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# Network Polydiacetylene Films: Preparation, Patterning, and Sensor Applications

Joosub Lee, Oktay Yarimaga, Cheol Hee Lee, Yang-Kyu Choi,\* and Jong-Man Kim\*

The synthesis, characterization, and functionalization of polydiacetylene (PDA) networks on solid substrates is presented. A highly transparent and cross-linked diacetylene film of DCDDA-bis-BA on a solid substrate is prepared first by tailoring the monomers with organoboronic acid moieties as pendant side groups and consequent drop-casting and dehydration steps. Precisely controlled thermal curing plays a key role to obtain properly aligned diacetylene monomers that are closely packed between the boronic acid derived anhydride structures. A second cross-linking, which occurs by polymerization of the diacetylene monomers with UV irradiation, induces a transparent to blue color shift. Accordingly, colored image patterns are readily available by polymerization through a photomask. The color change that takes place as a response to various organic solvents can be simply detected by naked eyes. The thermofluorescence change of PDA networks is demonstrated to be an effective method by which to obtain the microscale temperature distribution of thermal systems. The ease of film formation and stress-induced blue-to-red color change with a simultaneous fluorescence generation features of the network structure should find a great utility in a wide range of chemical and thermal sensing platforms.

blue-to-red color transition, which occurs with environmental perturbations such as heat (thermochromism),<sup>[23,24]</sup> mechanical stress (mechanochromism),<sup>[25–28]</sup> organic solvents (solvatochromism),<sup>[29–33]</sup> and ligand–receptor interactions (affinochromism).<sup>[34–45]</sup> These stress-induced responses that generate a simultaneous fluorescence signal have efficiently been applied to design of bio- and chemosensors,<sup>[34–45]</sup> molecular switches,<sup>[46,47]</sup> photonic materials,<sup>[48]</sup> and information displays.<sup>[49]</sup> Recent efforts on the utilization of thermofluorescence characteristic of PDAs have led to the development of diverse functional approaches to employ solution-based and film-embedded supramolecules as temperature indicators.<sup>[50–52]</sup>

Regardless of the sensing mechanism, formation of uniform and stable films of PDAs on solid substrates for most of the as-mentioned applications has been a common demand. However, PDAs, in general, are quite insoluble in common organic solvents due to their highly aggregating nature, which has put a severe

limitation on the fabrication of well-defined spin- and drop-cast layers. Relatively reliable examples of the soluble PDAs have been demonstrated by modification of side chain functionalities with substituted urethanes (alkoxycarbonylmethylurethanes (ACMUs) and aryl/alkyl urethanes),<sup>[53–56]</sup> carbazole derivatives,<sup>[57]</sup> and substituted phenoxyphenyl moieties.<sup>[58]</sup> The PDAs derived from these monomers are in general prepared from  $\gamma$ -ray irradiation of crystalline or powdered diacetylene monomers. Soluble PDAs are then obtained by extraction with organic solvents.

The Langmuir–Blodgett (LB) or Langmuir–Schaefer (LS) deposition method can yield transparent PDA films.<sup>[34]</sup> However, PDA films prepared from these methods are mechanically weak. Drop- or spin-casting of diacetylene monomers on a solid substrate followed by UV irradiation tends to result in opaque and poor quality PDA films because of the highly aggregating nature of the diacetylene monomers. Brinker and co-workers reported a new approach for the fabrication of transparent PDA films using alkoxysilane-containing diacetylene monomers.<sup>[59]</sup> The method described in that work requires acidic hydrolytic conditions and matrix monomers to prepare the transparent PDA nanocomposite films. Fabrication of transparent PDA layers without employing other

## 1. Introduction

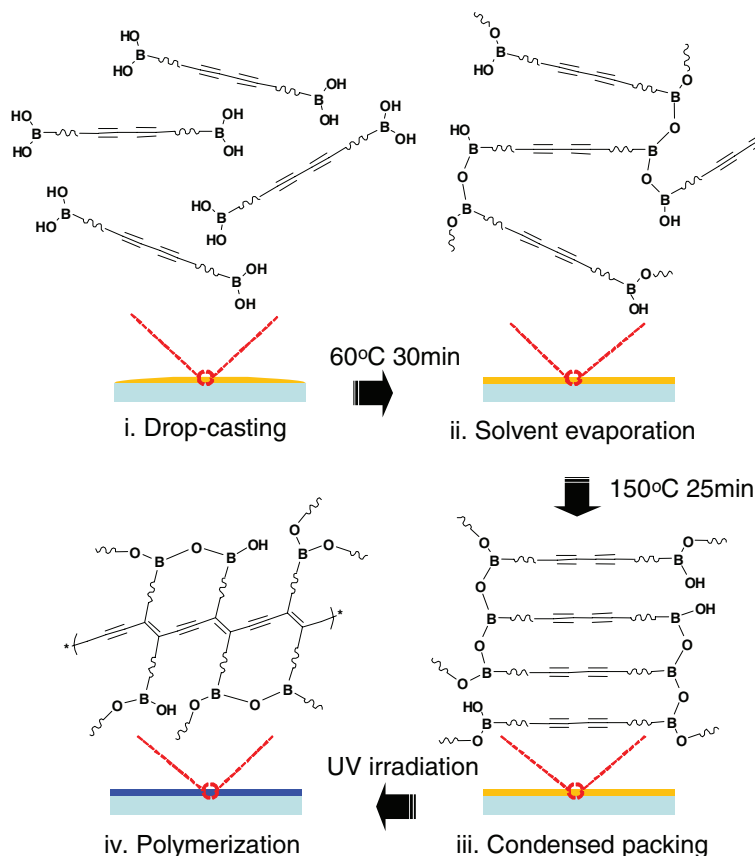
Polydiacetylenes (PDAs) are conjugated polymers with alternating ene–yne backbone structures. Unlike other conjugated polymers, PDAs are uniquely prepared by UV or  $\gamma$ -irradiation of molecularly assembled diacetylene monomers without employing additional catalysts or initiators.<sup>[1–22]</sup> Undoubtedly, the most attractive property of PDAs is their brilliant

