnetic field. Iron oxide nanoparticles have been widely studied for their superparamagnetic properties in recent years and represent one of the ideal candidates to meet this requirement.[17–20] Herein, we first incorporated Fe_3O_4 nanoparticles into PDA to produce high-quality composites that change colors in AC magnetic field through a ready and efficient self-assembly process. The synthetic procedures are shown in Figure 1. Diacetylenic monomers are first connected to the outer surfaces of Fe_3O_4 nanoparticles by hydrogen bonds, and the resulting core/shell nanoparticles assemble into films after evaporation of solvent. PDA/Fe_3O_4 composite films can be finally synthesized through topochemical polymerization of diacetylenic moieties under UV light. When exposed to AC magnetic field, the PDA/Fe_3O_4 nanomaterials change colors, for example, from blue to red.

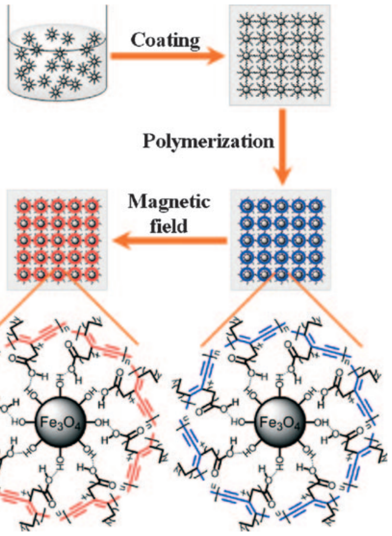

Figure 1. Schematic illustration to the synthesis of the magnetochromatic polydiacetylene by incorporation of Fe_3O_4 nanoparticles. The subscripts *x* and *y* refer to the numbers of methylene groups.

We synthesized Fe_3O_4 nanoparticles with controlled diameters from 4 to 13 nm by co-precipitation.[21,22] Figure 2a shows a typical transmission electron microscopy (TEM) image with average diameter of 8 nm. Powder X-ray diffraction was carried out to characterize the nanocrystalline

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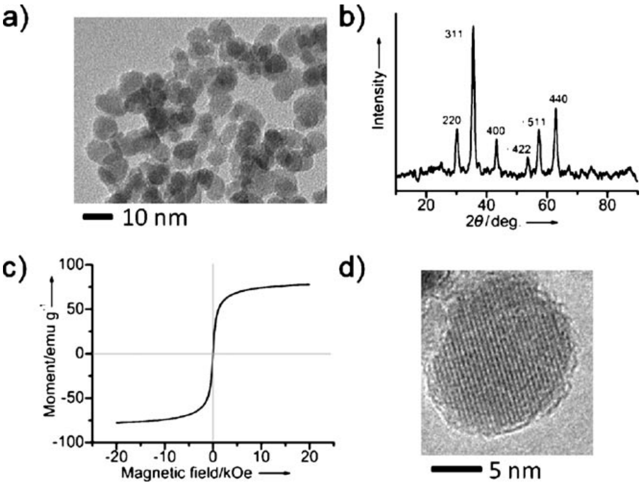

Figure 2. a) TEM image, b) XRD pattern, and c) hysteresis loop of Fe_3O_4 nanoparticles. d) TEM image of a Fe_3O_4 composite nanoparticle derived from $CH_3(CH_2)_9CCCC(CH_2)_3COOH$.

structure of the Fe_3O_4 nanoparticles. Figure 2b shows a representative pattern, which identifies the formation of Fe_3O_4 materials with a cubic inverse spinel structure with characteristic peaks of (220), (311), (400), (422), (511), and (440).[21] The magnetic properties of Fe_3O_4 nanoparticles were investigated by a superconducting quantum interference device at 300 K. As expected, the synthesized Fe_3O_4 nanoparticles exhibit superparamagnetic behavior confirmed by zero coercivity and remanence on the hysteresis loop (Figure 2c). A high saturation magnetization of 77.9 emu g^{-1} was found for these nanoparticles.

