Deliberately Designed Processes to Physically Tether the Carboxyl Groups of Poly(pentacosadiynoic acid) to a Poly(vinyl alcohol) Glassy Matrix to Make Poly(pentacosadiynoic acid) Thermochromically Reversible in the Matrix

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ABSTRACT: In this article, we demonstrate that by tethering carboxyl groups of poly(10,12-pentacosadiynoic acid) (PDA) to a poly(vinyl alcohol) (PVA) matrix, PDA, which is irreversible in its pure form, becomes reversible in the thermochromism. The tethering is realized by simple but deliberately designed processes: (1) Disperse the commercially available monomer 10,12-pentacosadiynoic acid (DA) nanocrystals in a PVA aqueous solution by the “NCCM” method invented in our laboratory. (2) Anneal and dry the mixture solution at a temperature higher than the melting point of pure DA crystal. (3) Polymerize the as-annealed DA/PVA blend films by UV irradiation. After the polymerization, PDA/PVA films with completely reversible thermochromism are obtained. The reversible PDA/PVA films can be easily dissolved in water, leading to water-dispersible nanoaggregates with the reversibility. Blends of PDA with other water-soluble polymers such as poly(ethylene oxide) (PEO), poly(acrylic acid) (PAA) and poly(allyamine) (PAM), were prepared respectively, by the same processes and under the same conditions. It is found that all these nanocomposites are irreversible or partially reversible in the thermochromism; either the relatively low glassy transition temperature of the polymer matrix (in the case of PEO) or the partial ionization nature of the polymer (in the cases of PAA and PAM) is responsible for the irreversibility or the partial reversibility.

1. INTRODUCTION

Polydiacetylenes have demonstrated intriguing properties such as color and fluorescence changes in response to external stimuli, which include heat, solvent, mechanical stress, and ligand–receptor interaction.1–14 These properties make polydiacetylenes promising in applications such as sensors for various purposes.15–21 In recent years, it is noted that most of the studies on polydiacetylenes started from diacetylene acids or diacetylene amines because they are commercially available. When properly packed, diacetylene acids can be topochemically polymerized into poly(diacetylene acid)s upon irradiation by UV, X-ray, or γ-irradiation.1,22,23 Poly(diacetylene acid)s often undergo an irreversible “blue-to-red” colorometric transition when environmental stimuli are applied. A great amount of effort has been devoted to making these originally irreversible color changes in poly(diacetylene acid)s reversible. This is not only encouraged by making the sensors reusable but also driven by the motivation to tailor the conformational change of a conjugated polymer backbone.24,25 These efforts reported in the literature can be roughly divided into two categories: (1) Chemical modification of the carboxyl groups of diacetylene acids to introduce multiple hydrogen bonding and strong aromatic or ionic interactions to enhance interactions among the head groups.2,3,6–30 In these cases, the modified diacetylene acids need to assemble into regular nanoaggregates such as vesicles, nanotubes, and thin films. In these nanoaggregates, the diacetylene segment must be properly packed to meet the requirements for the subsequent topochemical polymerization. Meanwhile, the neighboring head groups need to interact strongly with each other without disturbing the required packing of the diacetylene segments. Chemical modifications are thus needed. After the topochemical polymerization, the head groups of the modified diacetylene become the head groups in the side chains of the resultant polydiacetylene backbone. The strong interaction between neighboring head groups of the side chains controls the conformational change of the polydiacetylene backbone to make the thermochromism reversible. (2) Tethering either covalently or noncovalently the head groups of properly packed diacetylene
molecules to inorganic nano-objects such as carbon nanotubes, layered double hydroxides, or silica. The subsequent polymerization of these diacetylene molecules results in polyanions. The head groups of the side chains still being tethered onto the surfaces or the matrix of the inorganic nano-objects. The tethering makes the chromic transition of the polyanions reversible.

Despite the above successful examples, polymer blends containing poly(diacetylene acid)s with reversible chromatic transitions still remain challenging and attractive because they are expected to have the advantages possessed by many common polymer blends such as flexibility, easy processibility, and adaptability in a broad range of applications. Although great efforts have been made and a large number of poly(diacetylene acid)-containing polymer blends have been fabricated, there are rare examples that are thermochromically reversible. In recent communications, we reported that complete thermochromic reversibility in poly(10,12-pentacosadiynoic acid) (PDA) could be successfully achieved in its blend with poly(vinyl pyrrolidone) (PVPy) when an intercalated “brick-and-mortar” structure was properly formed. In this brick-and-mortar nanostructure, nearly all the side chains in the polyanions are tethered via hydrogen bonding to the PVPy matrix. To the best of our knowledge, PVPy is the only polymer matrix reported so far capable of converting irreversible PDA to completely reversible. Therefore, it is imperative to find other polymers that can form the brick-and-mortar or other nanostructures in their blends with DA and function similarly.

