

Thermochromatism and Structural Evolution of Metastable Polydiacetylenic Crystals

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Topochemically polymerized sodium 10,12-pentacosadiynoate (PCDA-Na) microcrystals show an irreversible red-to-blue chromatic transition accompanied by a distinct structural evolution upon initial thermal treatment, and show a subsequent completely reversible blue-to-red chromatic transition upon further thermal stimuli. Visible absorption spectroscopy, X-ray diffraction (XRD), and differential scanning calorimetry (DSC) are used to investigate the thermochromatic transition behavior of the polydiacetylenic microcrystals. Brief quantum mechanical geometry optimization is employed to explain the lattice dimensional change during the irreversible red-to-blue chromatic transition of the metastable polydiacetylenic crystals.

Introduction

Polydiacetylene (PDA) is of considerable interest for applications in molecular electronics, optical waveguides, and chromatic biosensors due to its unique electronic, chromatic, and optical nonlinear properties that result from its extended π electron conjugation and backbone alignment.^{1–5} PDA is usually synthesized by topochemical polymerization^{2,4,6} initiated by electromagnetic radiations (e.g., UV), which requires that the diacetylenic units are aligned in a reactive configuration. As the topochemical polymerization proceeds, internal chemical bond strain develops within the crystal lattice due to the molecular displacement and change of the bond angle derived from the reaction.⁷ As a result, either the crystal-lattice dimensions change gradually during the polymerization of diacetylenic units, or thermodynamically metastable polymer crystals are formed by the accumulation of internal strain even though part of this strain is often released by cracking of the crystals.^{6,7} Topochemically polymerized diene crystals were recently reported to show a very interesting crystal structure transition according to temperature.⁸ In this work we report the synthesis of metastable PDA crystals that demonstrate distinct lattice evolution and an irreversible chromatic transition from red to blue upon initial thermal stimulus.

Our strategy of capturing the metastable state of PDA crystals is based on the enhanced intermolecular interactions among the PDA side chains that increase molecular and bond angle constraints. This is achieved by reacting 10,12-pentacosadiynoic acid (PCDA) with excess NaOH in an aqueous medium followed by self-assembly (crystallization) and solid-state polymerization at room temperature. Furthermore, the enhanced intermolecular electrostatic interactions⁹ endow the polydiacetylene sodium salt (PDA-Na, specifically refer to polymerized PCDA-Na in this paper) microcrystals with a completely

reversible blue-to-red color change upon thermal stimuli after their transition to the blue state. The chromatic reversibility of PDA has been achieved recently through molecular design of diacetylene derivatives^{3,10,11} to add functional groups that are capable of additional hydrogen bonding. That design allows the supramolecule assemblies to restore their original molecular conformation after the removal of thermal stimuli. Since the synthesis of new diacetylene derivatives is sometimes tedious and expensive, this work demonstrates the easy formation of polydiacetylenic microcrystals with completely reversible blue to red chromatism by enhancing their intermolecular electrostatic interactions.⁹

Experimental Section

Synthesis. For a typical synthesis procedure, 0.072 g of purified colorless 10,12-pentacosadiynoic acid [PCDA, $\text{CH}_3\text{-(CH}_2\text{)}_{11}\text{C}\equiv\text{C-C}\equiv\text{C(CH}_2\text{)}_8\text{COOH}$, GFS Chemicals] monomer was dissolved in a mixture of 4.371 g of deionized water, 1.190 g of 1 mol/L NaOH aqueous solution, and 0.279 g of tetrahydrofuran (THF) to achieve a clear homogeneous solution after ca. 30 min of vigorous stirring. The molar ratio of PCDA: NaOH: H₂O: THF was kept at 1: 6: 1600: 20–40. After 2–4 h of continuous stirring at room temperature (ca. 25 °C), sodium 10,12-pentacosadiynoate (PCDA-Na) microcrystals began to precipitate from the solution by self-assembly. The mixture was covered by aluminum foil during the crystallization process to prevent polymerization due to light exposure. After 24 h of stirring, the cloudy mixture containing white precipitated crystals was cast on glass slides and dried at room temperature. Large-sized PCDA-Na single crystals were not obtained. The red polydiacetylene sodium salt (PDA-Na) microcrystals were formed via topochemical 1,4-addition polymerization of the diacetylenic units by exposure to both 254 and 365 nm UV radiation from a Spectronics Spectroline ENF-240C Ultraviolet lamp for ca. 15 h or exposure to room light in the laboratory for ca. 3 days at room temperature. Sometimes, a red-purple color occurred for the sample after polymerization by exposure to only 365 nm long-wave UV radiation for 20 h. This may result from the thermal effect from UV radiation that changes a small amount of the red microcrystals to blue.