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**Figure 1.** A scheme of the fabrication of a networked polydiacetylene film with DCDDA-bis-BA 1.

matrix polymers or harsh conditions has been a challenging task.

Here, we present a new approach for the preparation of PDA networks on solid substrates. The theoretical layout of this new method has been drawn by considering that organoboronic acids form anhydride structures by dehydration upon heating. As depicted in **Figure 1**, the strategy involves three distinct steps: formation of a solid film layer by drop-casting, a consequent thermal annealing, and polymerization of the diacetylene networks via UV irradiation. Accordingly, diacetylene monomers that are tailored to have two boronic acids at the ends are properly aligned during anhydride formation and closely packed into cross-linked networks. Spectral and optical analyses reveal that the compactness of the monomer chains is the key feature that affects the tendency toward highly uniform polymerization over a large distance. Adopting the method to a conventional photolithographic process, selectively cross-linked PDA optical and fluorescence image patterns can be obtained by polymerization of the monomer network through a photomask. The chemical sensitivity test of the samples to various organic solvents results in a distinguishable color contrast difference as observed by the naked-eye. In addition, we have successfully implemented the irreversible thermofluorescence transition feature of the PDA networks on a microheater system to monitor the temperature gradients on the device.

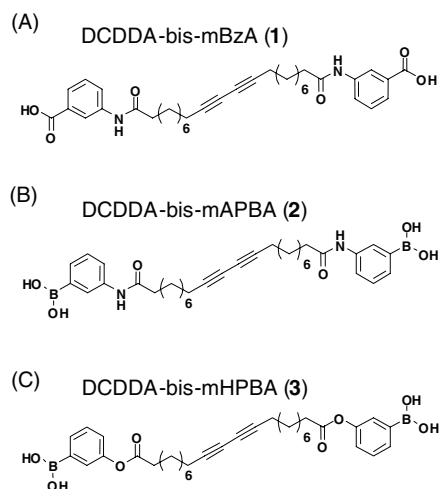
## 2. Results and Discussion

### 2.1. Structure, Stability, and Characterization of PDA Networks

Previous studies have shown that the polymerization of diacetylene chains is strongly affected by aromatic interactions, hydrogen bonding, and hydrophobic interactions especially between the adjacent functional groups.<sup>[60]</sup> Accordingly, a pronounceable polymerization is achievable only if the diacetylene monomers are properly tailored, well-aligned, and closely packed. In order to prove the effect of the packing density of the monomers and the functionality of boronic acid side groups on polymerization, a set of analog molecules of 10,12-docosadiynedioic acid (DCDDA) derivatives (DCDDA-bis-mBzA 1, DCDDA-bis-mAPBA 2, and DCDDA-bis-mHPBA 3) were investigated (**Figure 2**). The benzoic acid terminated diacetylene monomer DCDDA-bis-mBzA 1 was employed to compare its film-forming property with that of the structurally analogous phenylboronic acid containing monomer DCDDA-bis-mAPBA 2. Results obtained with the two diacetylene monomers, DCDDA-bis-mBzA 1 and DCDDA-bis-mAPBA 2, should reveal the significance of the boronic acid groups in terms of network forming ability. Additionally, the ester group containing diacetylene

monomer DCDDA-bis-mHPBA 3 was selected to gain information about the role played by amide hydrogen bonding interactions in the networked PDA supramolecules.

The diacetylene monomers 1–3 were readily prepared in one step by coupling 10,12-docosadiynedioic acid dichloride



**Figure 2.** The structures of diacetylene monomers investigated in this study. A) DCDDA-bis-mBzA 1. B) DCDDA-bis-mAPBA 2. C) DCDDA-bis-HPBA 3.