In this study, by testing different polymer matrices, mixing methods, and annealing temperatures, it was confirmed that only the nonionic water-soluble polymer with a relatively high glassy transition temperature (\(T_g\), such as poly(vinyl alcohol) (PVA), was capable of making the thermochromism in PDA reversible. Different from the DA/PVPy blends we reported before, no intercalated nanostructure was detected in the DA/PVA blends. However, the complete reversibility of the resultant PDA/PVA blends strongly suggests that the DA/PVA blends must have the nanostructure that individual crystallized DA bilayers are tethered by and dispersed in the PVA matrix (as explained below) because only this, besides the intercalated structure, can lead to complete reversibility. It is also demonstrated that the reversibility in PDA/PVA blends can be achieved in a larger annealing temperature range, compared with the PDA/PVPy blends. The PDA/PVA blends with complete reversibility can be in the forms of both films and water dispersible nanoggregates, which makes further solution-based applications of the blends possible.

2. EXPERIMENTAL SECTION

2.1. Materials. 10,12-Pentacosadiynoic acid (CH\(_3\)(CH\(_2\))\(_{11}\)C\(\equiv\)C\(\equiv\)C\(\equiv\)C\(\equiv\)C\(\equiv\)C\(\equiv\)C\(\equiv\)C\(\equiv\)C\(\equiv\)C\(\equiv\)C\(\equiv\)C\(\equiv\)O\(=\)H; DA) was purchased from GFS Chemicals, Inc. Poly(vinyl alcohol) (PVA, 124) was the commercial product of Kaurary Co., Japan, with a degree of saponification of 99% and a degree of polymerization of 2400. Poly(allylamine) (PAM, \(M_w = 65,000\), 20 wt % solution in water), poly(ethylene oxide) (PEO, \(M_w = 300,000\)) and poly(acrylic acid) (PAA, \(M_w = 100,000\), 35 wt % solution in water) were purchased from Aldrich. Anhydrous ethanol was purchased from Sinopharm Chemical Reagent Co., Ltd., China. Chemical reagents were used without any further purification.

2.2. Characterization. Before dynamic light scattering (DLS) measurements, all the sample solutions were filtered through 0.8 μm Millipore filters (hydrophilic Millex-LCR, mixed cellulose ester) to remove dust and then kept at 25 ± 0.1 °C for at least 10 min. The measurements were performed at 25 °C and at a fixed scattering angle of 90°. The colorless sample solutions and red sample solutions were measured by an ALV-5000 Laser light Scattering Spectrometer equipped with a multi-r digital time correlation (ALVS5000) and a He–Ne laser (\(\lambda = 632.8\) nm) light source. The hydrodynamic radius (\(R_h\)) and polydispersity index of the nanoggregate (PDI) were obtained by the CONTIN program. The blue sample solutions will absorb the light at 632.8 nm, which is the wavelength of the light source for the ALV-5000 instrument. Therefore, they were tested by a Malvern Autosizer 4700 (Malvern Instruments) equipped with a multi-r digital time correlator (Malvern PCS7132) and a solid-state laser (compass 315M-100, Coherent, Inc.; output power: 100 mW at 532 nm). The \(R_h\) and PDI were obtained by CONTIN mode analysis. A Mettler DSC-1 apparatus was used to determine the thermal properties of DA/PVA blends. Calibration for the temperature scale was performed using indium (\(T_m = 156.60\) °C and \(\Delta H_f = 28.45\) J/g) as the standard to ensure reliability of the data obtained. The accuracy of temperature measurement here is ±0.05 °C. All these experiments were carried out in a nitrogen atmosphere. spectrophotometer Lambda 35 (Perkin-Elmer) was used for UV–vis measurements. The highest temperature for the measurement is 85 °C due to the limitation of the instrument. 2F-1 UV Detector (Shanghai, Gucun Factory) was used as the UV source for the topochemical polymerization. Transmission electron microscopy (TEM) observations were conducted on a Philips CM 120 electron microscope. Before TEM observations, the aqueous suspension of the nanoggregates was dialyzed against water to remove free PVA chains. Then a drop of the suspension was deposited onto a carbon-coated copper grid. The samples were dried for 1 week at room temperature in a desiccator containing dried silica gel. All Fourier transform infrared (FT-IR) spectra 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.

