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Nanocomposites of Polydiacetylene and Rare Earth Ions with Reversible Thermochromism

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We report a facile approach to water-dispersible polydiacetylene/rare earth ions nanocomposites with reversible thermochromism. The nanocomposites were prepared by doping rare earth ions Dy^{3+} or Sm^{3+} into layer-structured 10,12-pentacosadiynoic acid (PCDA) nanoparticles to obtain PCDA/rare earth ions nanocomposites (PCDA-RE) and subsequently annealing PCDA-RE at the temperature slightly higher than the melting point of pure PCDA crystals, followed by topochemically polymerizing the annealed PCDA-RE. The polymerized PCDA-RE, *i.e.* poly(10,12-pentacosadiynoic acid)/rare earth ions nanocomposites (PDA-RE: PDA-Dy or PDA-Sm), are largely reversible (PDA-Sm) or even completely reversible (PDA-Dy) in the thermochromism, while, without the doping, pure PDA is completely irreversible. It is confirmed that, PDA-RE are also layer-structured with a *d*-spacing of 5.4 nm, higher than the *d*-spacing of pure PDA (4.7 nm). In PDA-RE, the rare earth ions form a layer in-between and interact strongly with the PDA bilayers, being responsible for the high degree or even the complete reversibility. This is the first example to make PDA completely reversible through the doping of rare earth ions; the annealing process is essential for the complete reversibility since it removes any defects in the structure.

Key words: Polydiacetylenes, Rare earth ions, Reversible thermochromism, Thermal annealing

I. INTRODUCTION

Polydiacetylenes, one kind of conjugated polymers, have attracted much attention in both theoretical and practical research fields. Polydiacetylenes have eminent optical and electrical properties, and are thus promising in nonlinear optical, photovoltaic and biomedical applications [1−4]. Besides, polydiacetylenes have a variety of chromism; they change their color when exposed to the external stimuli such as temperature, pH, metal ion, mechanical stress, and magnetic or electrical field [5−9], which make polydiacetylenes promising for chemical sensors or biosensors. Among the chromism, thermochromism, which makes polydiacetylenes change their color from blue to red when heated, is most widely studied. As the thermochromism of polydiacetylenes in their original form is irreversible and the irreversibility prevents them from being repeatedly used, considerable efforts are devoted to making the polydiacetylenes reversible. It is known that polydiacetylenes are the product of topochemical polymerization of diacetylenes (or their composites) as the precursors [10, 11]. For preparing polydiacetylenes with reversible thermochromism,

the structures of the precursors have to be deliberately controlled. The reversibility requires that, in the structures of precursors, the interaction among the side chains of diacetylenes is sufficiently enhanced (which was realized through chemically modifying the diacetylenes [12−18]), or the side chains of diacetylenes are fixed on a solid matrix including silica [19, 20], carbon nanotube [21], and polymers [22, 23]. It also requires that all the chemical and physical modifications should not prevent the backbone of diacetylenes from packing properly, otherwise they cannot be topochemically polymerized. These usually make the preparation of reversible polydiacetylenes difficult [24].

Herein, we report a convenient and robust approach to the nanocomposites PDA-RE (where PDA represents poly(10,12-pentacosadiynoic acid), and RE is the rare earth ions) with the completely reversible (PDA-Dy) or largely reversible (PDA-Sm) thermochromism. PCDA-RE (PCDA: 10,12-pentacosadiynoic acid) are simply prepared by mixing the rare earth ions with PCDA nanoparticles in water:ethanol (9:1) mixture solvent, followed by annealing the suspension at the temperature slightly higher than the melting point of pure PCDA crystals. After the topochemical polymerization, PCDA in the nanocomposites was polymerized into PDA, and PCDA-RE nanocomposites became PDA-RE nanocomposites, in which the carboxylic groups of the

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side chains of PDA conjugated backbone are non-covalently cross-linked and thus fixed by the multivalent rare earth ions. The cross-linking provides the restoring force for the PDA backbones to restore to their original conformation upon cooling back to room temperature, making the PDA-RE nanocomposites completely reversible (PDA-Dy) or largely reversible (PDA-Sm) in the thermochromism. The annealing is essential for the formation of the completely reversible PDA-Dy since it leads to the defects-free nanostructure, which ensures the full coordination interaction between Dy^{3+} and the carboxylic groups of PDA in the nanostructure.

II. EXPERIMENTS

A. Materials

10,12-pentacosadiynoic acid $(CH_3(CH_2)_{11}-C\equiv C-C\equiv C-(CH_2)_8-COOH$, PCDA) was purchased from GFS Chemicals, Inc. Dysprosium(III) chloride hexahydrate and samarium(III) chloride hexahydrate were purchased from J&K Chemical Ltd., China. Absolute ethanol was purchased from Sinopham Chemical Reagent Co., Ltd., China. All the reagents and solvents were used as received without further purification.

