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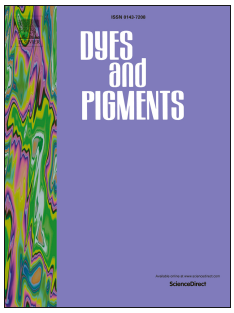

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PII: S0143-7208(19)30033-6

DOI: https://doi.org/10.1016/j.dyepig.2019.01.058

Reference: DYPI 7331

To appear in: *Dyes and Pigments*

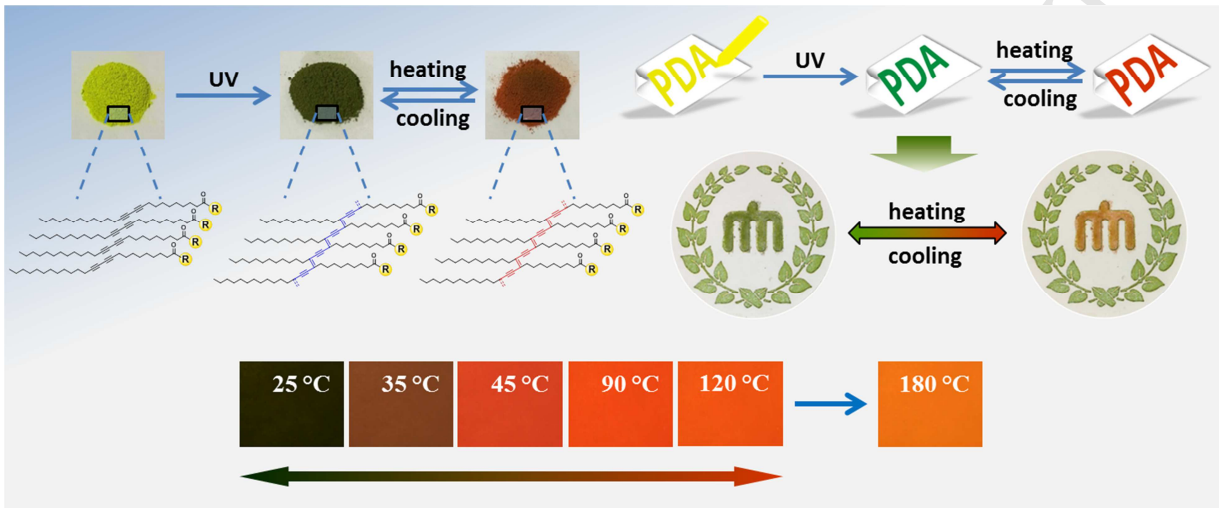
Received Date: 5 January 2019

Revised Date: 28 January 2019

Accepted Date: 30 January 2019

Please cite this article as: Mergu N, Kim H, Heo G, Son Y-A, Development of naphthalimide-functionalized thermochromic conjugated polydiacetylenes and their reversible green-to-red chromatic transition in the solid state, *Dyes and Pigments* (2019), doi: https://doi.org/10.1016/j.dyepig.2019.01.058.

Graphical abstract



Development of naphthalimide-functionalized thermochromic conjugated polydiacetylenes and their reversible green-to-red chromatic transition in the solid state

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Abstract

Development of PDAs has received great attention in many fields due to their optical and chromatic properties towards external stimuli. In this article, two novel PDAs (**NPI-PDA1** and **NPI-PDA2**) containing naphthalimide as a head group are designed and synthesized through self-assembly followed by topochemical polymerization, and these compounds show a reversible green-to-red colorimetric transition upon heating. PEO-embedded films are fabricated to facilitate the investigation of the thermochromic properties, and the surface morphologies of the films are observed by SEM analysis. The thermochromic behavior and color transitions are observed using photography and electronic absorption spectroscopy. The changes in the extended ene-yne conjugated system of the polymer during heat treatment are successfully monitored by Raman spectrometry. Moreover, PDA-embedded crayon wax-based hand-writable pens are fabricated and used efficiently on a solid substrate. **NPI-PDA1** and **NPI-PDA2** display excellent reversibility in the temperature ranges of 25–120 °C and 25–160 °C, respectively in the PEO polymer and paraffin wax matrices.

Keywords: Polydiacetylene, Thermochromism, Green-to-red color transition, PEO films, Crayon pen

1. Introduction

Polydiacetylenes (PDAs) are important conjugated polymers that have alternating double and triple bonds in the main polymer chain. PDAs are generally obtained by irradiation of self-assembled diacetylene monomers with UV (254 nm) or γ-rays, and these reactions do not require chemical initiators or catalysts nor are purification steps necessary to obtain pure PDAs. The polymerization takes place because the spacing between the monomer alkyl chains is small and similar to the spacing required for the diacetylene backbone to form and because of the intramolecular interactions among the monomer's sidechains [1–6]. However, for polymerization in the solid state, the diacetylene units must be properly oriented in relation to each other. A distance of 4.9 Å between the two reactive carbon atoms and an angle of 45° relative to the acetylene axis are required for this polymerization [7,8].

PDAs have received a substantial amount of attention since their discovery due to their facile self-polymerization and their optical and chromic properties including the unique blue-to-red and non-fluorescence to red-fluorescence transitions upon exposure to external stimuli such as heat, solvent, pH changes, mechanical stress, electrical current and ligand-receptor interaction [9–20]. The color change can easily be observed by the naked-eye. The color transformations of PDAs are due to the π-π* transition in the linear π-conjugated polymer backbone. The monomers alone do not show an absorption band, but an absorption band appears at approximately 650 nm upon polymerization. If the effective conjugation length is reduced due to strain or torsion applied to the backbone, the absorption maximum shifts to approximately 550 nm, which corresponds to a red color. These smart materials have been effectively used as temperature sensors and to monitor various biologically, chemically and environmentally important analytes [21–38]. To date, the majority of reported thermochromic PDAs show blue-to-red color changes

above room temperature (typically >40 °C). In the past few years, PDA-like conjugate polymers have been important materials for developing advanced systems and devices in various fields due to their intrinsic electronic, magnetic, photonic and spectroscopic properties [39–44].

To date, numerous PDAs were reported, which are mainly showing a reversible thermochromic behavior with a one-way blue-to-red color transitions. Also, the PCDA consisting of ethylene diamine was also reported, which showed blue-to-red color transition at room temperature [45]. In previous reports, aza-substituted PCDAs were used to achieve green-colored PDAs; however, due to steric hindrance, some of these compounds could not be polymerized, and some of those that did polymerize, produced regular blue-colored PDAs [46–49]. A green-to-red color transition was achieved by a subtractive color mixing method (external mixing) and reported recently by our research group [50]. From the knowledge of the color theory, we have extended the strategy to obtain PDAs that shows direct green-to-red color transition without mixing additional color. Recently, the development of directly writable techniques for depositing functional materials on solid substrates has attracted great attention [51–57]. In particular, pen-on-paper type approaches are very interesting since they enable the preparation of diverse patterned images on solid substrates with the flexibility afforded by drawing in an inexpensive manner [58].