2.3. Mixing DA with the Respective Polymers by the NCCM Method. PDA dried in vacuum at 60 °C for 1 week was dissolved in deionized water at 90 °C for 5 h. DA was dissolved in anhydrous ethanol. DA/PVA nanoggregates solutions were prepared by adding 0.4 mL DA solution in ethanol (1.25 mg/mL) (the solution was filtered through a 0.45 μm filter to remove any polymerized impurity prior to use) into a 5 mL PVA aqueous solution (at various concentrations ranging from 0.1 to 5.0 mg/mL) dropwise under stirring at 25 °C. DA/PAM, DA/PEO, and DA/PAA nanoggregates suspensions and blend films were prepared under the same conditions by the same processes as those for DA/PVA nanoggregates suspensions and films (processes for preparing the reversible PDA/PVA films is given below).

2.4. Preparation of PDA/Polymer Films. DA/polymer nanoggregate solutions were cast into polytetrafluoroethylene (PTFE) dishes and annealed in an oven at different temperatures (50 °C, 67 °C, and 85 °C) for different times. Colorless films could be stripped off dishes. All the preparation procedures described above were performed in darkness to avoid undesired polymerization of DA. Finally, the colored films were polymerized by exposure to UV irradiation (254 nm) for 10 min at room temperature.

2.5. Preparation of Water-Disperable PDA/Polymer Nanoggregates. Water-disperable PDA/polymer nanoggregates could be obtained by dissolving the DA/polymer film in water at 90 °C (for PDA/PVA films) or at room temperature (for other PDA/polymer films above-mentioned) for several minutes.

3. RESULTS AND DISCUSSION

3.1. Preparation of DA/PVA Nanoggregates. The present study started from a commercially available diacetylene monomer, DA. Obviously, preparation of PDA/polymer blends with...
thermochromic reversibility must begin from DA/polymer blends rather than PDA/polymer blends, because PDA is insoluble in nearly any solvents, and heating pure PDA above its melting point results in an irreversible color change. Usually, common solvent mixing and melt mixing are used for preparing polymer blends. However, we find that neither common solvent mixing nor melt mixing can prepare a DA/PVA blend that can finally lead to a reversible PDA/polymer blend. This is understandable for the following reasons: (1) Depending on the competition between the DA/polymer interaction and DA crystallizability, conventional common solvent mixing will result in either a miscible blend or macrophase separation. In a miscible blend, DA is molecularly dispersed in the polymer matrix, breaking the requirements for topochemical polymerization of diacetylenes. In a macrophase separated blend, DA crystallizes into its own crystals with relatively large sizes, which are known to be thermochromically irreversible. Therefore, common solvent mixing is not suitable for reversible thermochromism. (2) Melt mixing has to be above the glassy transition temperature ($T_g$) of the polymer. At such a high temperature, thermal polymerization of DA may occur, forming irreversible PDA. Fortunately, a solvent/nonsolvent method for preparing non-covalently connected micelles (denoted as the NCCM method) is able to disperse DA in aqueous solutions as nanocrystals by using water-soluble polymers as stabilizing chains. [When the weight ratio of DA to the polymer is relatively high, there will be free DA crystals (i.e., the DA crystals that are not interacting with the polymer matrix) in the DA/polymer blend. After polymerization, this free DA crystals will become irreversible PDA crystals (as mentioned in the introduction, the uninteracted (or pure) PDA crystals are irreversible). Additionally, when the weight ratio of DA/polymer is small enough for DA to form isolated domains in the polymer matrix, the mechanical properties of the resultant blend remains nearly unchanged.] After casting the solution under appropriate conditions and subsequent topochemical polymerization, these NCCMs can transform into the PDA/polymer blend with complete thermochromic reversibility.

In the NCCM method, two miscible solvents, A and B, are required, where A is a good solvent for the polymer but a nonsolvent for DA, and B is a good solvent for DA. Because DA is only insoluble in water, the solvent A should be water, and the polymer should be water-soluble. In this study, PEO, PAA, PAM, and PVA were chosen as the polymer matrices, and ethanol was chosen as the solvent B. As detailed below, the completely reversible thermochromism could only be achieved in the PVA matrix. Therefore, for the clarity of this paper, the DA/PVA system is described in detail, whereas other systems will be discussed briefly.