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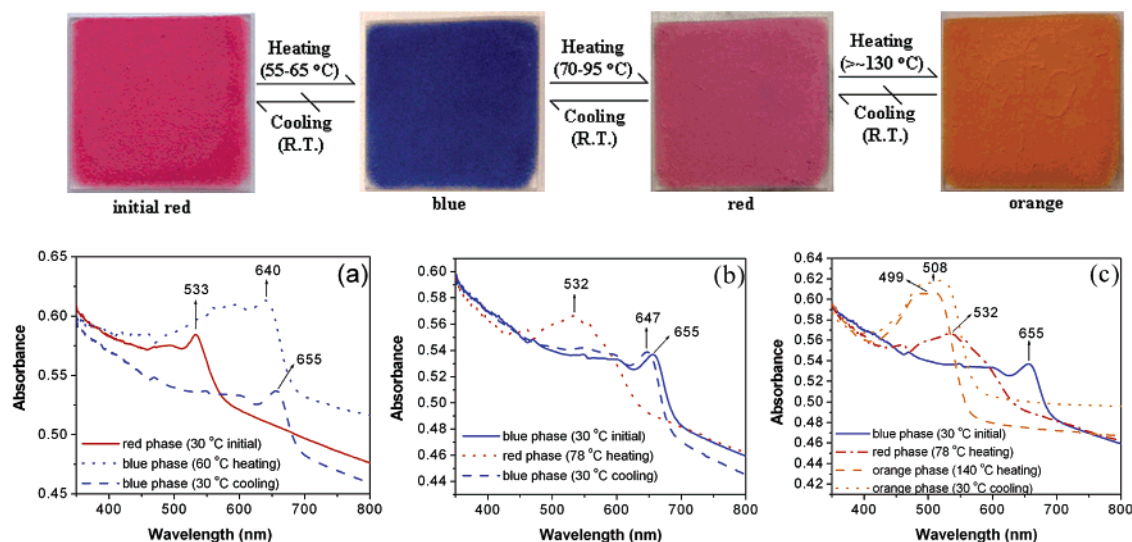


Figure 1. Photographs (top) of PDA-Na color transitions at different temperatures and the corresponding visible absorption spectra (bottom) for the color transitions: irreversible red to blue (a), reversible blue to red (b), and irreversible red to orange (c).

Characterization. The PDA-Na microcrystals were characterized by ^{13}C solid-state nuclear magnetic resonance (NMR) spectroscopy (Bruker DSX-300 spectrometer, with cross-polarization/magic angle spinning (CP/MAS) method), scanning electron microscopy (SEM, JEOL JSM-5410, operating voltage of 20 kV), transmission electron microscopy (TEM, JEOL JEM-2010, accelerating voltage of 120 kV), visible absorption spectroscopy (Beckman DU640B spectrophotometer), X-ray diffraction (XRD, Scintag XDS 2000 diffractometer, operating at 43 kV, 38 mA, Cu $K\alpha$ radiation, $\lambda = 0.15406$ nm), and differential scanning calorimetry (DSC, Thermal Analysis 2920 DSC instrument, heating rate of 5 $^{\circ}\text{C}/\text{min}$, cooling rate of 1 $^{\circ}\text{C}/\text{min}$, nitrogen flow rate of 100 cm^3/min). The samples for TEM observation were prepared by directly dispersing the microcrystals onto the Cu grid coated with carbon. The samples were not dyed before characterization. The MDI Jade5 software was used to seek the Miller indices and unit cell. The visible absorption spectroscopy measurement was conducted on a piece of glass slide coated with a very thin layer of crystal samples. The samples were heated by a flow of water with tunable temperature and the temperature of the samples was monitored by a thermocouple meter.