As designed, the Fe_3O_4 nanoparticles showed hydroxide groups on their outer surfaces.[23,24] The average weight content of hydroxide groups was determined to be about 6.5% by thermogravimetric analysis and differential thermal analysis (Figure S1 in the Supporting Information). The precursors, diacetylenic acids, were then connected to the Fe_3O_4 nanoparticles through hydrogen bonds between carboxy and hydroxide groups. According to our previous studies, the building monomers were critical to the sensitivity of resulting PDA materials.[14] Therefore, three different diacetylenic acids, namely, $CH_3(CH_2)_9CCCC(CH_2)_3COOH$, $CH_3(CH_2)_9CCCC(CH_2)_4COOH$, and $CH_3(CH_2)_{11}CCCC(CH_2)_8COOH$, were used and compared in this study. The formation of a layer of diacetylenic monomers on the outer surfaces of pure Fe_3O_4 nanoparticles was confirmed by Fourier transform infrared spectrometry (Figure S2). The characteristic peak at 1695 cm^{-1} for free carbonyl groups of diacetylenic acids moved to 1684 cm^{-1}, which corresponds to the formation of hydrogen bonds.[25] The complexation of diacetylenic acids on the Fe_3O_4 nanoparticles was also confirmed by high-resolution TEM analysis. As shown in Figure 2d and Figure S3, a thin layer of diacetylenic monomer molecules with relatively lighter contrast compared to the Fe_3O_4 nanoparticle was found on the outer surface. In fact, owing to the formation of Fe_3O_4/diacetylenic acid core/shell nanostructure, the composite nanoparticles could be well dispersed in tetrahydrofuran and further assembled into uniform black brown films (the color originated from iron oxide, and diacetylenic monomers were colorless) after evaporation of solvent.

Under UV irradiation, the diacetylenic moieties underwent topochemical polymerization to produce polydiacetylene with an apparent color change to blue. The high-quality PDA/Fe_3O_4 nanocomposites were characterized by optical microscopy, fluorescent microscopy, and scanning electron microscopy (SEM), as shown in Figure 3. The composite films are uniform and show a crystalline-like structure (Figure 3a,b). The SEM image in Figure 3c reveals that Fe_3O_4 particles are uniformly dispersed in the PDA matrices. Before exposure to the magnetic field, PDA/Fe_3O_4 films from the three monomers are not visible under fluorescent microscopy. Interestingly, upon exposure to an AC magnetic field (e.g., 15 kA m^{-1}, 55 kHz), the composite films derived from $CH_3(CH_2)_9CCCC(CH_2)_3COOH$ were visible under fluorescent microscopy, and Figure 3d shows a typical fluorescent image. However, the composite films obtained from $CH_3(CH_2)_9CCCC(CH_2)_4COOH$ and $CH_3(CH_2)_{11}CCCC(CH_2)_8COOH$ remained invisible. It has been known that blue-phase PDA materials are nonfluorescent whereas their red-phase counterparts exhibit fluorescence.[2] Therefore, a color change from blue to red in the case of $CH_3(CH_2)_9CCCC(CH_2)_3COOH$ may occur after the above process. In fact, the above blue-to-red transition in the derived PDA/Fe_3O_4 film could be also easily observed by the naked eye. Figure 3e,f shows photographs of the composite film in blue and red phases, respectively.

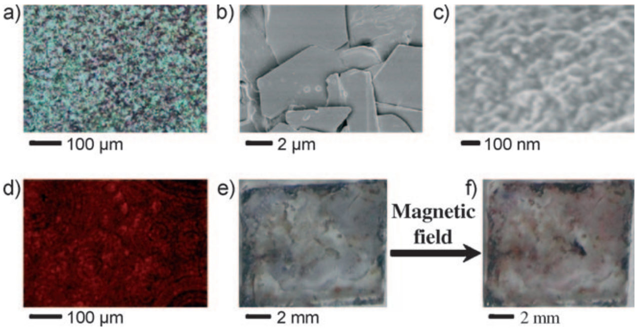

Figure 3. Characterization of the PDA/Fe_3O_4 composite film derived from $CH_3(CH_2)_9CCCC(CH_2)_3COOH$: a) Optical microscopy image. b) SEM image. c) SEM image at higher magnification. d) Fluorescent microscopy image. e,f) Photographs of the PDA/Fe_3O_4 composite film before (e) and after (f) color changes upon exposure to an AC magnetic field.

The chromatic transition was further confirmed by UV/Vis spectrometry. Figure 4a compares the UV/Vis spectra of a PDA/Fe_3O_4 film derived from $CH_3(CH_2)_9CCCC(CH_2)_3COOH$ with a weight ratio of PDA to Fe_3O_4 of 100:1. Before exposure to an AC magnetic field, the composite films mainly showed a characteristic peak at about 631 nm for the blue phase; after exposure to the magnetic field, a new peak corresponding to the red phase appeared at about 550 nm. The exposure time depended on the thickness of the composite film and was up to 60 min. With an increase of

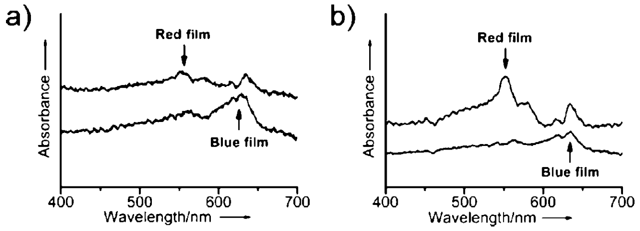

Figure 4. UV/Vis spectra of the composite films derived from $CH_3(CH_2)_9CCCC(CH_2)_3COOH$ at weight ratios of PDA to Fe_3O_4 nanoparticles of a) 100:1 and b) 10:1.