In the present work, we have developed new PDAs (**NPI-PDA**) containing naphthalimide as a head group by a condensation reaction using 10,12-pentacosadiynoic acid (PCDA) (see **Figure S1** in the SI). This is the first example of a PDA with a reversible green-to-red color transition at 45 °C instead of a blue-to-red transition, and the compound can return to its initial color (green) when temperature is decreased. Furthermore, thermochromic color transitions

displayed by **NPI-PDA**-embedded PEO films are highly reversible and occur over a short temperature range (25 to 45 °C).

2. Experimental Section

2.1. Materials and Instruments

4-Bromo-1,8-naphthalic anhydride, n-butylamine, anhydrous ethylenediamine, anhydrous piperazine, N,N′-dicyclohexylcarbodiimide and 4-dimethylaminopyridine were purchased from TCI. 10,12-Pentacosadiynoic acid (PCDA) was purchased from Sigma-Aldrich. All other solvents were purchased from commercial sources and used without further purification. The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were collected on a Bruker AVANCE III spectrometer at 300 and 600 MHz, and $CDCl_3$ was used as the solvent. Mass spectra were recorded on AB Sciex 4000 QTRAP and Bruker micrOTOF-Q mass spectrometers. Solid-state absorption spectra were acquired on a SolidSpec-3700 diffuse reflectance UV-vis-NIR spectrophotometer. UV-vis spectra of the PEO films were collected using a Shimadzu UV-2600 spectrophotometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were conducted on a Mettler-Toledo TGA/DSC1 thermal analyzer at a heating/cooling rate of 10 °C/min in a nitrogen stream. SEM analysis for the polymer thin films was conducted using a Zeiss MERLIN field emission scanning electron microscope. Raman spectra were obtained on a Horiba Jobin Yovn LabRAM HR-800 Raman spectrometer with excitation at 785 nm laser under ambient conditions.

2.2. Preparation of diacetylene

Synthesis of naphthalimide (A): **A** was prepared according to the literature method [59]. A mixture of 4-bromo-1,8-naphthalic anhydride (2.77 g, 10 mmol) and butylamine (0.88 g, 12 mmol) in ethanol (50 mL) was refluxed for 8 hours. Then, the reaction mixture was concentrated under reduced pressure and purified by column chromatography using a mixture of hexane/DCM (7:3) as the eluent. After drying under reduced pressure, the reaction yielded **A** as a white solid (3.0 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.55 (dd, *J* = 1.2, 7.2 Hz, 1H; Ar H), 8.45 (dd, *J* = 1.2, 8.4 Hz, 1H; Ar H), 8.31 (d, *J* = 8.1 Hz, 1H; Ar H), 7.94 (d, *J* = 7.8 Hz, 1H; Ar H), 7.75 (t, *J* = 7.2 Hz, 1H; Ar H), 4.09 (t, *J* = 7.5 Hz, 2H; CH_2), 1.69–1.59 (m, 2H, CH_2), 1.37 (sext, *J* = 7.5 Hz, 2H; CH_2), 0.90 (t, *J* = 7.5 Hz, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$, δ): 133.1, 131.9, 131.1, 131.0, 130.5, 130.1, 128.9, 128.0, 123.1, 122.2, 40.3, 30.1, 20.3,13.8.

Synthesis of naphthalimide derivative (B): **A** (1.0 g, 3 mmol), ethylenediamine (1.8 g, 30 mmol), and piperazine (1.3 g, 15 mmol) were refluxed in ethanol (30 mL) for 72 hours. The mixture was then concentrated and purified by column chromatography using DCM/MeOH (90:10 for **B1** and 95:5 for **B2**) as the eluent, and **B** was isolated as a yellow solid (0.79 g, 84% of **B1** and 0.89 g, 87% of **B2**).

B1: ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.53 (d, *J* = 7.2 Hz, 1H; Ar H), 8.41 (d, *J* = 8.4 Hz, 1H; Ar H), 8.15 (d, *J* = 8.4 Hz, 1H; Ar H), 7.57 (t, *J* = 7.2 Hz, 1H; Ar H), 6.65 (d, *J* = 8.4 Hz, 1H; Ar H), 6.19 (s, 1H, NH), 4.14 (t, *J* = 7.8 Hz, 2H; CH_2), 3.39 (q, *J* = 6.0 Hz, 2H; CH_2), 3.16 (t, *J* = 6.0 Hz 2H; CH_2), 1.72–1.67 (m, 2H, CH_2), 1.56 (s, 2H, NH_2), 1.42 (sext, *J* = 7.8 Hz, 2H; CH_2), 0.96 (t, *J* = 7.8 Hz, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$, δ): 164.7, 164.1, 149.6, 134.4, 131.0, 129.7, 126.2, 124.6, 123.1, 120.4, 110.3, 104.4, 44.9, 40.2, 39.9, 30.3, 20.4, 13.8. ESI-MS *m/z*: $[M + H]^+$ calcd for $C_{18}H_{21}N_3O_2$, 312.2; found, 312.3.

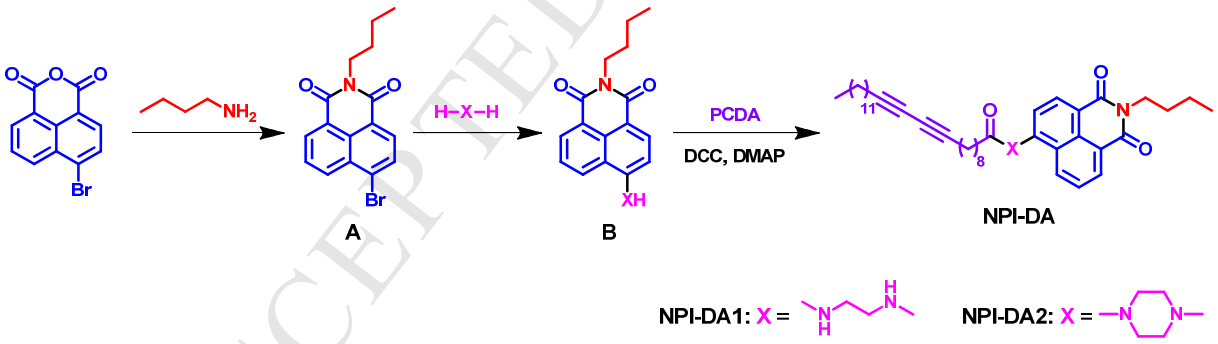
B2: ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.57 (d, *J* = 7.2 Hz, 1H; Ar H), 8.51 (d, *J* = 7.8 Hz, 1H; Ar H), 8.41 (d, *J* = 8.4 Hz, 1H; Ar H), 7.68 (t, *J* = 7.8 Hz, 1H; Ar H), 7.20 (d, *J* = 7.8 Hz, 1H; Ar H), 4.16 (t, *J* = 7.2 Hz, 2H; CH_2), 3.24–3.19 (m, 8H, CH_2), 1.70 (qn, *J* = 7.8 Hz, 2H; CH_2), 1.44 (sext, *J* = 7.2 Hz, 2H; CH_2), 1.24 (s, 1H, NH), 0.96 (t, *J* = 7.2 Hz, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$, δ):164.5, 164.0, 156.3, 132.5, 131.20, 130.2, 129.9, 126.2, 125.6, 123.3, 116.8, 114.9, 54.4, 46.2, 40.1, 30.3, 20.4, 13.8. ESI-MS *m/z*: $[M + H]^+$ calcd for $C_{20}H_{23}N_3O_2$, 338.2; found, 337.8.