B. Preparation of PCDA-RE and PDA-RE

In a typical preparation experiment of PCDA-RE, PCDA was dissolved in absolute ethanol at the concentration of 1 mmol/L. The PCDA ethanol solution was filtered through 0.45 μm filter to remove any polymerized impurity just before use. PCDA nanoparticles were prepared by dropwise adding 20 mL of the PCDA ethanol solution into 180 mL water under stirring at 25 °C. The suspension of the nanoparticles in $9/1$ (V/V) mixture solvent was stirred for a few hours. Then, to the suspension of the PCDA nanoparticles, 1 mL $DyCl_3$ or 1 mL $SmCl_3$ aqueous solution at the concentration of 20 mmol/L was added, and the resultant nanocomposites PCDA-Dy or PCDA-Sm in the mixture solvent was stirred for additional 2−4 h. Afterwards, the glass vessel containing the suspension of PCDA-Dy or PCDA-Sm was sealed and annealed in an oven at 68 °C (the melt point of PCDA is 65 °C) for 6 h. After the annealing, the suspensions were stored in a refrigerator at 4 °C overnight. Just after the storing, the respective suspensions were exposed to UV irradiation at room temperature for 2 min, leading to PDA-RE.

C. Instruments and characterizations

Dynamic light scattering (DLS) was performed on an ALV-5000 Laser scattering spectrometer equipped with a multi-τ digital time correlation and a He-Ne laser (λ=632.8 nm) light source. A JEOL 2000FX transmission electron microscope (TEM) was used to characterize the morphology of PCDA-RE nanocomposites without or with the annealing at 68 °C. Before the TEM observations, the PCDA-RE solution was dialyzed against water to remove free rare earth ions. Then, the dialyzed solution was deposited onto a carbon-coated copper grid. X-ray powder diffraction (XRPD) was conducted on a X'Pert PRO (X'Celerator diffractometer, operating at 40 kV, 40 mA, Cu Kα radiation, λ=0.15406 nm). Fourier transform infrared spectroscopy (FTIR) were recorded in the range 4000−400 cm^{-1} on a Nicolet Nexus 470 spectrometer with a resolution of 4 cm^{-1}, and 64 scans were available for an acceptable signal-to-noise ratio. A mettler differential scanning calorimetry (DSC) apparatus was used to determine the thermal properties. All the DSC experiments were carried out in a nitrogen atmosphere. DSC samples were heated to 100 °C at the heating rate of 10 °C/min. Shimadzu UV-2550 Spectrophotometer was used for UV-Vis measurements. The highest temperature for the measurement was 85 °C.

III. RESULTS AND DISCUSSION

A. Preparation of PCDA-RE nanocomposites

Nano- or micro- sized crystal of a small molecular organic compound with a certain degree of amphiphilicity can be prepared by adding a dilute solution of the organic compound in a water-soluble organic solvent into its non-solvent water [25]. In the present study, PCDA is amphiphilic and the PCDA particles are prepared by slow addition of PCDA solution in ethanol into water, as described in the experiment section. The as-prepared PCDA particles in the mixed solvent (water/ethanol=9/1, V/V) have an average hydrodynamic diameter of 32 nm by DLS. Then, rare earth ions Dy^{3+} and Sm^{3+} were added into the suspensions, respectively. After the addition of the rare earth ions, the size of nanoparticles increased, aggregation between the PCDA nanoparticles took place due to the bridging coupling by the multivalent rare earth ions. DLS measurements demonstrated that the hydrodynamic radius of PCDA-Dy was 155 nm, and that of PCDA-Sm was 152 nm.

TEM observation reveals that both PCDA-Dy and PCDA-Sm (Fig.1 (a) and (b)) nanoparticles are with a spherical morphology. After the annealing at 68 °C, the sizes of PCDA-Dy and PCDA-Sm particles further increased to 1.4 μm (PCDA-Dy) and 1.5 μm (PCDA-Sm), respectively, according to TEM observations (Fig.1 (c) and (d)). After the annealing, the PCDA-RE nanocomposites became more regular in the morphology, and can be well-dispersed in the suspensions, because no precipitates were observed in the suspensions during the storing for several days.