Fe_3O_4, (e.g., weight ratio of 10:1), the composite blue films became red more quickly with higher efficiency (see Figure 4b). It should be noted that the peaks of the blue phase greatly decreased but did not disappear. This result may be explained by the fact that not all PDA backbones closely surrounded the Fe_3O_4 nanoparticles, and those a little far away from the Fe_3O_4 nanoparticles would not be heated enough to change their conformations. This limitation can be solved by increasing the quality of Fe_3O_4 nanoparticles (e.g., more uniform sizes), and improving the uniformity of composite films according to our previous work.[4] As a comparison, almost no red peaks were found for the PDA/Fe_3O_4 film derived from $CH_3(CH_2)_9CCCC(CH_2)_4COOH$ and $CH_3(CH_2)_{11}CCCC(CH_2)_8COOH$ in a range of weight ratios between 10:1 and 100:1 after exposure to the same AC magnetic field (Figure S4). Nevertheless, it should be noted that the PDA nanocomposites derived from $CH_3(CH_2)_9CCCC(CH_2)_4COOH$ and $CH_3(CH_2)_{11}CCCC(CH_2)_8COOH$ could change colors by varying the experimental parameters according to power dissipation equation for a superparamagnetic nanoparticle [Eq. (1)],[26] where μ_o is

$$P = \mu_o \pi f \chi'' H^2 \tag{1}$$

constant, f is frequency of magnetic field, χ'' is out-of-phase component of the susceptibility, and H is amplitude of magnetic field. Because χ'' is a material-related parameter, the compositions, shapes, sizes, and size distributions of the nanoparticles greatly influence their heating efficiencies. Therefore, the chromatic transitions of PDA nanocomposites prepared from both $CH_3(CH_2)_9CCCC(CH_2)_4COOH$ and $CH_3(CH_2)_{11}CCCC(CH_2)_8COOH$ can be induced by increasing the frequency of the AC field, the amplitude of the field or decreasing the particle polydispersity. For example, an increase of frequency from 55 to about 100 kHz may induce the chromatic transitions of PDA nanocomposites prepared from both $CH_3(CH_2)_9CCCC(CH_2)_4COOH$ and $CH_3(CH_2)_{11}CCCC(CH_2)_8COOH$.

On the basis of the above phenomena, the magnetochromatic mechanism in PDA can be summarized as follows. It is well known that superparamagnetic nanoparticles produce heat internalized in and localized near them through Néel relaxation under an AC magnetic field, and the heat may induce the color change of surrounding PDA. For the three monomers of $CH_3(CH_2)_9CCCC(CH_2)_3COOH$, $CH_3(CH_2)_9CCCC(CH_2)_4COOH$, and $CH_3(CH_2)_{11}CCCC(CH_2)_8COOH$, the resulting pure PDA materials began to change colors at 41–42 °C, 45–46 °C, and 53–54 °C, respectively. That is, the PDA/Fe_3O_4 nanocomposite derived from $CH_3(CH_2)_9CCCC(CH_2)_3COOH$ is more sensitive to heat and may change colors at lower temperature relative to the other two monomers. As a result, the PDA composite films from $CH_3(CH_2)_9CCCC(CH_2)_3COOH$ showed a magnetochromatic transition at low frequency of 55 kHz, whereas the resulting PDA composite films from the other two monomers did not. Moreover, it can be also concluded that the temperatures of composite materials should be higher than 41 but lower than 45 °C under the AC magnetic field. The PDA/Fe_3O_4 nanocomposites derived from the three monomers could be readily used to indicate the environmental temperatures from 41 to 54 °C along this conception.