In the present study, DA was dissolved in ethanol at a concentration of 1.25 mg/mL, and PVA was dissolved in water at various concentrations, ranging from 0.1 to 5 mg/mL. Subsequently, 0.4 mL of DA in ethanol was added dropwise into a 5 mL water solution of PVA. When the concentrations of PVA in the aqueous solution were 0.1, 0.5, 1.0, 2.0, and 5.0 mg/mL, the weight ratios of DA/PVA in the mixture solutions were 1/1, 1/5, 1/10, 1/20, and 1/50, respectively. DLS showed that the Z-averaged hydrodynamic radius ($\langle R_h \rangle$) for an individual PVA chain ($M_w = 105 \ 600 \ \text{g/mol}$) in the aqueous solution was 13 nm (Figure 1a). After adding the ethanol solution of DA to the aqueous solutions of PVA, DA started to aggregate (or nucleate) into nanosized particles because it was insoluble in the mixture solvent (ethanol/water = 0.08/1 vol/vol). However, further growth of DA beyond nanosized aggregates was arrested due to the hydrogen bonding between the carboxyl groups in DA and the hydroxyl groups of PVA. In other words, DA NCCMs were stabilized by PVA in the aqueous solution. The $\langle R_h \rangle$ values of the PVA-stabilized DA nanoaggregates at 24 h after mixing were measured by DLS (Figure 1a), and they were 93, 121, 174, 233, and 347 nm, respectively.
Figure 3. DSC curve of DA/PVA blend film prepared by drying the suspension of DA/PVA nanoaggregates (S3) at room temperature. At room temperature, a relatively large amount of water was absorbed in the PVA matrix, resulting in a very broad endothermic peak between 50 and 100 °C due to water evaporation.

182, and 230 nm for the DA/PVA weight ratios of 1/1, 1/5, 1/10, 1/20, and 1/50 (denoted as S1, S2, S3, S4 and S5, respectively). The \( R_h \) value of the DA nanoaggregates increased with increasing concentration of PVA. The number of PVA chains that participated in complexing and stabilizing DA nanocrystals increased when the concentration of PVA increased, leading to the increase in the \( R_h \). Note that after mixing, there were still free PVA chains in the aqueous solution. However, the scattering intensity from free PVA chains was very weak in the Z-averaged DLS curves as compared to the large scattering intensity from much larger DA/PVA nanoaggregates.45 From Figure 1b, it was found that the \( R_h \) values of the DA/PVA nanoaggregates also changed with time; they increased rapidly in the early stage but leveled off after \(~7\) h.

The DA/PVA nanoaggregates were basically spherical with some irregular shapes, as observed by TEM (Figure 2). As mentioned before, without PVA, DA would precipitate out of the mixture solution. With PVA, the DA nanoaggregates were stabilized by PVA, which interacted favorably with DA due to the hydrogen-bonding between carboxyl groups in DA and hydroxyl groups in PVA.45,46 Therefore, the DA/PVA nanoaggregates should have a core—shell structure with DA as the core and PVA as the shell.

3.2. Formation of PVA-Tethered and Crystallized DA in PVA Matrix. DA in the nanoaggregates in the ethanol/water suspensions could be polymerized into PDA by exposing to UV irradiation at 254 nm. DA in the nanoaggregates should exist as nanocrystals because the crystalline structure is necessary for topochemical polymerization. The suspension of the freshly formed PDA/PVA nanoaggregates in solution was blue in color. Upon heating to above 60 °C, the suspension changed into red color. However, this thermochromic transition turned out to be irreversible. Differential scanning calorimetry (DSC) curve of DA/PVA nanoaggregates in Figure 3 shows a melting peak at 62 °C, suggesting that DA in the nanoaggregates largely existed as pure (i.e., noninteracted) DA nanocrystals,42 which eventually transformed into pure PDA crystals upon UV irradiation. The irreversibility in thermochromism of pure PDA crystals and the defects existed in the hydrogen bonded crystals (as explained below) should be responsible for the irreversibility observed for the suspensions of the polymerized nanoaggregates. On the basis of our recent report, we considered that to make the PDA/PVA blend completely reversible, it is necessary to “tether” all the side chains of PDA to the PVA matrix. For this purpose, the carboxyl groups of DA in the DA/PVA blend, as the precursor of the reversible PDA/PVA blend, should be tethered to the PVA matrix. Meanwhile, the DA should crystallize to meet the requirements for topochemical polymerization. In principle, PVA-tethered DA nanocrystals should have an increased melting point, because the tethering could lead to a reduced entropy change during melting. Annealing the DA/PVA blend at a temperature above the melting point of pure DA crystals but below the melting point of PVA-tethered DA crystals would be able to remove pure DA nanocrystals (some of them may be transformed into PVA-tethered DA nanocrystals and the other become molecularly solubilized in PVA matrix). In the present study, we annealed the DA/PVA nanoaggregates in the suspensions instead of in the bulk, because both DA and PVA molecules in the suspensions had a higher mobility than those in the bulk. The annealing was conducted at 50 °C (below the melting point of pure DA crystals at 62 °C), 67 °C (slightly higher than the melting point of pure DA crystals), and 85 °C (proven to be significantly higher than the melting point of PVA-tethered DA nanocrystals), respectively. The respective nanoaggregate suspensions at the DA/PVA weight ratios of 1/1 (S1), 1/5 (S2), 1/10 (S3), 1/20 (S4) and 1/50 (S5) were annealed open in the air at each temperature for 7 h. During this annealing process, the suspension eventually dried into a solid film. It was noted that annealing S1 and S2 cannot yield uniform DA/PVA films because of too high DA content. Therefore, S3—S5 samples were used for further study.