Synthesis of diacetylene monomers (NPI-DA): As shown in **Scheme 1**, a dichloromethane (DCM) solution containing **B** (1.5 mmol), 10,12-pentacosadiynoic acid (PCDA) (0.56 g, 1.5 mmol), N,N′-dicyclohexylcarbodiimide (DCC) (0.5 g, 2.5 mmol) and 4-(dimethylamino)pyridine (DMAP) (30 mg) was stirred overnight at room temperature. The mixture was concentrated under reduced pressure and purified by column chromatography (DCM/MeOH; 99:1) to afford **NPI-DA** as green-yellow solid (750 mg, 75% of **NPI-DA1** and 821 mg, 79% of **NPI-DA2**).

NPI-DA1: ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.56 (d, *J* = 7.2 Hz, 1H; Ar H), 8.38 (d, *J* = 7.8 Hz, 1H; Ar H), 8.23 (d, *J* = 8.4 Hz, 1H; Ar H), 7.63 (t, *J* = 7.2 Hz, 1H; Ar H), 7.20 (s, 1H, NH), 6.48 (d, *J* = 8.4 Hz, 1H; Ar H), 6.37 (t, *J* = 6.6 Hz, 1H; NH), 4.15 (t, *J* = 7.2 Hz, 2H; CH_2), 3.76 (q, *J* = 6.0 Hz, 2H; CH_2), 3.42 (q, *J* = 4.2 Hz, 2H, CH_2), 2.28 (t, *J* = 7.2 Hz, 2H; CH_2), 2.23 (t, *J* = 7.2 Hz, 2H; CH_2), 2.16 (t, *J* = 7.2 Hz, 2H; CH_2), 1.73–1.69 (m, 2H, CH_2), 1.67–1.63 (m, 2H, CH_2), 1.50 (qn, *J* = 7.2 Hz, 2H; CH_2), 1.46–1.38 (m, 4H, CH_2), 1.37–1.13 (m, 23H, CH_2), 1.15–1.08 (m, 3H, CH_2), 0.96 (t, *J* = 7.2 Hz, 3H; CH_3), 0.87 (t, *J* = 7.2 Hz, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$, δ): 176.6, 164.8, 164.3, 150.1, 134.4, 131.1, 129.8, 127.2, 124.9, 122.8, 120.4, 109.9, 103.1, 77.6, 77.3, 65.4, 65.2, 46.7, 39.9, 38.9, 36.6, 33.9, 31.9, 30.3, 29.6, 29.6, 29.5, 29.4, 29.3,

29.1, 29.0, 28.9, 28.8, 28.8, 28.6, 28.4, 28.2, 25.7, 25.6, 24.9, 22.7, 20.4, 19.1, 14.1, 13.9. HRMS *m/z*: $[M + Na]^+$ calcd for $C_{43}H_{61}N_3O_3$, 690.4611; found, 690.4600.

NPI-DA2: ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.60 (dd, *J* = 1.2, 7.2 Hz, 1H; Ar H), 8.52 (d, *J* = 7.8 Hz, 1H; Ar H), 8.42 (dd, *J* = 1.2, 8.4 Hz, 1H; Ar H), 7.72 (t, *J* = 7.2 Hz, 1H; Ar H), 7.22 (d, *J* = 8.4 Hz, 1H; Ar H), 4.16 (t, *J* = 7.2 Hz, 2H; CH_2), 3.94 (s, 2H, CH_2), 3.79 (s, 2H, CH_2), 3.25–3.21 (m, 4H, CH_2), 2.24 (t, *J* = 7.8 Hz, 2H; CH_2), 2.23 (q, *J* = 7.8 Hz, 4H; CH_2), 1.73–1.65 (m, 4H, CH_2), 1.50 (sext, *J* = 7.2 Hz, 4H; CH_2), 1.44 (q, *J* = 7.2 Hz, 2H; CH_2), 1.41–1.25 (m, 26H, CH_2), 0.97 (t, *J* = 7.2 Hz, 3H; CH_3), 0.87 (t, *J* = 7.2 Hz, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$, δ): 171.9, 164.3, 163.9, 155.1, 132.3, 131.2, 129.8, 129.7, 126.3, 126.1, 123.5, 117.7, 115.4, 77.6, 77.4, 65.3, 65.2, 53.1, 53.1, 45.8, 41.7, 40.1, 33.3, 31.9, 30.2, 29.6, 29.6, 29.6, 29.4, 29.4, 29.3, 29.2, 29.1, 28.9, 28.8, 28.7, 28.3, 28.3, 25.3, 22.7, 20.4, 19.2, 14.1, 13.8. HRMS *m/z*: $[M + Na]^+$ calcd for $C_{45}H_{63}N_3O_3$, 716.4767; found, 716.4767.



Scheme 1. Synthesis route for the preparation of PCDA derivatives containing a naphthalimide unit.

2.3. Preparation of polymerized NPI-DAs

The **NPI-DA** monomer was ground into a fine powder using a mortar and pestle and then polymerized with UV irradiation using a 254 nm lamp for 1 h at room temperature. Finally, a green-colored **NPI-PDA** was collected, and it was used without further purification.

2.4. Preparation of the NPI-DA-embedded PEO film

Poly(ethylene oxide) was used as the polymer matrix to prepare the polymeric films. As depicted in the schematic representation (**Figure 1**), to the stirred solution of $CHCl_3$ (3 mL) containing 100 mg of PEO was added 20 mg of **NPI-DA** monomer. After the PEO had completely dissolved, the transparent solution was poured into a petri dish. The solvent was allowed to slowly evaporate under a vacuum dryer for 1 h. The thin PEO films were cut into 2×2 cm square pieces and then removed from the petri dish.

2.5. Fabrication of an NPI-DA-embedded hand-writable pen

For drawing purposes, a paraffin wax-based hand-writable pen containing **NPI-DA** monomer was constructed. As demonstrated in **Figure 1**, a hot solution of paraffin wax (90%) containing DA monomer (10%) was poured into a mold. After cooling to room temperature, the yellow-colored stick was removed from the mold and could then be used as a thermochromic drawing tool. As shown in the figure, the color transition takes place upon heating a solid surface that has already been drawn with the PDA-wax pen and polymerized.