The crystal structure of the annealed PCDA-RE was characterized by XRPD. As exhibited in Fig.2, the diffraction patterns of PCDA-Dy and PCDA-Sm were
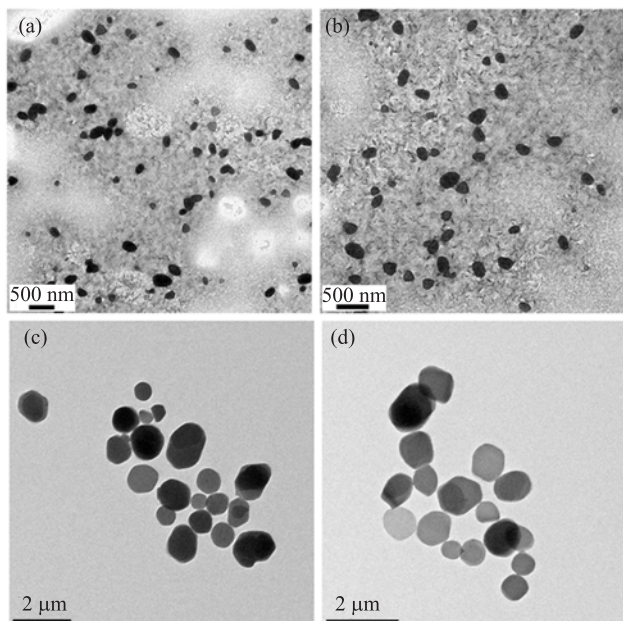
FIG. 1 TEM images of PCDA-RE before (a,b) and after (c,d) annealing at 68 °C. (a) and (c) PCDA-Dy, (b) and (d) PCDA-Sm, respectively.
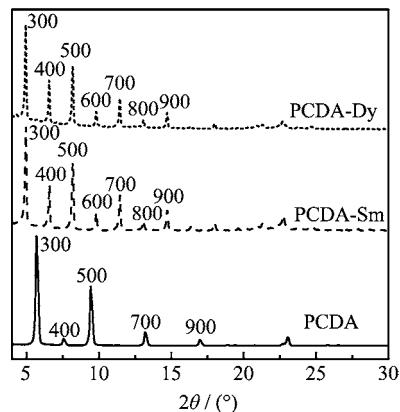

FIG. 2 XRPD spectra of the PCDA, PCDA-Dy, and PCDA-Sm.

FIG. 3 (a) FTIR spectra of PCDA and (b) DSC curves, the annealed PCDA-DY and the annealed PCDA-Sm.

remarkably different from the pattern of pure PCDA crystal. The peaks in the small angle range of the patterns of the nanocomposites could be indexed to the $(00l)$ planes (l=1, 2, 3...), which indicates the lamellar structure along the c-axis in the crystalline phase. The d-spacing of the PCDA-Dy and that of the PCDA-Sm are 5.4 nm, much larger than the d-spacing of pure PCDA crystals, which is 4.7 nm. Obviously, the rare earth ions inserted into the layered structure of PCDA crystals.

According to FT-IR measurements of the nanocomposites, the insertion of the rare earth ions into the layered structure of PCDA results from the complexation of the rare earth ions with the carboxylic groups. In the FT-IR spectra of PCDA-Dy and PCDA-Sm (Fig.3(a)), the carbonyl stretching band (ν(C=O)) appears at 1538 cm^{-1}, while that of COOH of pure PCDA is located at 1693 cm^{-1}. This indicates the complexation between the carboxyl groups and rare earth ions [24]. Besides, the carboxyl groups in PCDA-Dy and PCDA-Sm are deprotonated, because the wavenumber of ν(C=O) is in the range of ν(C=O) of COO^{-} (much less than ν(C=O) protonated carboxyl groups (COOH), which should be around 1720 cm^{-1}). And the bands appearing at 1478 cm^{-1} can be ascribed to the symmetric stretching vibrations of carboxylate ν_{ss}(COO^{-}). Furthermore, the coordination type of COO^{-} in its complex with a kind of rare earth ions can be reflected by the wavenumber difference between the antisymmetric stretching vibration and the symmetric stretching vibrations of carboxylate [26]. It has been reported that, when the wavenumber difference is in the range

of 40−110 cm^{-1}, COO^{-} is a bidentate ligand. Therefore, COO^{-} in PCDA-Dy and PCDA-Sm complexes is a bidentate ligand, since the wavenumber difference is 60 cm^{-1} (1538−1478 cm^{-1}).