DA/PVA films obtained by annealing S3—S5 at different temperatures for 7 h were studied by DSC. As shown in Figure 4a, DSC curves of S3—S5 films annealed at 50 °C for 7 h exhibited two melting peaks at 62 and ca. 72 °C, respectively. By annealing at 67 °C, DSC curves of S3—S5 films showed a single melting peak at 73—78 °C (Figure 4b). It is known that the melting point and glassy transition temperature observed for PVA are 228 and 155 °C, respectively. Therefore, the signals observed in Figure 4 should be attributed to the melting points of DA crystals in PVA matrix. The signal peaked at ~62 °C was assigned to pure DA crystals. Obviously, pure DA nanocrystals could survive through the annealing at 50 °C since it was lower than the melting point of pure DA crystals. Another signal appearing in Figure 4a at 71—73 °C was assigned to the hydrogen bonded DA crystals (i.e., the tethered DA crystals), which were stabilized due to the hydrogen bonding with the glassy PVA matrix and thus had a higher melting temperature. The DSC curves for the films annealed at 67 °C have a single peak at 73—78 °C, indicating that only the hydrogen-bonded DA nanocrystals could remain after the annealing at the temperature (67 °C) higher than the melting point of pure DA crystal. At 67 °C, before the drying of the systems, we believed that melted DA molecules were movable and diffused into the interacting PVA matrix so that the pure DA nanocrystals could finally disappear in the system, as evidenced by the complete reversibility of the resultant PDA/PVA blend films. Additionally, the DSC curves of the samples prepared by annealing at 85 °C displayed no signal because both the unhydrogen bonded DA nanocrystals and hydrogen-bonded DA nanocrystals could not survive through the annealing treatment at 85 °C, which was apparently higher than the melting points of both pure DA crystals and hydrogen-bonded DA crystals. The disappearance of both the pure and the hydrogen-bonded DA crystals after
annealing at 85 °C demonstrated that the melted DA molecules in the system, both un-hydrogen-bonded and hydrogen-bonded, were movable. The DA/PVA blend films resulting from the annealing at 67 °C were repeatedly characterized by small-angle X-ray scattering (SAXS) using Shanghai Synchrotron Radiation Facility, but no signal related to the lamellar structure of either pure DA crystals or the intercalated structure reported in our previous communication was detected. (During preparing samples for SAXS analysis, most of free PVA polymer chains were removed by dialysis against water.) This indicated that the tethered DA crystals in the films obtained by annealing at 67 °C must exist as individually dispersed tethered DA bilayers. [It is noted that, in all the reversible systems reported, polydiacetylene backbones, which should result in the irreversibility. In PVA matrix, PDA that is completely reversible should have bilayered crystal structure in which the hydrocarbon side chains (i.e., the side chains without carboxyl groups) aggregate together without being exposed to the polar PVA matrix. Additionally, each of the PDA bilayers should be tethered to PVA for complete reversibility. Of course, in the precursor PVA/DA blends, each of DA bilayers should be tethered by the PVA matrix. When the tethering is realized in the nanostructure where polymer matrix layers are sandwiched between DA bilayers, and the polymer layers are with similar thickness, the periodicity can be kept and detectable by SAXS; the nanostructure is the intercalated nanostructure. Otherwise, when the DA bilayers are separated by the polymer matrix to different distances or/and the DA bilayers are thus oriented differently, the periodicity is lost although each of DA bilayers is also tethered. This nanostructure should be described as individually dispersed tethered DA bilayers.]