Quantum Mechanical (QM) Geometry Optimization. Approximate geometry of the fully extended 10,12-pentacosadiynoate was initially optimized by using the GAFF force field of AMBER 8.¹² We then employed the quantum mechanical density functional theory method (B3LYP/6-311G**) to perform high-level geometry optimizations. The geometry-optimized structure was then used to determine the packing structure of 10,12-pentacosadiynoate monomers through energy minimization.

To get the geometry of the 10,12-pentacosadiynoate after polymerization and thermal treatment, the energy-minimized packing structure of four monomers was connected with the corresponding double bonds. This structure represents part of the PDA after polymerization at room temperature. To obtain the relaxed geometry of PDA after thermal treatment, we followed the same geometry optimization procedure for the monomer. However, the number of atoms in this structure is too big to be optimized at the DFT/B3LYP/6-311G** level. Since we believe that the major structure difference between the optimized and unoptimized PDA molecule is located around the conjugated backbone, atoms which are 8 Å away from the

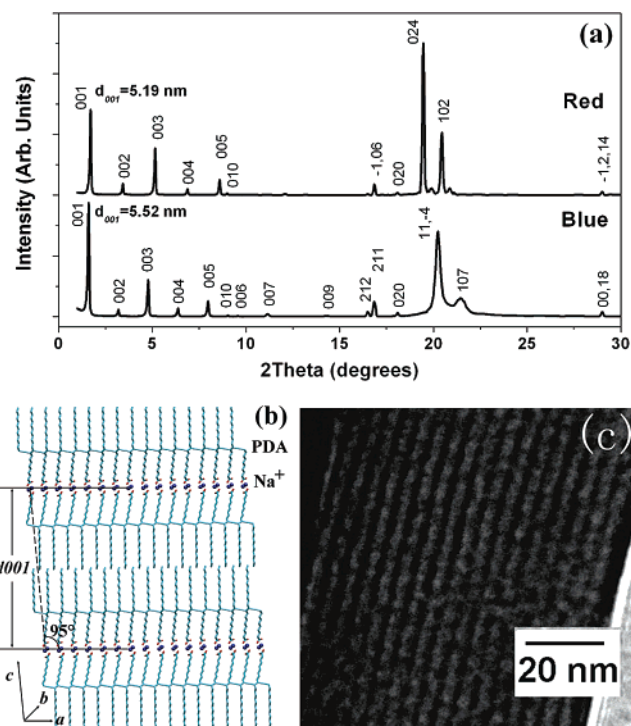


Figure 2. (a) XRD patterns of the as-polymerized PDA-Na microcrystals on glass slides before (initial red) and after (blue) a brief thermal treatment at about 60 $^{\circ}\text{C}$; (b) a schematic molecular packing structure of the blue PDA-Na microcrystals; and (c) a representative TEM image of a blue PDA-Na microcrystal.

conjugated backbone were excluded from the high-level geometry optimization. These atoms were then mapped back after the optimization of the conjugated part based on the conformation of monomer.

Results and Discussion

Polymerization of the PCDA-Na at room temperature was demonstrated by a white-to-red chromatic transition² and was confirmed by ^{13}C solid-state NMR spectroscopy¹³ (Supporting Information, Figure SI-1). The red color results from the conjugated polydiacetylenic backbone that absorbs blue light. The PDA-Na microcrystals exhibit a microsized sheet- or strip-like morphology from SEM (Supporting Information, Figure