The above tunable chromatic properties of PDA materials in the temperature range of 41–45 °C by engineering the building monomers are promising for a broad spectrum of sensing applications. The superparamagnetic Fe_3O_4 nanoparticles have been extensively used in the biomedical field; for example, they were delivered to treat cancers.[19,27] The produced heat from these nanoparticles in AC magnetic fields is expected to kill cancer cells, and the mechanism has been well studied.[28] The desired temperature typically ranges from 41 to 45 °C. However, it is challenging to safely determine and control the above environmental temperature from the superparamagnetic Fe_3O_4 nanoparticles by tuning AC magnetic fields. At this point, if PDA nanomaterials are integrated into the therapeutic Fe_3O_4 nanosystems, the resulting nanothermometers would be very sensitive to the change of environmental temperature. Therefore, it is safe, convenient, and accurate to tune the produced heat to kill the cancer cells more efficiently.

The structure of the above nanothermometer is shown schematically in Figure S5. The nanothermometer is composed of three main parts, namely, Fe_3O_4 as the core, PDA as the middle shell, and a hydrophilic polymer used to stabilize the nanosystem in aqueous solution as the outer shell. As discussed, the magnetocaloric temperature exactly matches the sensing temperature range of 41–45 °C indicated by PDA materials prepared from $CH_3(CH_2)_9CCCC(CH_2)_3COOH$ and $CH_3(CH_2)_9CCCC(CH_2)_4COOH$. That is, the environmental temperature may be readily controlled between 41 and 45 °C by varying the AC magnetic fields to make PDA materials derived from $CH_3(CH_2)_9CCCC(CH_2)_3COOH$ change colors while not for PDA materials derived from $CH_3(CH_2)_9CCCC(CH_2)_4COOH$. Note that the PDA materials prepared from $CH_3(CH_2)_9CCCC(CH_2)_3COOH$ change colors from blue to red, whereas those from $CH_3(CH_2)_9CCCC(CH_2)_4COOH$ change colors from blue to orange, so it is easy to detect the difference of chromatic transitions by spectrometer. As designed, these nanothermometers could monitor a safe and efficient cancer therapy. In addition, the used frequencies to induce the chromatic transitions of the PDA/Fe_3O_4 nanoparticles derived from the three monomers range from 55 to 100 kHz, which fall in the typical frequency range of a wide variety of biomedical applications (50–100 kHz) other than cancer treatment.[29] The typical UV/Vis spectra of PDA nanomaterials before and after chromatic transitions derived from three building monomers are shown in Figure S6. As expected, the magnetochromatic response has met the requirements of the above applications. Nevertheless, the response speed may be further improved for more applications compared to the other new stimuli, such as current. The above issues will be studied in detail later.

In conclusion, this work reports a novel magnetochromism in PDA nanocomposites through incorporation of superparamagnetic Fe_3O_4 nanoparticles. The color changes could be easily detected by spectrometer and observed by the naked eye. These composite nanomaterials show promising applications in a wide variety of fields, such as intelligent and sensing devices.

Experimental Section

The Fe_3O_4 nanoparticles were synthesized through a co-precipitation method. Typically, $FeCl_2\cdot 4H_2O$ (5.6 mmol) and $FeCl_3\cdot 6H_2O$ (11.2 mmol) were dissolved in deionized water (150 mL) in a 250 mL three-neck flask. The resulting mixture solution was heated to 50 °C and vigorously stirred under a nitrogen atmosphere. Aqueous ammonia solution (25 %; 12.5 mL) was rapidly added to the solution with an immediate color change to black. The reaction solution was cooled down to room temperature after reaction for 30 min, and the Fe_3O_4 nanoparticles were collected by magnetic separation. The nanoparticles were further washed with deionized water three times.

The PDA/Fe_3O_4 composite films were fabricated through a simple solution process. Diacetylenic acids were dissolved in THF with concentration at about 20 $mg\,mL^{-1}$ and then filtered with a membrane (pore diameter of 0.22 μm) to remove impurities and precipitants. The resulting monomer solutions were diluted to 10 $mg\,mL^{-1}$, and the Fe_3O_4 nanoparticles were then added to the monomer solutions with weight ratios of PDA to Fe_3O_4 of 100:1 or 10:1, depending on the requirements. The mixture solutions were cast onto glass slides to fabricate films after evaporation of solvent at room temperature. Finally, the blue PDA/Fe_3O_4 nanocomposite films were prepared by topochemical polymerization of diacetylenic moieties under UV light at wavelength of 254 nm typically for minutes (10 cm between the sample and the UV lamp). The blue PDA materials synthesized from the three building monomers of $CH_3(CH_2)_9CCCC(CH_2)_3COOH$, $CH_3(CH_2)_9CCCC(CH_2)_4COOH$, and $CH_3(CH_2)_{11}CCCC(CH_2)_8COOH$ showed chromatic transitions of blue to red, blue to orange, and blue to red in appearance, respectively, upon exposure to environmental stimuli.

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