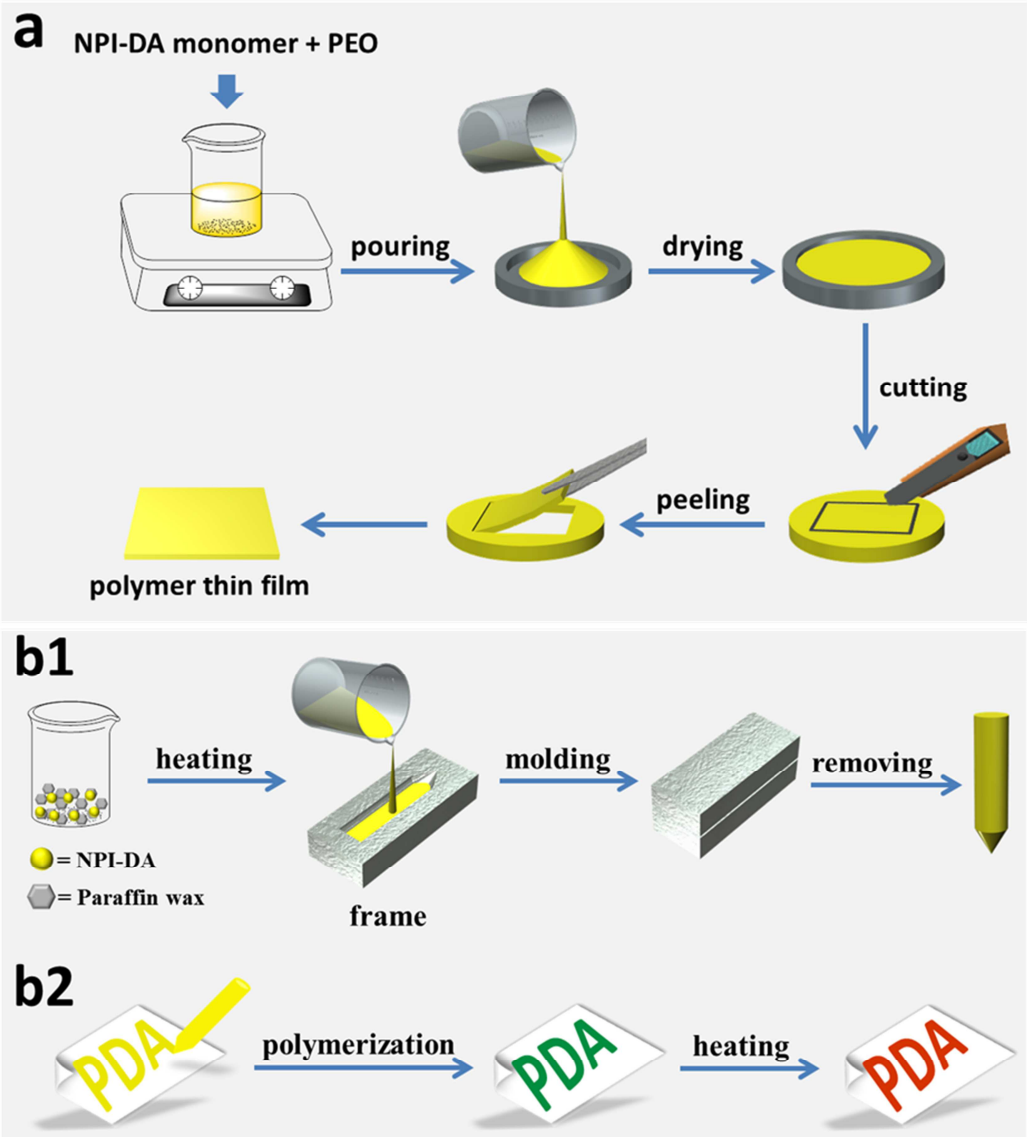


Figure 1. (a) Schematic representation of the steps involved in the preparation of polymer thin film. (b1) Fabrication of a diacetylene monomer-embedded paraffin pen. (b2) Color transition of the paraffin wax drawing upon polymerization and heating.

3. Results and Discussion

3.1. Thermochromism of green PDAs

Green PDAs were obtained upon polymerization of the diacetylene monomers **NPI-DA1** and **NPI-DA2** under UV light irradiation. To date, the majority of PDAs and their derivatives are blue in color, and this is the first report of using a yellow-colored naphthalimide derivative as a head group to prepare green PDAs. The topochemical polymerization initiated and accelerated by UV irradiation generates the conjugated polymer network [7,8]. To gain a better understanding of the development of green PDA, an illustration showing the self-assembly of the **NPI-DA** monomer, the polymerization and the color transition upon heat treatment is shown in **Figure 2**. As seen in the figure, the monomers approach each other in a single plane upon self-assembly. Under UV irradiation, the adjacent highly ordered monomers join together to produce polymer of **NPI-DA**. The developed green-colored PDAs turns red under thermal stress in the solid state.