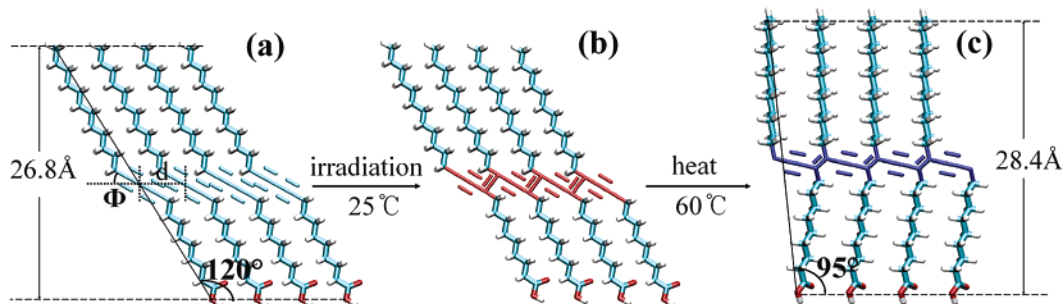


Figure 3. A proposed molecular structural evolution mechanism during the irreversible red to blue color change: (a) before polymerization, (b) after polymerization at room temperature (red), and (c) after thermal treatment (blue). The d is the monomer separation distance, and Φ is the angle between the diacetylenic unit and the stacking axis.

SI-2). Figure 1 shows photographs of the PDA-Na microcrystals deposited on glass slides at different temperatures and the corresponding visible absorption spectra. The microcrystals, which are initially red at room temperature, undergo an irreversible color transition to blue when the crystals are heated to ca. 55–65 °C, which remains upon cooling to room temperature. As shown in the corresponding visible absorption spectra (Figure 1a), the absorption peak at 533 nm for the original red sample shifts to 640 nm upon heating at 60 °C, consistent with the red to blue transition observed. When the sample is cooled to room temperature, the absorption peak remains at 655 nm corresponding to the blue phase microcrystals at room temperature.^{1,3,9–11} Most PCDA derivatives show a blue color after polymerization and undergo either an irreversible or reversible blue to red color transition when subjected to thermal stimuli;^{1,10,11,14,15} to the best of our knowledge, this is the first example of PDA derivatives that show an irreversible red-to-blue chromatic transition upon a heating–cooling cycle. The enhanced intermolecular interactions also endow the PDA crystals with a reversible blue-to-red thermochromatism after their transition to the blue state. For example, subjecting the blue crystals to multiple temperature cycles (e.g., between 70 and 95 °C and room temperature) results in a completely reversible blue to red color transition.^{10,11} The absorption band shifts from 655 to 532 nm and back to 647 nm during a thermal cycle between 30 and 78 °C (Figure 1b). Heating the crystals to temperatures above 105 °C limits the degree of reversibility. For example, if the sample is heated at a temperature higher than ca. 130 °C, a further irreversible chromatic transition from red to orange occurs. As shown in Figure 1c, the absorption peak of the crystals irreversibly shifts to 499 nm after heating at 140 °C. Such unique thermochromatic transitions may be of great interest for use in thermal sensors or for other potential applications.

We are very interested in the structural change during the irreversible red-to-blue color transition. Figure 2a shows the powder XRD patterns of the initial red and the thermally treated blue PDA-Na microcrystals. The red crystals possess a monoclinic structure with unit cell parameters of $a = 5.29$ Å, $b = 9.80$ Å, $c = 57.37$ Å, and $\beta = 120^\circ$; the blue crystal possesses a similar monoclinic structure with unit cell parameters of $a = 5.10$ Å, $b = 9.79$ Å, $c = 55.65$ Å, and $\beta = 95^\circ$. Figure 2b shows a schematic molecular packing structure of the blue PDA-Na microcrystals based on brief geometry optimization and energy minimization (see details in the Experimental Section). It is anticipated that the a -axis is parallel to the extended PDA backbone chain direction while the c -axis is parallel to the extended side chain direction of PDA. Most significantly, the powder XRD patterns demonstrate a significant lattice dimensional change along the c -axis. The intense diffraction peaks indexed as $00l$ planes at the low angle range are contributed by

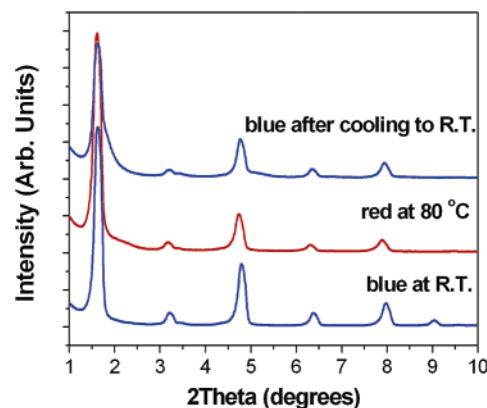


Figure 4. XRD patterns for the blue PDA-Na microcrystals upon heating to 80 °C and cooling to room temperature, demonstrating no obvious difference in the lamellar mesostructure during the reversible blue to red color transitions.