Furthermore, the annealed nanocomposites and pure PCDA crystals were characterized by DSC. As demonstrated in the DSC curves, the melting points of annealed PCDA-Dy and PCDA-Sm are 88 °C, being much higher than the melting point of pure PCDA crystals (Fig.3(b)). Obviously, the complexation with rare earth ions restricts movement of PCDA molecules in the crystals. This makes the melting of the PCDA crystal in the

nanocomposites difficult, and thus increases the melting points of PCDA crystals in the nanocomposites. As exhibited in Fig.3(b), no pure PDA signal was detected in the DSC curves of the annealed nanocomposites; excess DyCl$_3$ or SmCl$_3$ was used, which ensured that all the PDAC molecules in the systems were complexed. However, in the DSC curves of the un-annealed nanocomposites, two signals were observed: one was located at the temperature near the melting point of pure PCDA crystals, and the other appeared at the temperatures about 74 °C, which should be assigned to pure PDA crystals and the crystals of PCDA-RE complexes, respectively (data not shown). Obviously, there are defects in the un-annealed PCDA-RE complexes, so that the melting points are much lower than those of annealed PCDA-RE. The annealing can remove pure PCDA crystals and decrease or even remove defects in the systems. It should be mentioned here that since the pure PDA is irreversible, the existence of pure PCDA will result in incomplete reversibility since it will change to pure PDA after the polymerization. Besides, the defects will cause irreversible relaxation during heating, and thus results in irreversibility in the thermochromism. Therefore, as further confirmed below, the annealing is necessary for the reversibility.

B. Thermochromism of PCDA-RE

The annealed PCDA-Dy and PCDA-Sm nanocomposites were topochemically polymerized by exposing the respective suspensions to UV irradiation at 254 nm for 2 min, leading to PDA-Dy and PDA-Sm, respectively. The suspensions of PDA-Dy and PDA-Sm nanocomposites are blue colored. At 25 °C, the UV-Vis spectrum of PDA-Dy has a maximum absorption peak at 644 nm and a shoulder peak at 591 nm (Fig.4(a)), and the corresponding peaks in the spectra of PDA-Sm are located at 646 and 592 nm, respectively; the two spectra are almost the same. Upon heating from 25 °C to 85 °C, both the suspensions underwent blue-to-red color transition, and the maximum absorption peaks shift to 554 nm. After cooling the suspensions to 25 °C, the color of the suspension of PDA-Dy nanocomposites change back to the blue color, and its UV-Vis curve recovers the original curve before the heating; the thermochromism of PDA-Dy nanocomposites are completely reversible [22]. Regarding the suspension of PDA-Sm nanocomposites, after the heating-cooling cycle, the color goes back to a blue color, and the UV-Vis curve largely recovers the original one; a small peak at 551 nm still exists after the heating-cooling cycle. The PDA-Sm exhibits incompletely but largely reversible thermochromism.

C. Mechanism of the reversible thermochromism

The complete reversibility of PDA-Dy reveals that the PDA-Dy nanostructure should have no considerable
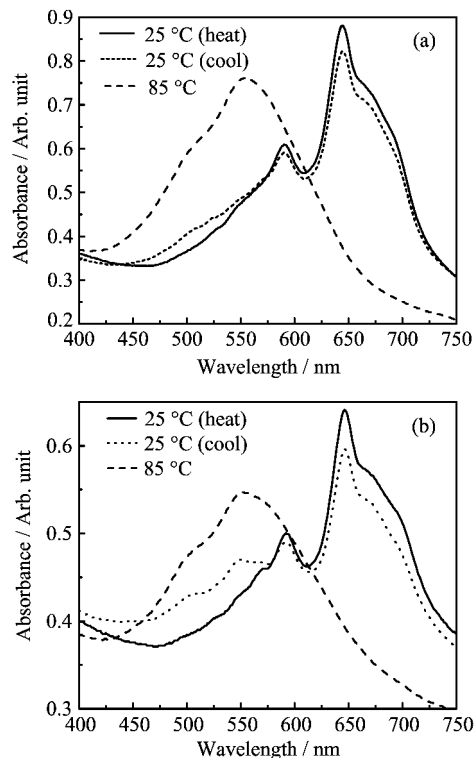

FIG. 4 UV-Vis spectra of (a) the annealed PDA-Dy and (b) the annealed PDA-Sm during heat-cool cycle.

defects (the defects will cause relaxation in the nanostructure during the heating and thus the irreversibility or incomplete reversibility in the thermochromism) [27]. Such a PDA-Dy nanostructure requires that: in the precursor (the annealed PCDA-Dy nanocomposites) (i) no considerable defects exist, and (ii) the PCDA molecules are properly packed (the defects in the PCDA-Dy will lead to defects in the resultant PDA-Dy, and the proper packing is required for the topochemical polymerization). Therefore, Dy^{3+} ions should form a layer sandwiched between two PCDA bilayers (Fig.2); it is unimaginable that any other manner of the insertion can meet these two requirements. This is also supported by the XRPD results (the insertion leads to a 0.7 nm increase in the d-spacing), and also necessitated by the complete reversibility, which requires that all the carboxyl groups have to be tethered to a solid matrix.