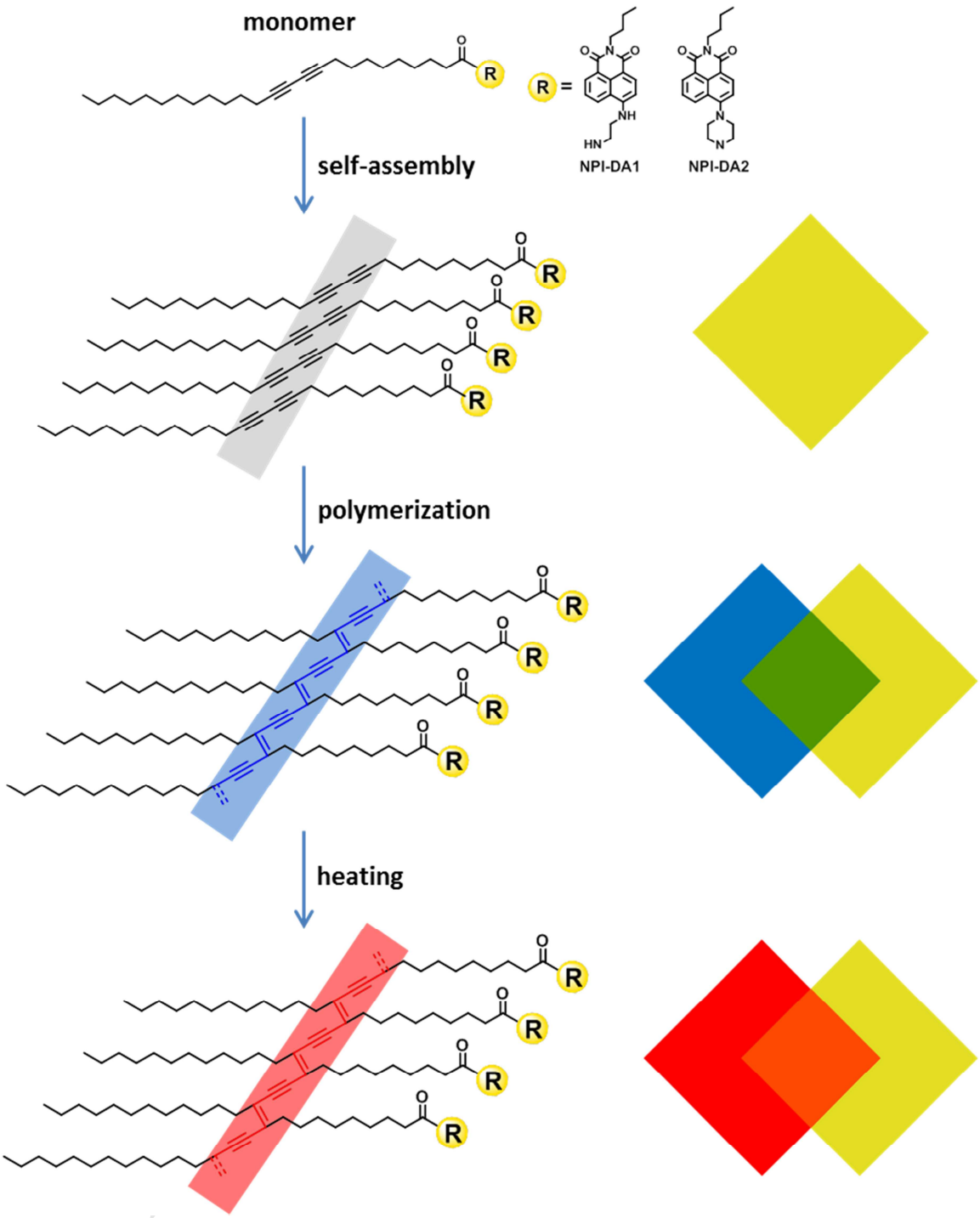


Figure 2. A detailed schematic illustration of the steps involved in producing a green PDA from the DA monomer and its thermochromic behavior.

Initially, the monomers are yellow, and they turn green upon polymerization (see **Figure S1** in the SI). UV-vis absorption spectra corresponding to the green and red phases of the PDAs in the powder state were recorded and are shown in (see **Figure S2** in the SI). For the green phase, the most prominent spectral features are two broad peaks centered at approximately 450 and 620 nm for **NPI-PDA1** and 400 and 600 nm for **NPI-PDA2**. The PDA undergoes a color transition from green to red when the temperature is increased to 45 °C, and the PDA can be returned to its original green color by decreasing the temperature. The **NPI-PDA**s displayed excellent thermochromic reversibility in the temperature range of 25–160 °C. In the red phase, unexpected absorption shifts were observed due to inadequate polymerization in the powder phase. To avoid this, we then prepared and characterized PEO polymer thin films doped with **NPI-DA** monomer. Additionally, the thin polymer films are clear to the naked-eye and show good spectral properties. Notably, higher temperatures of 180 and 160 °C, which are equal to the melting points of **NPI-PDA1** and **NPI-PDA2**, respectively, will cause irreversible thermochromic behavior in the solid state.

To determine the thermal stability of the synthesized PDAs, thermogravimetric analysis (TGA) was conducted over the range of 25–800 °C. As shown in **Figure 3a**, **NPI-PDA1** and **NPI-PDA2** have similar thermal decomposition behavior, and both compounds started decomposing at approximately 350 °C. In the DSC curve of **NPI-PDA1**, two endothermic peaks were observed at 98.39 and 131.26 °C, while **NPI-PDA2** displayed a single endothermic peak at 84.24 °C (**Figure 3b**). According to the obtained TGA and DSC data, the prepared PDAs can be analyzed and display their thermochromic properties at reasonably high temperatures.

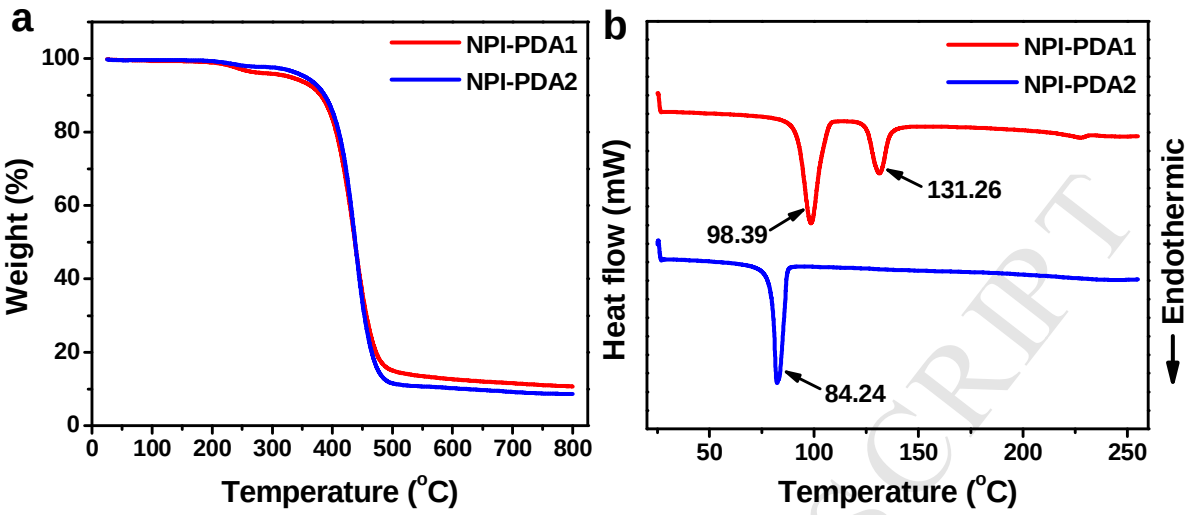


Figure 3. TGA (a) and DSC (b) curves of **NPI-PDA1** and **NPI-PDA2**. The heating rate was 10 °C/min.