the highly ordered mesoscopic lamellar structure along the c -axis. The interlamellar distance (i.e., d -spacing) calculated from the Bragg equation extends from 51.9 Å to 55.2 Å during the irreversible color transition from red to blue, which is very reproducible. This uniform lamellar mesostructure of both the red and the blue crystals has been confirmed by transmission electron microscopy (TEM) (Figure 2c) even though the difference of 3.3 Å in the interlamellar distance is not distinguishable in TEM images. The diffraction peaks at the high 2θ angles correspond to the in-plane molecular ordering.

Compared with the polymerized pure PCDA that is blue after polymerization at room temperature (results not shown),¹ the introduction of sodium ions promotes the formation of PDA-Na crystals with stronger intermolecular interactions, in particular, electrostatic interactions. Since the polymerization is conducted at room temperature and the monomers are arranged in a highly ordered crystalline form, the electrostatic interactions between sodium ions and carboxylic groups restrict the molecular mobility. As a result, the monomer packing is mostly frozen during the topochemical polymerization process; thereby, internal strain is generated along the ene–yne backbone due to the unfavorable reacting bond angle, resulting in the formation of metastable PDA crystals. This argument is confirmed by the unchanged XRD patterns before and after the polymerization at room temperature (Supporting Information, Figure SI-3). Upon thermal agitation, the strain relaxes and the structure settles into the stable blue state, creating a longer effective π electron conjugative length and the resultant irreversible red-to-blue color transition. We observed that reducing pressure (e.g., subjected to evacuation) also facilitates the molecular movement and internal strain release and produces a similar red-to-blue color transition.