The detailed structure of PCDA-Dy can be determined if the COO$^-$/Dy molar ratio in the nanocomposites is determined. Unfortunately, our efforts to determine the molar ratio accurately fail; the repeatability of the obtained molar ratios is unsatisfactory although different methods to remove free Dy^{3+} were tried. However, the molar ratio in the nanocomposites can be evaluated according to the fact that the coordination number of rare earth ions in a confined structure was 6 [28]. Furthermore, FT-IR results reveal that, in PCDA-Dy nanocomposites, COO$^-$ is a bidentate ligand, as mentioned before. Therefore, the Dy^{3+}/COO$^-$ molar ratio
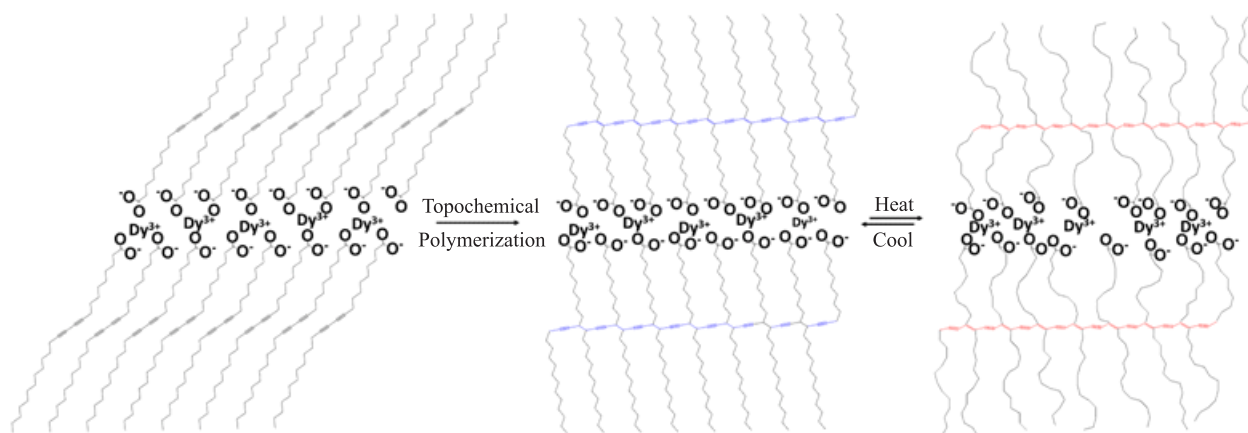
FIG. 5 Schematic description of the structures of PCDA-Dy, PDA-Dy in the blue form and PDA-Dy in the red form, respectively.

should be 1/3, which is also required for neutralization of the nanocomposites and the reversibility. Thus, the structure of PCDA-Dy can be proposed as Fig.5. The structure of PDA-Dy in blue form and that in red form can be determined accordingly. In the nanostructure described in Fig.5, the head group of each side chain of PDA backbone is tethered by coordination between the COO^- and the Dy^{3+}, which is responsible for the reversibility [22]. The annealing at 68 °C removes any pure PCDA nanocrystals (which will result in irreversible pure PDA crystals) and defects in the system, because they cannot survive at 68 °C. This leads to the complete reversibility.

As indicated in Figs. 2−4, the XRPD, FT-IR, and DSC results of PCDA-Sm nanocomposites are the same as the respective results of PCDA-Dy nanocomposites. The structure of PCDA-Sm should be the same as that of PCDA-Dy. The slight difference in the reversibility between PDA-Dy and PDA-Sm should result from the difference between the structures or/and sizes of Dy^{3+} and Sm^{3+}, which may have subtle effects on the reversibility.

IV. CONCLUSION

Polydiacetylenes with reversible thermochromism are prepared by inserting rare earth ions into the layered structure of diacetylenes and then annealing these nanocomposites at proper temperature, followed by the topochemical polymerization. When Sm^{3+} is used, the thermochromism is largely reversible, and the complete reversibility is achieved when Dy^{3+} is used. The strong complexation between rare earth ions and PCDA, and the removal of any defects in the nanostructures and pure PCDA nanocrystals from the systems by the annealing at temperature slightly higher than the melting point of pure PCDA crystals are essential for the reversibility. To the best of our knowledge, this is the first

example to make PDA completely reversible through the insertion of rare earth ions, which also provides a convenient way to introduce the functional species into polydiacetylenes.

V. ACKNOWLEDGEMENTS

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