The hydrogen bonding in DA/PVA mixtures annealed at 50, 67, and 85 °C were characerized by FT-IR. Changes in the signal of C=O stretching vibrations of DA are especially noteworthy since it is sensitive to the hydrogen bonding state of the carboxyl groups of DA. However, in samples S3, S4 and S5, the molar ratio of DA to the repeat units of PVA is less than 1:85. In the FTIR spectra of S3−5, DA signals are buried in PVA signals. For solving this problem, we prepared DA/PVA nanoaggregates at a molar ratio of carboxyl groups of DA to hydroxyl groups of PVA of 5:7. The change in the molar ratio should have no remarkable effect on hydrogen bonding in the system; largely excess PVA was used for forming the uniform films. The DA/PVA nanoaggregates at a \( -\text{COOH/\text{OH}} \) molar ratio of 5:7 were prepared using the same method under the same conditions. Then, the nanoaggregates suspension were annealed and dried on CaF2 plates at 50, 67, and 85 °C, followed by FT-IR measurements at room temperature to give spectra A, B, and C, respectively (Figure 5). In spectrum A, signal of carboxyl groups appears at 1692 cm\(^{-1}\), the same position as that of pure DA crystal (spectrum D). This indicates the existence of pure DA crystals in the sample annealed at 50 °C, which is consistent with the conclusion obtained by the above-mentioned DSC measurements. In the spectra of the samples annealed at 67 and 85 °C (spectra B and C), the signal of carboxyl groups shifts to 1697 cm\(^{-1}\), which should be assigned to C=O stretching vibrations of the carboxyl groups hydrogen bonded with the hydroxyl groups of PVA. It is noted that in spectrum A, there is a shoulder at 1697 cm\(^{-1}\), indicating the existence of COOH−OH hydrogen bonding in the sample annealed at 50 °C, which should happen at the interface of the nanocrystals and PVA matrix. It is noted that in the DSC curve of S3−5 annealed at 50 °C (Figure 4), the intensity of the signal at 72 °C is even stronger than that at 62 °C, indicating that DA crystals are largely tethered. However, in spectrum A, the intensity of the signal at 1697 cm\(^{-1}\) is lower than that at 1692 cm\(^{-1}\). This implicates that the specific interface area of DA crystallites in the sample at a COOH/\text{OH} molar ratio of 5:7 is less than that in S3−5; in S3−5, COOH/\text{OH} is less than 1/85, and DA is fully dispersed in the PVA matrix as smaller nanocrystals. It is also noted that in each of spectra B and C, there is a shoulder at 1722 cm\(^{-1}\), which

![Figure 4. DSC curves for DA/PVA films, S3 (black line), S4 (red line), and S5 (blue lines), at (a) 50, (b) 67, and (c) 85 °C for 7 h.](image)

![Figure 5. FT-IR spectra of DA/PVA films at a COOH/OH molar ratio of 5/7 annealed at 50 (A), 67 (B) and 85 °C (C). D and E are FT-IR spectra of pure DA crystals and pure PVA, respectively. The FT-IR measurements were conducted at room temperature.](image)
should be attributed to the carboxyl groups that are free from hydrogen bonding. Due to the reversibility of the hydrogen bonding, there should be a certain amount of un-hydrogen-bonded COOH groups at relatively high temperatures such as 67 and 85 °C. After the sample was cooled to room temperature, the hydrogen bonding cannot form again since the mobility of the DA and the repeat units of PVA is restricted in the solid system.

As indicated in Figure 6, the DSC curves of the samples annealed at the same temperature but for different times were similar. For example, all the DSC curves of the samples prepared by annealing S3 at 50 °C but for different annealing times displayed two signals peaked at ~62 and 73 °C (Figure 6a), respectively, and those at 67 °C exhibited only one signal at 73–78 °C. It was concluded that prolonged annealing time did not change the nanostructure of DA/PVA as well as the thermochromic behavior of the corresponding PDA/PVA blends (Figure 10) as described below.