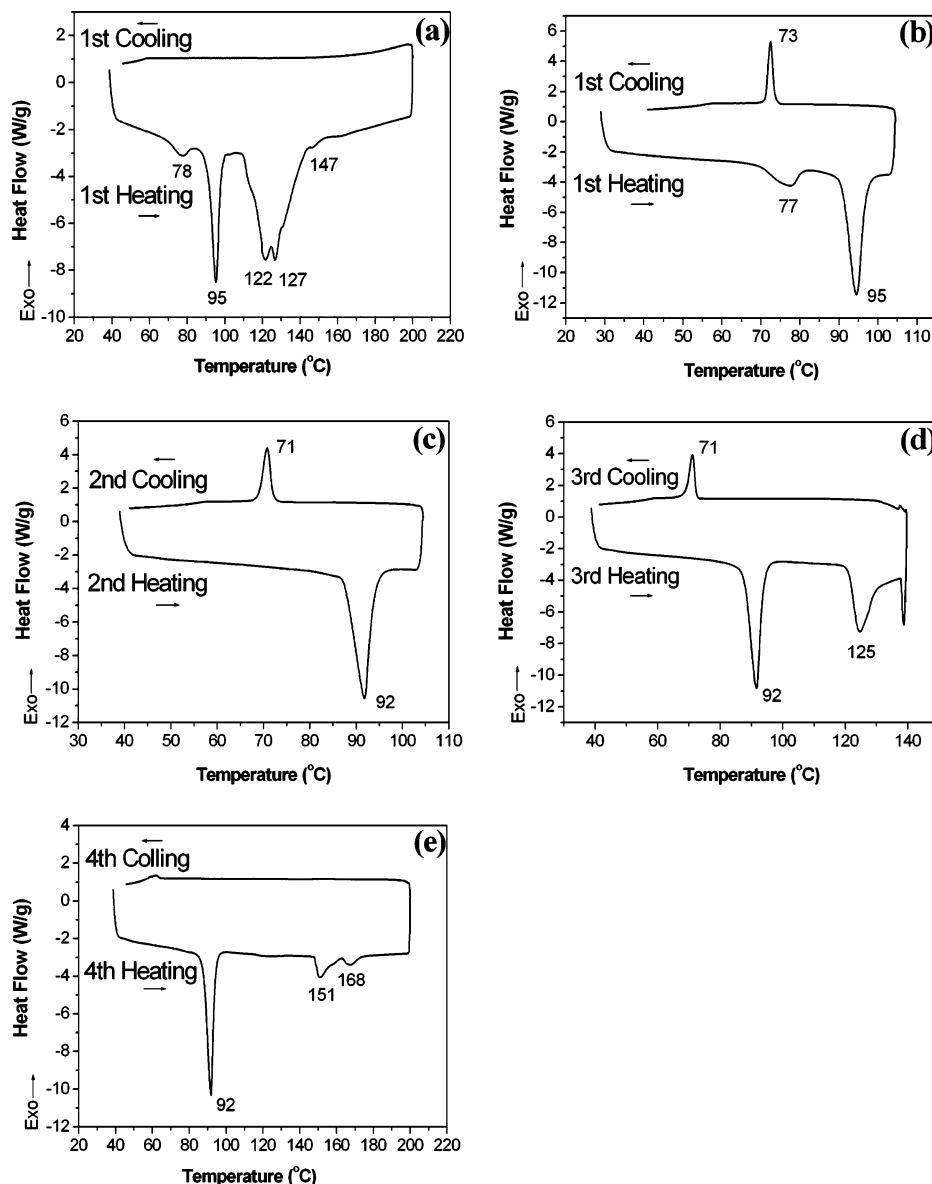


Figure 5. DSC curves for different heating and cooling cycles of the PDA-Na microcrystals: full thermal cycle to 200 °C (a); first partial thermal cycle to 105 °C (b); second partial thermal cycle to 105 °C (c); third partial thermal cycle to 140 °C; and (d) fourth full thermal cycle to 200 °C (e).

A mechanism (Figure 3) is proposed to explain the structural evolution during the irreversible red to blue color transition. Since the dimensional change is caused by the topochemical polymerization, we use four 10,12-pentacosadiynoic acid molecules and deduce the molecular packing based on preliminary quantum mechanical (QM) geometry optimizations (at DFT/B3LYP/6-311G** level) and energy minimization (see details in the Experimental Section).¹² As shown in Figure 3, the monomers before polymerization are arranged in a fashion with a tilt angle of 120° between the molecular direction and the packing array direction. The monomer separation distance (d) is about 5.06 Å, and the angle (Φ) between the diacetylenic unit and the stacking axis is about 43°, both of which satisfy the geometric requirement for the topochemical polymerization of diacetylene monomers.⁶ After polymerization at room temperature, the molecular packing does not change significantly due to the strong intermolecular interactions within the crystals. From the view of chemical reaction, as the diacetylenic units are polymerized, the outer acetylenic carbons of the diacetylenic units change from sp hybridized carbon atoms to sp^2 hybridized carbon atoms (i.e., olefinic carbons). Therefore the bond angle

of the outer carbons of diacetylenic units needs to change (e.g., from 180° to 120°) to obtain a stable molecular confirmation. As a result, the pendant side chains adjust their positions under the provision of external energy in order to release the bond strain along the ene-yne backbones. The optimized tilt angle of 95° between the adjusted side chain direction and the PDA backbone is consistent with the β angle obtained from XRD. Furthermore, the *ab initio* geometry optimization clearly demonstrates the increased repeat distance perpendicular to the conjugated backbone direction with the molecular movement. The calculated dimensional increase in one layer of diacetylene molecules is 1.6 Å, which is in excellent agreement with half the observed d -spacing change of 3.3 Å for two layers of diacetylene molecules in the crystal unit cell (see Figure 2b). We believe that the internal strain subjected on the PDA backbone constrains the π -electron delocalization, resulting in the initial red crystals. After molecular rearrangement, the PDA molecules are packed in the more stable (i.e., low-energy) blue state.