3.2. Thermochromism of NPI-DA-embedded PEO films

Due to its uniformity and the availability of higher surface area to polymerization, we prepared **NPI-DA**-embedded PEO films. These thin films displayed an extremely quick response to UV irradiation to yield a green color. The fabricated yellow-colored PEO-based films were irradiated with a UV lamp (254 nm) at room temperature for 5 min to achieve the polymerized green-colored films, and the corresponding UV spectra are shown in **Figure 4**. The naphthalimide moiety connected to ethylenediamine (primary amine) produced brighter green compared to piperazine (secondary amine) due to the difference in their original yellow colors. The color of PDA is also depends on the intermolecular hydrogen bonds between two adjacent polymerizable monomers [60]. Thus, a strong color observed for **NPI-PDA1** could be due to the formation of strong intermolecular hydrogen bonds that induces the polymerization of monomers. The **NPI-DA** monomer showed a very broad and more intense peak in the region of 400–500 nm that can be attributed to the naphthalimide chromophore, no peak was observed in

the range of 550–700 nm, and a peak centered at 640 nm with a shoulder at approximately 590 nm was observed during the polymerization process. In general, a very strong absorption appears at around 650 nm for PDA macromolecules. Instead, a broad absorption peak in the 550–700 nm region was observed, which mainly due to the overlap with the broad and strong absorption band of naphthalimide chromophore. As shown in the spectra, the λ_{max} at approximately 640 nm gradually increased and reached a maximum, and the yellow-colored thin films dramatically turned green after 5 min of UV irradiation. SEM analysis was carried out to observe the morphology of only the thin films of PEO, **NPI-PDA1**-embedded PEO and **NPI-PDA2**-embedded PEO (**Figure 5**). The SEM results of PEO show that the surface is an aggregated sheet. The morphology of the PDA/PEO mixture is completely different, and they show aggregated needles-type morphology. The obtained green PDA-embedded PEO solid film was further heated for the thermochromic observations. The thermochromic transition of the successfully fabricated and polymerized thin films were carried out using photography and electronic absorption spectroscopy.

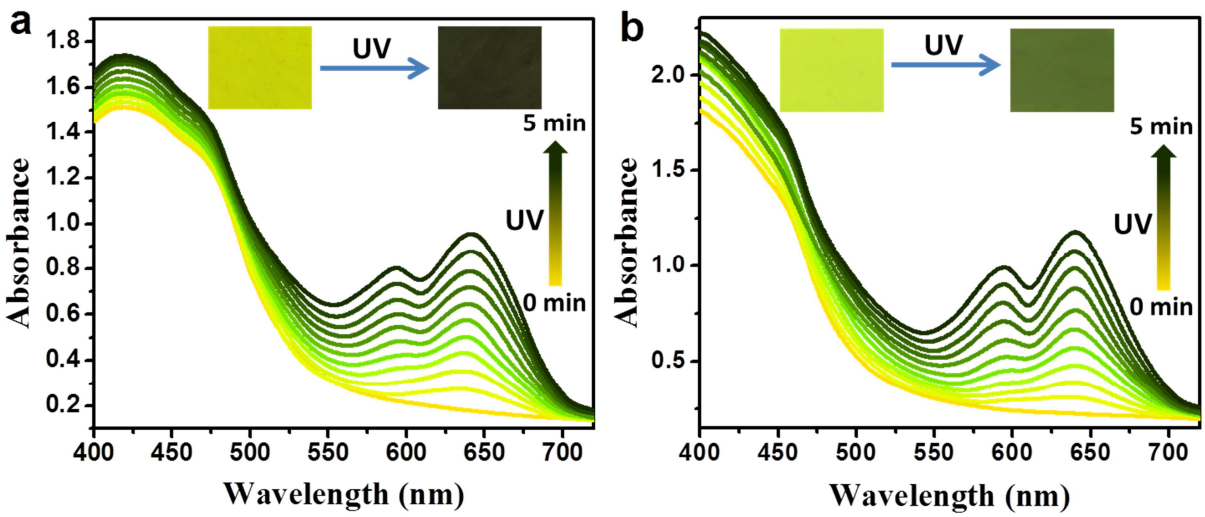


Figure 4. UV-vis spectral changes of (a) **NPI-DA1-** and (b) **NPI-DA2-**embedded PEO films under UV irradiation for 5 min. Inset: The color changes of the thin films from yellow to green upon polymerization.

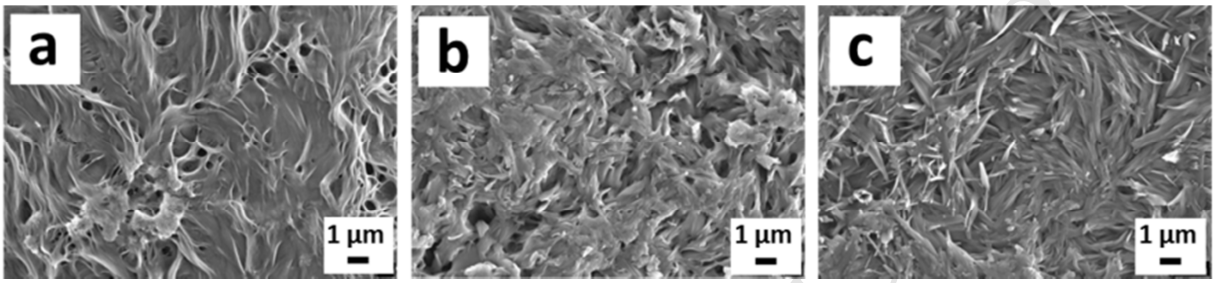


Figure 5. SEM images of PEO (a), **NPI-PDA1**-embedded PEO (b) and **NPI-PDA2-**embedded PEO (c) films at room temperature.

As depicted in **Figure 6**, the reversible significant color transition and the changes in its absorption spectrum were observed and recorded at 2 °C increments in the temperature range of 25–45 °C. Initially, at 25 °C, the film was green and showed a broad absorption peak centered at 640 nm. The color slowly turned orange-red, and the absorbance at 640 nm gradually decreased, and a new absorption peak at approximately 550 nm (blueshift) appeared as the temperature increased. The peak at 640 nm almost disappeared, and the new peak at 550 nm reached its maximum intensity at 45 °C. The band corresponding to the naphthalimide did not change as the temperature increase, which means that the naphthalimide group was not affected during polymerization or heat treatment. The original spectral pattern and color were completely recovered upon cooling from 45 °C to 25 °C. It is commonly believed that the side chains that are directly linked to the backbone of the polymer undergo twisting upon thermal treatment. Due to the presence of twisted side chains, the conjugation within the polymer decreases, causing a

blueshift in the absorption spectra [61–63]. On further increasing the temperature from 45–120 °C, the orange-red color slowly became orange. The thermochromic reversibility of the PDA-embedded PEO films was successfully demonstrated up to 120 °C. Finally, upon further heat treatment of the orange **NPI-PDA1-** and **NPI-PDA2**-embedded PEO films at 180 and 160 °C, respectively, an irreversible yellow-orange color developed. The thermal stability for PEO films was found to be 180 and 160 °C respectively for **NPI-PDA1** and **NPI-PDA2**. Thus, the PDA in the PEO polymer matrix exhibited a rapid green-to-orange response and a reversible orange-to-green thermochromic transition. The color transition of the PDA in the polymer matrix was the same as that observed in the powder form, and compared to the powder form, it showed promising spectral characteristics when embedded in the polymer matrix.