3.3. Thermochromism of PDA/PVA Films. Each of the films prepared by annealing S3, S4, and S5 at different temperatures was irradiated by UV at a wavelength of 254 nm for 10 min. After irradiation, the original uncolored films became blue, indicating that DA was polymerized into PDA. The thermochromism between 30 and 85 °C (the highest temperature allowed by the instrument) was checked by UV−vis spectroscopy measurement. As shown in Figure 7, films all underwent blue-to-red color transition when heated from 30 to 85 °C. Specifically, at 30 °C, the spectra of all the PDA/PVA films before the heating−cooling cycles present a maximum absorbance at 634 nm, responsible for the blue color. Upon heating, the maximum absorbance shifted to lower wavelengths, and the absorbance intensity at 634 nm

Figure 6. DSC curves of DA/PVA films obtained by annealing S3 for different times (5−24 h) and at different temperatures ((a) 50 °C, (b) 67 °C and (c) 85 °C).

Figure 7. UV−vis spectra of PDA/PVA films derived from the DA/PVA films obtained by annealing each of S3, S4, and S5 at 50, 67, and 85 °C for 7 h, respectively.
decreased. At 85 °C, the 634 nm absorbance completely disappeared, the absorbance at 534 nm increased to a maximum, and the color became red. UV–vis spectra of the films obtained by annealing at 67 °C exhibited reversible thermochromism, i.e., the color changed back to blue again after the films were cooled from 85 to 30 °C. The thermochromic reversibility between 30 and 85 °C for the films annealed at 67 °C was also demonstrated by the parameter of “colorimetric response” (CR) in different thermal cycles (Figure 8). The thermochromism reversibility was attributed to the formation of hydrogen bonded DA nanocrystals, which led to the tethering of the side chains of resultant PDA backbone to the glassy PVA matrix. After the tethering and the crystallization of the side chains, the conformation of the PDA backbone was almost fixed. Upon heating, the crystal of the side chains melt. The thermo agitation led to fluctuation in the conformation of the PDA backbone, leading to the decrease in the efficient conjugation length of the PDA backbone and the color changed from blue to red. However, once the exterior stimulus was withdrawn, the tethered side chains crystallized again and forced the backbone to change back to the conformation in the blue form; the color changed back from red to blue.

In the DSC curves of the films prepared by annealing at 50 °C (Figure 4a), we noted that the relative signal intensity of the hydrogen bonded DA nanocrystals (at 71–73 °C) was higher than that of unbonded DA nanocrystals (at 62 °C). However, the resultant polymerized films were nearly completely irreversible; the hydrogen bonded PDA resulting from the annealing at 50 °C should be largely irreversible in the thermochromism since only very small reversible peaks could be seen in the spectra (indicated by blue arrows in Figure 7). Obviously, there should be defects in the structure of DA hydrogen bonded nanocrystals. The defects could not be removed by annealing at 50 °C since the movement of DA molecules was restricted at a temperature below the melting point of pure DA crystals. It is understandable that the thermochromism is very sensitive to the defects because only a small fraction of the defects should make the permanent conformational change of PDA backbone at the color change temperature possible. When annealed at 67 °C, a temperature slightly higher than the melting point of pure DA nanocrystals, the defects could be removed by the annealing and the resultant PDA/PVA films were completely reversible. It should be mentioned here that the films annealed at 85 °C, which gave no signals in the DSC curves, also exhibited a complete reversibility in the thermochromism (Figure 7) after the polymerization. However, the colors of the films obtained by annealing at 85 °C were much lighter than that of films at 67 °C (Figure 9). Note that the thicknesses of the films in a and b are similar. Actually, DA is miscible with PVA due to the interaction between them. When annealed at 67 °C, which was below the melting temperature of the hydrogen bonded DA nanocrystal (~73 °C), the diffusion of DA was stopped once the DA molecules formed the hydrogen bonded nanocrystals. When annealed at 85 °C, which was higher than the melting point of hydrogen bonded DA nanocrystals, the hydrogen-bonded DA nanocrystals melted. It is known that hydrogen bonds, especially some weak hydrogen bonds such as that between hydroxyl groups and carboxyl groups in a polar solvent (such as water or water/ethanol mixture), are reversible, especially at a relatively high temperature. Due to the reversibility in the hydrogen bonding, before the dry of the systems, for melted DA molecules, there should be a balance between the hydrogen-bonded DA molecules and un-hydrogen-bonded DA molecules. With the diffusion of the un-hydrogen-bonded DA molecules into the PVA matrix, to keep the balance, some of the originally hydrogen-bonded and melted DA molecules become the un-hydrogen-bonded ones, which would continue to diffuse into the matrix. As the result, at 85 °C, a large part of DA molecules diffused and molecularly dispersed in the matrix, as evidenced by the fact that the resultant PDA/PVA films were very light in color (the molecularly dispersed DA molecules are unpolymerizable). The diffusion of DA molecules would become much slower or be stopped once the film was dried. Therefore, there were still some places in the PVA matrix where the local concentration of DA molecules was relatively high so that they formed a few hydrogen-bonded nanocrystals after the cooling of the films; the amount of the nanocrystals is too low to give a clear signal in the DSC curves. The processes for dispersing DA nanocrystals in the PVA matrix into various nanostructures by annealing at different temperatures are schematically described in Scheme 1.