These thermally treated blue crystals can undergo subsequent structural and chromatic transitions (Figure 1) upon further

thermal stimuli similar to that reported before.^{9,10} The subsequent blue-to-red color change is completely reversible due to the enhanced electrostatic interactions; to our knowledge, however, only a few examples have been reported.^{3,9–11} XRD studies demonstrate no obvious change for the lamellar mesostructure during the reversible blue-to-red color transitions (see Figure 4). Since the blue to red color change arises from the fluctuating or melting of the ordered pendant side chains within the polymerized PDA-Na molecules, the distance perpendicular to the backbones may remain similar during these chromatic transitions. However, the degree of structural ordering slightly decreases along the *a*- and *b*-axes as indicated by the broadening of the peaks in the high-angle XRD pattern (results not shown). Heating the crystals to a much higher temperature (>130 °C) results in an ordered to disordered structural change accompanied by an irreversible red to orange color transition. The XRD patterns for orange samples exhibit a very broad diffraction peak at 2θ of ca. 2° without any diffractions at the high angle range (results not shown). The irreversible transition from red to orange microcrystals corresponds to the entangling of the side chains and the disordering of the PDA backbones.¹ Since the side chains are entangled around the backbones during this process, the structure hardly reverts to its ordered state of either red or blue form upon cooling.

Phase transitions corresponding to the color changes were investigated at a molecular level through differential scanning calorimetry (DSC). Figure 5 shows the DSC curves of the PDA-Na microcrystals subjected to different heating and cooling cycles. For a first complete heating–cooling cycle (from room temperature to 200 °C and then to room temperature), the DSC curve shows several distinct endothermic peaks at about 78, 95, 122–127, and 147 °C (Figure 5a), which are relative to the observed thermochromatic transitions. To further understand the nature of these molecular transitions, the microcrystals were tested at different temperature segments. As shown in Figure 5b, the DSC curve shows endothermic peaks at 77 and 95 °C when the as-synthesized red crystals are heated from room temperature to 105 °C. The former peak is attributed by the structural evolution to release the bond strain along the ene–yne backbones as discussed above, corresponding to the irreversible red-to-blue color transition. The endothermic peak temperature at 77 °C is higher than that observed visibly by melting-point meter (about 60 °C) because of the different heating rate. The latter endothermic peak in Figure 5b corresponds to the melting of the side alkyl chains. Upon cooling, only an exothermic peak at 73 °C is observed corresponding to the recrystallization of the side chains. This fluctuating (before 95 °C) melting and recrystallization of the ordered pendant side chain structure within the polymerized PDA-Na molecules¹ reversibly changes the effective conjugated ene–yne length of the polydiacetylenic backbone, resulting in the observed reversible chromatic transition from blue to red.^{1,14} The reversibility of this structure transition is further demonstrated by the DSC curve of the crystals subjected to a second heating–cooling cycle (Figure 5c). It shows a similar endothermic peak at 92 °C and an exothermic peak at 71 °C. During the third thermal cycle shown in Figure 5d, the transition is also observed with an endothermic peak at about 92 °C and a new endothermic peak at 125 °C. Cooling the crystals from 140 °C results in a similar exothermic peak as that in Figure 5b,c, corresponding to the local crystallization of the side chains. Subjected to a fourth heating–cooling cycle to 200 °C, the DSC curve shows the side chain melting peak at 92 °C; however, the endothermic peak at 125 °C is no longer present (see Figure 5e). Considering

the chromatic transitions described in Figure 1, we believe the irreversible structure change at about 125 °C is due to the wobbling and entangling of the side chain groups over the PDA backbones.¹ This structural change is difficult to recover since the entangled side chains are locked into each other, which causes an irrecoverable shortening of the conjugation length and therefore an irreversible red to orange color change. The polymer backbone structure may also be changed as evidenced by the endothermic peaks above 150 °C (Figure 5e).

Conclusions

In summary, both the experimental and the brief QM geometry optimization results demonstrate the lattice dimensional change of the metastable PDA crystals prepared by topochemical polymerization of PCDA-Na microcrystals. Releasing the internal strain by thermal agitation increases the effective conjugative length, producing an irreversible red-to-blue color change. The electrostatic interactions also result in the stable PDA crystals that show a reversible blue-to-red thermochromatism. This work provides some insights into the solid-state polymerization of diacetylenes and offers new responsive materials for sensors, optics, and adaptive devices, which are worth investigating further.

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Supporting Information Available: NMR, SEM, and XRD results of the microcrystals. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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