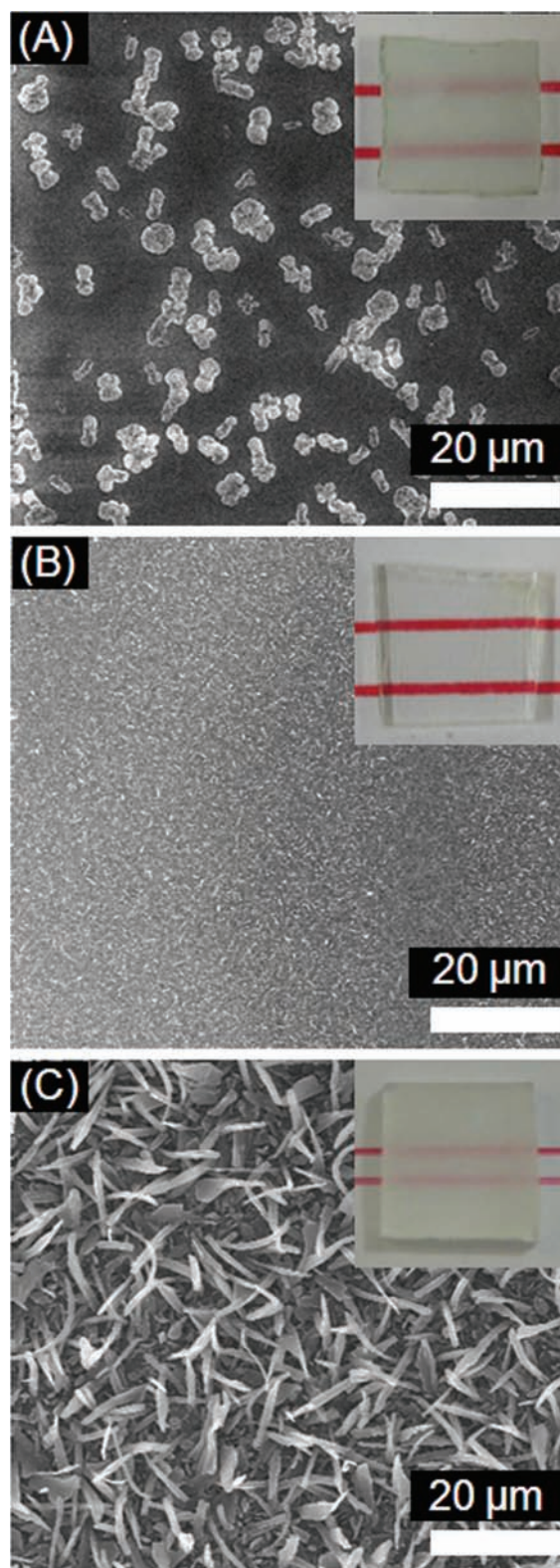
(DCDDA-Cl) with the corresponding amino or hydroxy benzoic acids or phenylboronic acids.

A monomer solution (50 mm) in 2-methoxyethanol was prepared before drop-casting on a glass substrate. In contrast to the previously reported coating methods of thin PDA film structures, such as thermal evaporation,<sup>[61]</sup> self assembly,<sup>[16,34]</sup> and spin-coating,<sup>[62]</sup> here, drop-casting was employed for several advantages. LB deposition is highly sensitive to substrate and fabrication conditions. The drawback of spin-coating is the low material efficiency due to loss of almost 95% of the materials during spinning, while only the remaining is used to obtain a thin 10,12-pentacosadiynoic acid (PCDA) layer. Spin-coating also lacks processability on topographically nonplanar surfaces, which constitutes a certain constraint on the use of the method for device-based applications. Drop-casting, being the simplest of all, produces very reliable and relatively thicker layers of several micrometers. It is also cost effective and can be applied on not only the planar substrates but also the surface of microfabricated devices with varying heights. Following the drop-casting, a two-step curing was performed at 60 °C for 30 min and 150 °C for 25 min.

Scanning electron microscopy (SEM) images of the drop-cast and cured films are shown in **Figure 3**. Isolated microcrystals can be clearly seen from the DCDDA-bis-mBzA **1** derived film (**Figure 3A**). In addition, the photograph of the film prepared from DCDDA-bis-mBzA **1** demonstrates that only an opaque film can be achieved from the monomer (**Figure 3A**, inset). The two red lines shown in the inset of the figure are drawn on a paper and the glass substrate coated with diacetylene monomer is placed on the paper to test the transparency of the film. In contrast, drop-casting and curing of the thin film derived from DCDDA-bis-mAPBA **2** result in formation of isolated microcrystals and yield a transparent film, as seen in **Figure 3B**. The observations described above demonstrate the significance of the boronic acid groups for the formation of a transparent diacetylene film. Interestingly, similar to the monomer DCDDA-bis-mBzA **1**, an opaque film with grass-like giant polymeric leaves was obtained with the ester-functionalized boronic acid DCDDA-bis-mHPBA **3** (**Figure 3C**). This indicates that the hydrogen-bondable internal amide groups, as well as the boronic acid moieties, are necessary in the diacetylene monomer for the preparation of a transparent film.