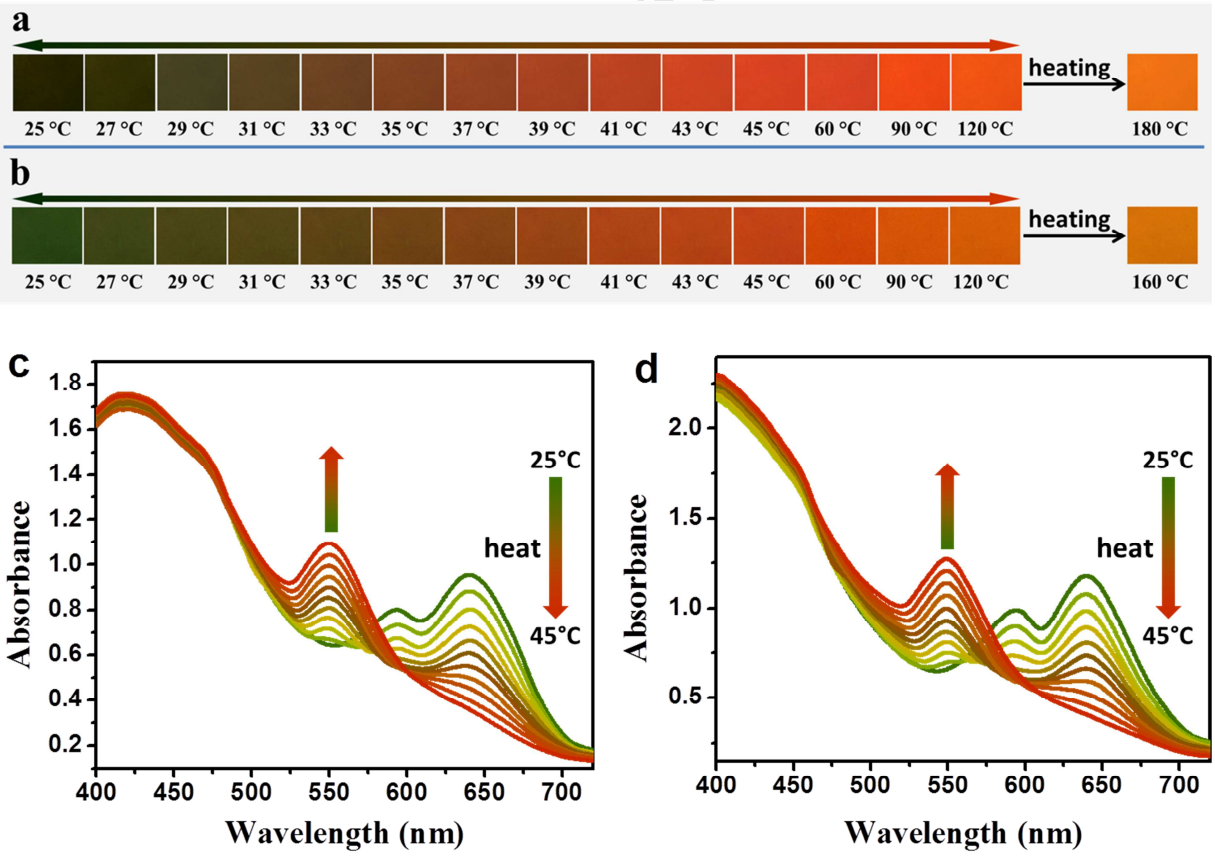


Figure 6. The color transition (a,b) and UV absorption spectral changes (c,d) of polymerized thin films under heating; a and c correspond to **NPI-PDA1**, and b and d correspond to **NPI-PDA2**.

Moreover, the thin films consisting of the monomer and polymer were further characterized using Raman spectrometry. For this study, to generate irreversibly orange films, **NPI-PDA1-** and **NPI-PDA2-**embedded films were heat treated at 180 and 160 °C, respectively. As can be seen in **Figure 7**, peaks corresponding to the alkene and alkyne groups in the **NPI-DA1** monomer appeared at 1455 and 2092 cm^{-1}, respectively, and green **NPI-PDA1** showed Raman shifts similar to those of the monomer. The alkene and alkyne bands in the typical orange **NPI-PDA1** appeared at 1512 and 2117 cm^{-1}, respectively, and the bands typical of the initial green polymer were also present. Similarly, the **NPI-DA2** monomer and polymer (green phase) produced signals at 1454 and 2082 cm^{-1} corresponding to the alkene and alkyne groups, respectively. The orange **NPI-PDA2** exhibited the same Raman bands along with shoulder peaks at 1501 and 2107 cm^{-1}. The spectral changes corresponding to the color transition are commonly due to the thermal-induced conformational changes in the alkyl side chains causing changes in the PDA backbone [64–67].

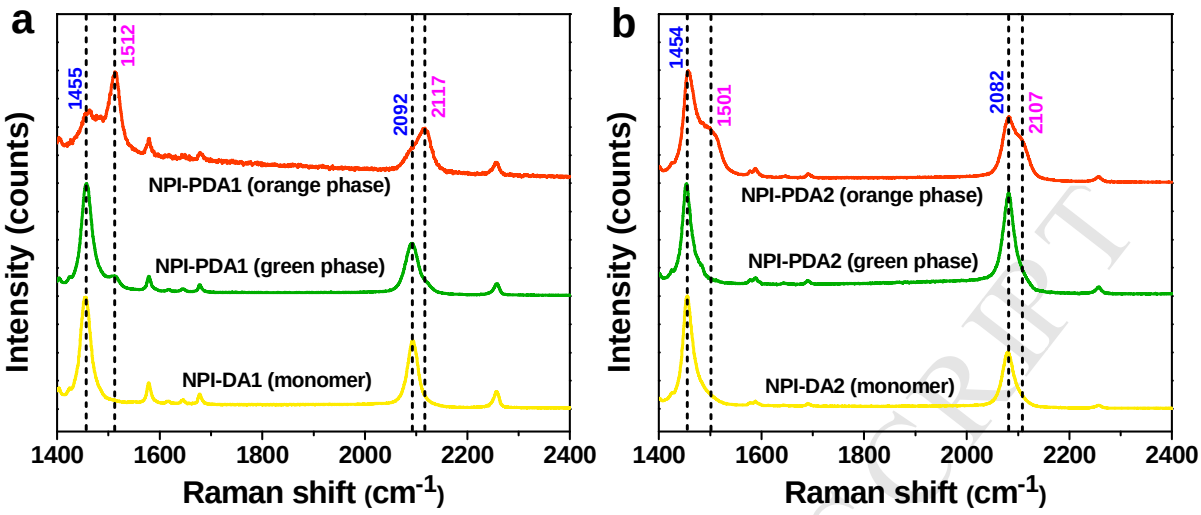


Figure 7. Raman spectral changes of (a) **NPI-DA1-** and (b) **NPI-DA2**-embedded PEO thin films before and after polymerization (green and orange phase).