**3.4. Effects of Polymer Matrix on the Thermochromic Reversibility of the Resultant PDA/Polymer Blends.** To achieve complete thermochromic reversibility for PDA in a polymer matrix, the nanostructure in which all the PDA bilayers are tethered to polymer matrix though interaction between carboxyl groups of DA and the polymer should be realized. Furthermore, the polymer matrix should have a relatively high glassy transition temperature ($T_g$) so that the matrix can remain...
in a glassy state at the color change temperatures; the glassy state polymer matrix can provide restoring force to help the tethered polydiacetylene backbones resume its conformation in the blue-color form once the exterior stimulus is withdrawn. Additionally, as mentioned before, the NCCM method is necessarily applied and the polymers should be water-soluble. The water-soluble polymers used in the present study were PEO, PAA, and PAM. The conditions and the procedures for preparing PDA/polymer films were identical to those for preparing PDA/PVA blend films. All thus-prepared PDA/PEO films were completely irreversible, whereas all the PDA/PAA and PDA/PAM films were partially reversible. The complete irreversibility of PDA/PEO blends is due to the low \( T_g \) of the PEO matrix. At a temperature higher than the \( T_g \) of the polymer matrix, when PDA is in the red form, the chains of the polymer matrix in a rubber state bound to the PDA backbone are able to adjust their conformation to fit the conformation of the PDA backbone. The restoring force that is necessary for reversibility is thus lost. In the case of PDA/PAA and PDA/PAM blends, a partial reversibility resulted from the partial ionization of PAA and PAM in water. The ionization introduced defects into the tethered PDA nanocrystals, leading to the partial reversibility. Therefore, for complete reversibility, in the precursor DA/polymer blends, every DA crystallized bilayer should be tethered. Additionally, there should not be considerable defects in the nanostructure of the tethered DA crystals.

### 3.5. Thermochromic Behavior of PDA/PVA Nanoaggregates in Aqueous Solutions

All the polymerized films could be easily dissolved in water at 90 °C (PDA/PVA films) or room temperature (other PDA/polymer films). In the solutions, the films dissociated into PDA/PVA nanoaggregates. Compared with the respective DA/PVA nanoaggregates, the final PDA/PVA nanoparticles had similar sizes; diffusion of DA during the annealing was limited within NCCMs (Figure 11). Additionally, the PDA/PVA water-dispersible nanoaggregates had the same reversibility in the thermochromism as their respective PDA/PVA films (Figure 12). This makes any further solution-based applications of the reversible PDA/PVA blends possible.
4. CONCLUSION

Realization of the complete thermochemical reversibility of poly(diacetylene acid) in a common polymer matrix requires preparing the precursor diacetylene acid/polymer blends with a nanostructure in which every DA crystallized bilayer is tethered to the polymer matrix. For complete reversibility, the glass transition temperature of the polymer matrix should be high enough, and there should not be considerable defects in the tethered DA crystals. When a water-soluble and unionizable interacting polymer is used, complete reversibility can be realized by mixing DA with the polymer using the NCCM method and then annealing the mixture solution into films at a temperature higher than the melting point of pure DA crystal. The annealing not only helps the formation of tethered DA bilayers but also removes pure DA nanocrystals from the system and eliminates the defects that existed in the tethered DA nanocrystals. This makes the resultant PDA/PVA blend films completely reversible. Annealing at a temperature higher than the melting point of tethered DA crystals can also lead to complete reversibility. However, the higher annealing temperature will decrease the efficiency of using DA to functionalize the polymer since more DA molecules are molecularly dispersed in the polymer matrix and thus become unpolymerizable.

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Figure 12. UV–vis spectra of the PDA/PVA nanoaggregate suspension derived from S5 annealed at (a) 67 °C and (b) 85 °C.