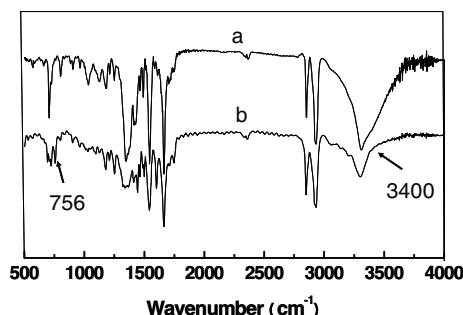
Fourier transform infrared (FTIR) analysis of the molecule DCDDA-bis-mAPBA **2** before (a) and after (b) the curing step, depicted in **Figure 4**, provides additional evidence for the development of cross-linked sites through anhydride formation. Indeed, the intensity of –OH peak of boronic acid at around 3400 cm<sup>-1</sup> was weakened and a new absorption peak at 734 cm<sup>-1</sup> was generated and can be assigned to the boronic anhydride structure.<sup>[63]</sup>

We observed even more eminent evidence showing the effect of thermal treatment on the packing density, and hence on the polymerization, of the network film prepared with monomer DCDDA-bis-mHPBA **3**. It should be noted that well-arranged diacetylene monomers, in general, shift to blue color when polymerized, whereas any disorder in the arrangement may cause a distortion of the color transition. **Figure 5** shows the films that were obtained by UV irradiation of the samples after annealing temperatures of 100 °C, 120 °C, and 150 °C. As



**Figure 3.** SEM images and photographs (inset) of drop-cast and cured films obtained with DCDDA-bis-mBzA **1** (A), DCDDA-bis-mAPBA **2** (B), and DCDDA-bis-mHPBA **3** (C). The two red lines shown in the inset of each figure are drawn on a paper and the glass substrate coated with diacetylene monomer is placed on the paper to test the transparency of the film.





**Figure 4.** FTIR spectra of the monomer DCDDA-bis-mAPBA **2** before (a) and after (b) thermal curing.

confirmed by the different responses of the samples, the best arrangement of the monomers occurred at 150 °C with the blue transition, and the other two samples were proved to be in disordered states with purple and red colors. The results presented in Figure 5 also provide some useful information about color control of the PDA film. It is interesting that red-, purple-, or blue-colored PDA films can be readily achieved by simply manipulating the annealing temperature of the monomer film. To the best of our knowledge, this is the first example of PDA color control based on the annealing temperature strategy.

Intriguingly, although the preheating of the drop-cast solution of monomer DCDDA-bis-mAPBA **2** afforded a transparent solid film as a result of solvent evaporation, the sample did not show any polymerization phenomena via UV irradiation. The

reason was considered to be that the monomers were cross-linked through anhydride side groups, yet were not closely packed enough to provide polymerization among the diacetylene backbones. Thus, a post-heating process was applied that yielded a transparent and also polymerizable monomer network structure. As shown in the visible spectra of the film in Figure 6A, the absorption gradually increases and reaches a maximum after ca. 10 min of irradiation with an intense blue color at a characteristic absorption peak of around 640 nm.

The stress-induced color change of the network structure was investigated in the next phase of our studies. The thermochromic behavior of a polymerized blue-colored film of monomer DCDDA-bis-mAPBA **2** is shown in Figure 6B. The film undergoes an irreversible blue-to-red color transition as a response to thermal stress, which generates a shift of the absorption peak from 640 nm to 540 nm. As illustrated in Figure 6B and in the inset picture, there is a temperature margin of about 70 °C from 50 °C to 120 °C over which the red transition occurs.

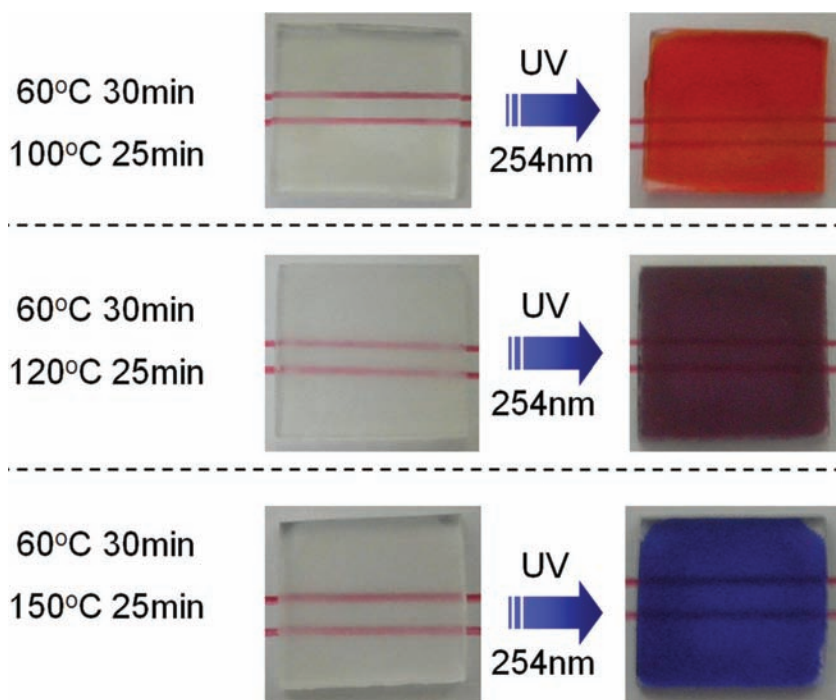
## 2.2. Fabrication of Patterned Images

We also made an effort to fabricate colored micropatterns on the film by UV irradiation via a photomask.<sup>[62,64]</sup> Figure 7 shows the obtained optical and corresponding fluorescence images of the film with sequential irradiation and heating steps. Depicted in Figure 7A are the images taken after the first irradiation through a photomask. As a weak fluorescence was observed