3.3. Thermochromic properties of NPI-DA-embedded hand-writable pen

Due to the unreactive solid matrix, we used crayon wax to fabricate a hand-writable pen based on the diacetylene monomer and investigated its thermochromic behavior on solid substrates such as paper. The drawings of **NPI-DA2**-wax crayon on paper showed color changes upon UV irradiation and thermal treatment, which are photographed step-by-step at various temperatures (**Figure 8**). As demonstrated in **Figure 9**, images of a parrot and a rose were drawn using the **NPI-DA1-** and **NPI-DA2**-wax crayons, respectively, and were initially yellow. The drawings turned green immediately upon UV irradiation (254 nm). The obtained green images exhibited reversible thermochromic behavior over a wide range of working temperatures from 25–160 °C and 25–180 °C for **NPI-DA1-** and **NPI-DA2**-embedded wax crayons, respectively. The color of each of the green drawings was monitored over various temperature ranges as shown in the figure. The images turned greenish-red and orange-red at 35 and 45 °C, and these color changes are completely reversible. On further heating, the parrot and rose turned orange at

180 and 160 °C, respectively, and they returned to green upon cooling. The images corresponding to **NPI-DA1** and **NPI-DA2** irreversibly turned yellow-orange at approximately 190 and 170 °C, respectively. The images drawn using crayon pens exhibited similar thermochromic properties as the monomers showed in the powder state. Thus, due to their high thermal stability and immediate thermochromic reversibility, it is possible to utilize in the identification and authentication of documents.

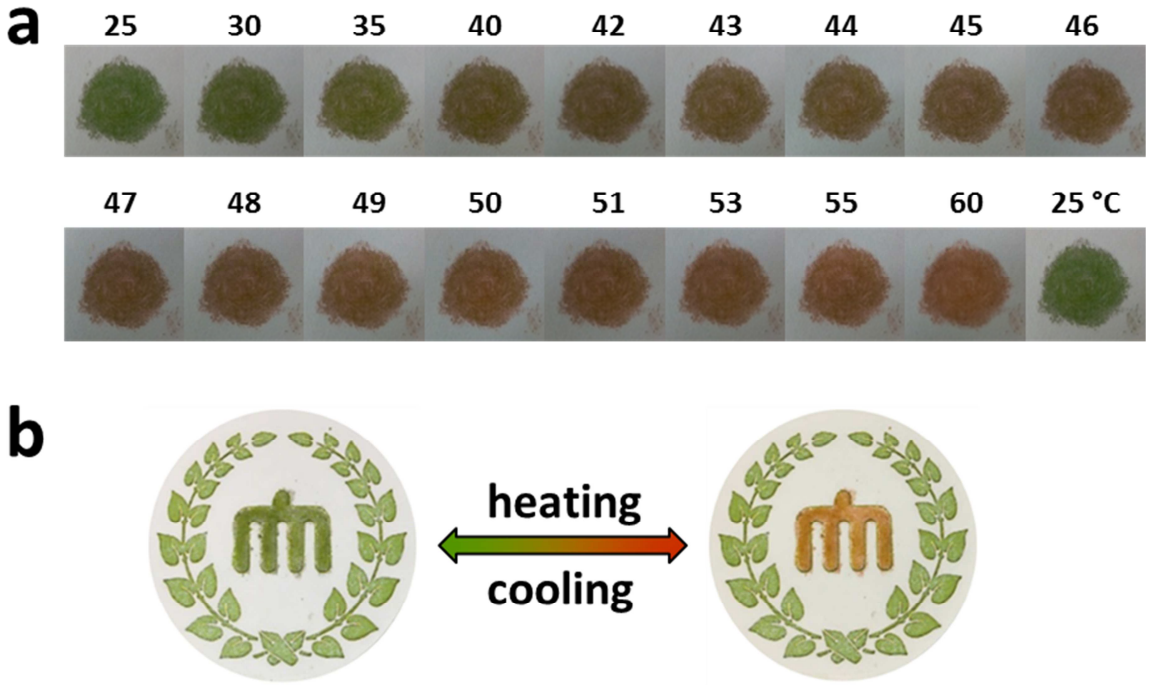


Figure 8. Photographs of a PDA image on paper derived from **NPI-PDA2-**wax upon heating and cooling.

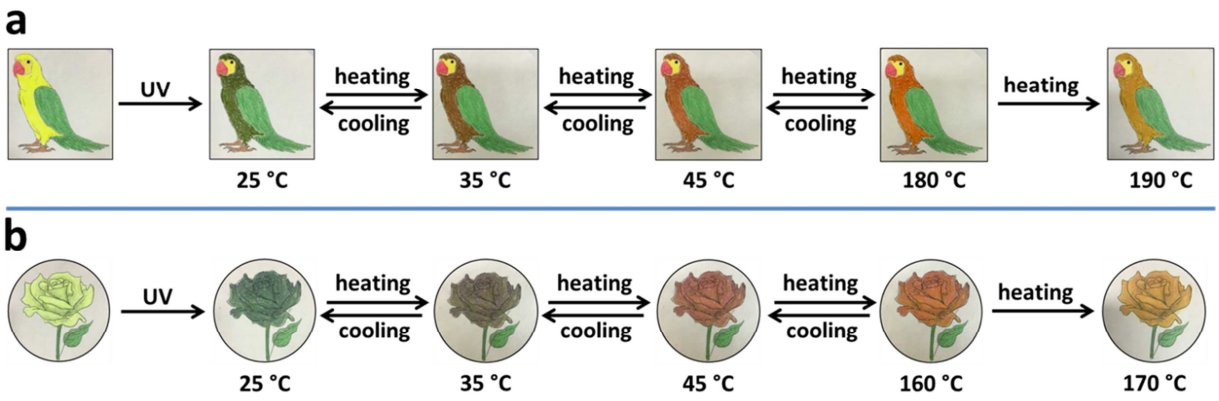


Figure 9. Photographs of PDA images drawn using the hand-writable pens derived from (a) **NPI-DA1-** and (b) **NPI-DA2**-wax crayons at various conditions.

4. Conclusion

In the studies described above, the thermochromic behavior of newly synthesized PDAs was investigated in the solid state as well as in a polymer matrix. PDA-embedded polymer thin films were fabricated and characterized by SEM, UV absorption and Raman spectroscopic studies. Obvious spectral changes corresponding to the color transition from green-to-red and red-to-orange upon heating were observed. Thermochromic reversibility was successfully monitored in the range of 25–120 °C in the polymer matrix. In addition, **NPI-DA1-** and **NPI-DA2**-embedded paraffin wax-based hand-writable pens were constructed, and they exhibited excellent reversible thermochromic performance over a wide temperature range (25–160 °C). Due to their high thermal stability and immediate thermochromic reversibility, these materials can be used in the identification and authentication of documents.

Acknowledgements

This study was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (Grant No. NRF-2017R1E1A1A01074266).

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Highlights

- Novel PDAs show reversible green-to-red colorimetric transition upon heating.
- PEO films are fabricated and characterized by SEM, UV and Raman spectroscopy.
- Crayon hand-writable pens are fabricated and used efficiently on a solid substrate.
- PDAs work efficiently and reversibly in the ranges of 25–120 °C and 25–160 °C.