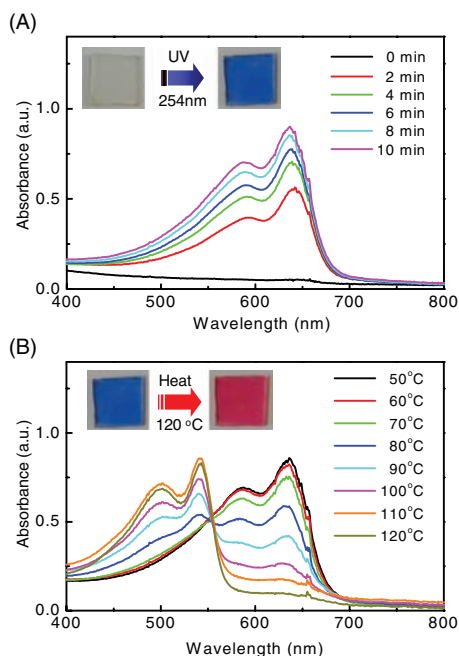
from the monomer film, the blue phase did not emit any fluorescence, which meant polymerization phenomenon quenched the original fluorescence from the transparent diacetylene film. As expected, heating the film at 130 °C caused a transition of blue images to red with an intense fluorescence signaling from the image patterns (Figure 7B). At first, it seems that the red fluorescence from the non-irradiated transparent part in Figure 7B was quenched due to heating. However, this is simply due to the fact that intense red fluorescence of the optically red patterns screens relatively weak fluorescence of the monomer region. Additionally, a second maskless UV irradiation of the overall film produced dual-colored optical patterns with clear-edged fluorescence images because polymerization of the monomer part quenched the weak background fluorescence of that region (Figure 7C). As a result, both positive and negative fluorescence images were obtainable using a single photomask.

## 2.3. Application of PDA Networks for Differentiation of Organic Solvents

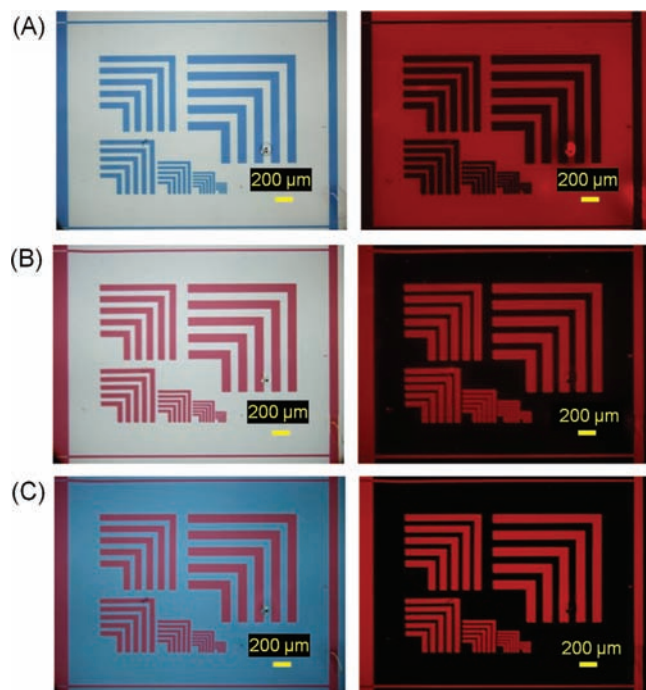
Fabrication of efficient chemosensors to detect various materials that have environmental,



**Figure 5.** Photographs of the films prepared with monomer DCDDA-bis-mHPBA **3** on glass by drop-casting and different thermal curing conditions and the corresponding color responses after 254 nm UV irradiation for 10 min. Note that perfect polymerization with the blue color shift occurs after curing at 60 °C for 30 min and 150 °C for 25 min.



**Figure 6.** Visible absorption spectra of the networked film prepared with monomer DCDDA-bis-mAPBA **2** and irradiated with UV (254 nm) for varying expose times (A) and the visible absorption change as the blue phase film was heated from 50 °C to 120 °C for 10 s at each step (B). The insets show photographs of the films after UV irradiation for 10 min (inset of (A)) and heat treatment of 120 °C for 10 min (inset of (B)).

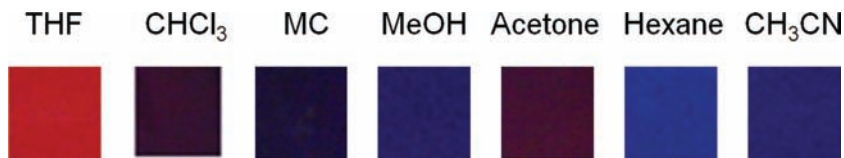


**Figure 7.** The optical (left) and fluorescence (right) images of the micropatterns fabricated on the network film of monomer DCDDA-bis-mAPBA **2**. A) After UV (254 nm) irradiation through a photomask for 10 min. B) After heating the film in (A) at 130 °C for 10 s. C) After maskless UV (254 nm) irradiation of the film in (B) for 10 min. Exposure times of the fluorescence images in (A–C) were 1/5 s, 1/25 s, and 1/12 s, respectively.

biological, or diagnostic significance has a great impact among many scientists. We have recently reported a new strategy for colorimetric detection of volatile organic compounds (VOCs) based on PDA-embedded electrospun microfibers.<sup>[30,65]</sup> Accordingly, differentiation of the organic solvents had been achieved by arising color patterns that were distinguishable with respect to several VOCs, such as chloroform, hexane, ethyl acetate (EA), and tetrahydrofuran (THF). Here we anticipated that if the PDA network film exhibits a selective solvatochromic feature in such organic solvents then it would lead to the development of a simple strategy for a color contrast-based chemosensor. **Figure 8** shows the colorimetric responses of the PDA film samples prepared with monomer DCDDA-bis-mAPBA **2** that were exposed to common organic solvents. Preserving the morphological stability, the samples displayed vivid color changes, which were detectable by eye, in varying and combinational tones of blue and red. THF was apparently superior to other solvents in disturbing the blue-phase PDA network.

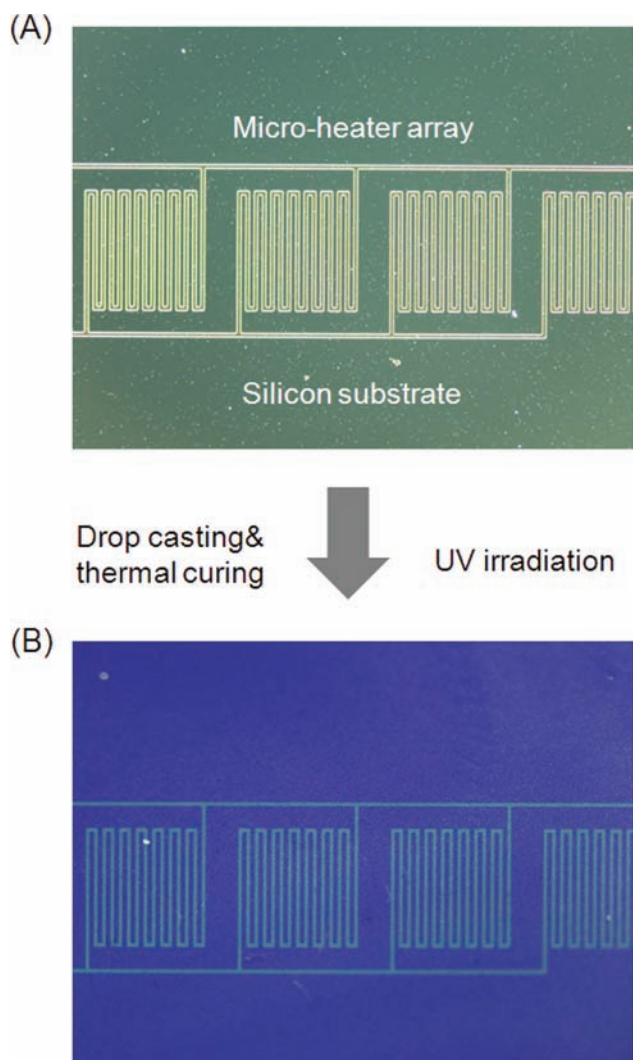
#### 2.4. Temperature-Monitoring System Using the Thermofluorescence Feature of PDA Networks

To date, the thermochromic and thermofluorescence features of PDAs have been extensively investigated and proposed as temperature sensors in the forms of solutions, mono- and multi-layer films, and even vesicles that are embedded in polymer matrices.<sup>[50–52,66]</sup> However, the feasibility of the reported features still remains at the primitive state due to the technical challenges coming from the film-forming methods, which are usually substrate selective, and the lack of detectable color contrast. Quantification of the color contrast is another constraint on the utilization of PDAs as efficient temperature-sensitive materials. In addition to optical color transitions, a thermally induced non-fluorescence to fluorescence transition of PDAs can be harnessed as a very useful tool for temperature-monitoring systems. In parallel efforts aimed at the functionalization of PDAs as temperature indicators, we successfully implemented the thermofluorescence property of PDA networks to obtain the temperature profile of a solid surface. A simple heat source was designed and fabricated as an array of serpentine-type Au microheaters on a silicon substrate as shown in **Figure 9**. A film of monomer DCDDA-bis-mAPBA **2** was then prepared on the device and polymerized by UV irradiation to obtain a blue-phase PDA network structure (**Figure 9**). The microheaters were supplied with varying current levels to generate heat deviations on the substrate surface, and the corresponding fluorescence images were acquired and are shown in **Figure 10** (left column). The figures indicate that due to continuous heat generation from the microheaters, the network film exhibits an increasing trend of fluorescence intensity on the overall surface. This result is in good agreement with the well-known thermofluorescence feature of PDAs. However, more precise temperature-dependent fluorescence profiles of the surface can be extracted by quantification of the images with a software program. As illustrated in **Figure 10** (right column), the fluorescence intensity diagrams reveal the mechanism of heat conduction from microheaters to the silicon substrate. While the fluorescence



**Figure 8.** Photographs of the PDA network films after exposure to various organic solvents for 30 s.

intensity peaks in the regions where the heat sources are populated in Figure 10A, increasing the current level on the microheaters causes heat transfer from the center to corners through silicon and creates thermal contours, as depicted in Figure 10B. Figure 10C shows that a further increase in the current level produces new contours, but with smaller fluorescence intensity differences due to good thermal conductivity of silicon ( $149 \text{ W m}^{-1} \text{ K}^{-1}$ ).

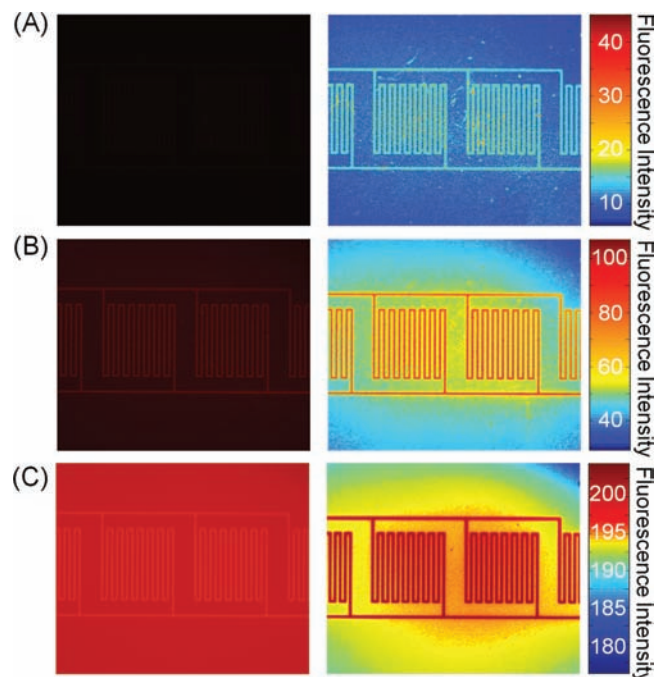


**Figure 9.** Optical microscopy images of the microheater array fabricated on a Si substrate before (A) and after (B) coating the substrate with a PDA network film prepared with monomer DCDDA-bis-mAPBA 2.

### 3. Conclusions

Using a new concept for tailoring diacetylene monomers with boronic acid pendant side groups, we successfully prepared drop-cast and photopolymerizable diacetylene network films on solid substrates. The compactness of the monomers forming the network was particularly arranged by thermal annealing, which was shown to be a crucial

step for proper polymerization. Using the difference of the film structure before and after polymerization, a photolithographic process was adopted to generate colored images. The intriguing chromatic and fluorescence features of the polymer network afforded the construction of efficient chemo- and thermal sensors. Selective color transition in response to various organic solvents was employed to develop a color-contrast-based differentiation of the solvents. In addition, in contrast to previous reports on the use of PDA films as thermochromic indicators, the irreversible non-fluorescence to fluorescence switching feature of the network film provided a simple method by which to monitor heat deviations of a thermal system. Accordingly, the fluorescence intensity variations of the PDA film were correlated with the temperature gradients of the underlying surface. In this way the thermal fluctuations on a device surface were promptly monitored and quantified using the thermal sensitivity of the PDA network. This method should find great utility in the thermal systems, especially where the detection of regional



**Figure 10.** Fluorescence images (left) and the corresponding fluorescence intensity diagrams (right) of the microheater array coated with PDA network film. The fluorescence intensity contours appeared depending on the surface temperature variations after supplying the microheater array with the current levels of A) 0.150 A, B) 0.175 A, and C) 0.200 A for 10 s at each step.



temperature elevations is critical such as power semiconductor chips and thermal microelectromechanical (MEMS) devices.

## 4. Experimental Section

**Materials:** 10,12-Docosadiynoic acid (DCDDA) was purchased from GFS Chemicals. DCDDA-bis-mBzA **1** was prepared according to the published protocol.<sup>[67]</sup> Oxalyl chloride, 3-aminophenylboronic acid, 3-hydroxyphenyl boronic acid, and 4-hydroxyphenyl boronic acid were purchased from Aldrich.

**Synthesis of Docosa-10,12-Diynediyl Dichloride (DCDDA-Cl):** Oxalyl chloride (612.8 mg, 4.8 mm) was added dropwise to the methylene chloride solution containing DCDDA (500 mg, 1.4 mm). After 30 min of stirring, one drop of dimethylformamide (DMF) was added to the solution and the resulting mixture was stirred for another 4 h. Removal of the solvent in vacuo afforded the desired DCDDA-Cl in 100% yield and the product was used for the next reaction without further purification.

**Synthesis of DCDDA-bis-mAPBA **2**:** 3-Aminophenylboronic acid hemisulfate salt (717.9 mg, 4.1 mm) and triethylamine (1.4 g, 13.8 mm) were dissolved in methylene chloride and DCDDA-Cl (551 mg, 1.4 mm) was dissolved in a small amount of THF. The THF solution containing DCDDA-Cl was added dropwise into the methylene chloride solution. The resultant solution was stirred at room temperature overnight and concentrated in vacuo. The crude residue was dissolved in a small amount of methanol and added dropwise to water. The precipitates formed were collected and subjected to column chromatography on a silica gel with 1:1 ethyl acetate:hexane as an eluent to give the desired product (yield = 60%). Melting point (m.p.): 178–179 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 1.20–1.62 (m, 24H), 2.18 (t, 4H), 2.21–2.38 (m, 4H), 7.22 (t, 2H), 7.45 (d, 2H), 7.72 (d, 2H), 7.82 (s, 2H), 8.00 (s, 4H), 9.79 (s, 2H); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 19.00, 25.88, 28.43, 28.93, 29.06, 29.39, 34.37, 37.04, 66.06, 78.71, 121.85, 125.88, 128.26, 129.47, 139.19, 165.60, 171.84, 175.19; IR (KBr) 3487, 2947, 2846, 2158, 1682, 1527, 1489, 1018, 962, 903, 800 cm<sup>-1</sup>.

**Synthesis of DCDDA-bis-mHPBA **3**:** 3-Hydroxyphenylboronic acid (571 mg, 4.1 mm) and triethylamine (1.4 g, 13.8 mm) were dissolved in methylene chloride. A THF solution containing DCDDA-Cl (551 mg, 1.4 mm) was added dropwise into the methylene chloride solution. After stirring for overnight, the reaction mixture was concentrated in vacuo. The crude residue was dissolved in a small amount of methanol and the methanolic solution was added dropwise to water. Addition of small amount of aqueous dilute HCl solution resulted in the formation of solid precipitates. The precipitates were collected and dried to yield the desired product. (yield = 77%). m.p.: 82–83 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 1.20–1.66 (m, 24H), 2.28 (t, 4H), 2.56 (t, 4H), 7.12 (d, 2H), 7.37 (t, 2H), 7.45 (s, 2H), 7.66 (d, 2H), 8.17 (s, 4H); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 19.24, 25.35, 28.67, 29.16, 29.27, 29.53, 34.44, 66.31, 78.92, 124.44, 127.93, 129.58, 132.39, 150.98, 172.90, 172.92; IR (KBr) 3437, 2939, 2850, 1763, 1608, 1576, 1491, 1470, 1105, 1026, 1001, 941, 899, 806 cm<sup>-1</sup>.

**Preparation of PDA Network Film on a Glass Substrate:** DA monomer was dissolved in 2-methoxyethanol (50 mm) and applied to the glass substrates (0.8 × 0.8 cm) with an amount of 20  $\mu$ L. The glass substrate was then heated on a temperature-controllable hotplate at 60 °C for 30 min. A second annealing was performed at 150 °C for 25 min to create diacetylene monomers that were cross-linked and closely packed for polymerization.

**Generation of Patterned Color and Fluorescence Images:** A drop-cast and thermally cured thin film (ca. 10  $\mu$ m) prepared following the procedures described above was irradiated with 254 nm UV light (1 mW cm<sup>-2</sup>) for 10 min through a photomask. The film was then heated to 130 °C for 10 s to induce the blue-to-red phase shift of the PDA. The heat-treated film was further irradiated with 254 nm UV light (1 mW cm<sup>-2</sup>) for 10 min without a photomask. An optical and fluorescent microscope (Olympus BX51W/DP70) was used to observe the patterned images.

**Fabrication of a Microheater Array on Si:** After a cleaning process Si, Ti (10 nm), and Au (200 nm) layers were deposited on the substrate using thermal evaporation. The microheaters were then patterned by

conventional lithography and wet-etching processes. The resultant resistance of the microheater array was measured to be 45.6  $\Omega$ .

**Preparation and Thermal Monitoring of the Microheater System:** A PDA network film was coated on a microheater array using the same method of film forming as on glass. The microheaters were supplied with a potential through a power supply while being monitored with a fluorescence microscope, (Olympus BX51W/DP70). The array was supplied with three current levels of 0.150 A, 0.175 A, and 0.200 A, each for 10 s. The fluorescence measurements after each step were performed after cooling the substrate to room temperature.

**Scanning Electron Microscopy (SEM):** SEM images of the PDA films were obtained by using a JEOL (JSM-6330F) microscope. Samples were coated with Pt for 30 s before analysis.

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