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FULL PAPER

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# Patterned Color and Fluorescent Images with Polydiacetylene Supramolecules Embedded in Poly(vinyl alcohol) Films**

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Poly(vinyl alcohol) (PVA) films embedded with functional polydiacetylene (PDA) are efficiently prepared for color and fluorescence imaging. Intensely blue films are obtained by mixing and drying solutions containing PDA vesicles and PVA. A blue-to-red color transition is observed upon heating the polymer films. In addition, selective UV irradiation (through a photomask) of PVA films containing diacetylene monomer results in the generation of micropatterned color (without heating) and both color and fluorescent images (after heating the films at 120 °C for 10 s). Patterned two-color (blue and red) images in the polymer film are readily obtained by a sequential process of photomasked irradiation, heating, and unmasked irradiation.

## 1. Introduction

The generation of patterned functional images in polymer films is of great technological importance in fundamental and applied research areas. Since the first report of the "precursor approach" by Kim et al. for fabricating patterned fluorescent images in a polymer film,[1] the strategy, which allows development of micrometer-sized patterned functional images without employing wet developing processes, has been actively investigated by many researchers.[2] The key concept of the precursor approach is to induce a fluorescence change (either intensity or wavelength) of the precursor molecules in the UV-exposed areas. The fluorescence of the precursor molecules has been manipulated by the following photoinduced processes: i) acid-catalyzed removal of protecting groups;[1,2a–c,2j,2k] ii) keto–enol tautomerization;[2d,2f] iii) oxidation of main-chain[2h] or side-chain fluorophores;[2i] and iv) radical generation.[2e]

Polydiacetylenes (PDAs) are π-conjugated polymers that have alternating double- and triple-bond groups in the main polymer chain.[3] PDAs are unique in terms of their method of preparation, their molecular structure, and the output signal associated with their color transitions. Unlike other conjugated polymers, functionalized PDAs are prepared by irradiation of self-assembled diacetylene monomers with UV light (for thin films/vesicle solutions) or γ-rays (for solid powders). If PDAs are prepared under optimal conditions, they have an intense blue color with a maximum absorption wavelength at ca. 640 nm. In addition, the blue-colored PDAs undergo a color shift to a red phase (ca. 550 nm maximum absorption wavelength) upon environmental stimulation. Owing to their intriguing stress-induced chromic transition (blue-to-red) and nonlinear optical properties, PDAs have been extensively investigated as potential chemosensors and photonic materials.[3–10]

Another important feature of PDAs that has not gained much attention compared to the colorimetric transition is their *fluorescence*. PDAs are non-fluorescent in the "blue phase" and fluorescent in "red phase".[11] The stress-induced fluorescence change of PDA was reported only recently by our group[12] and others.[13] Since blue-colored, non-fluorescent PDAs can be readily prepared by UV irradiation, we hypothesized that selective irradiation of a diacetylene assembly using a photomask would generate a patterned, blue-colored image in the exposed areas. Furthermore, heating the blue-colored PDA film would induce a blue-to-red color transition with simultaneous appearance of a fluorescence signal. Accordingly, the generation of both color and fluorescence images would be possible using this method. As color and fluorescence images could be obtained only by a sequential irradiation and heating process, no wet development process would be required. As part of an ongoing program of research in the area of patterned functional imaging using precursor molecules[1,2a–c] and PDAs,[12,14] we report here a new methodology for constructing patterned color and fluorescent images using PDA supramolecular systems in polymer films. For this purpose, we used poly(vinyl alcohol) (PVA) as a host molecule. The use of PVA as the matrix polymer has several advantages that derive from i) its hydrophilic nature, which allows the incorporation of a variety of aqueous-based guest molecules; ii) its ready formulation as a hydrogel film; iii) its water solubility, leading to environmental friendliness; and iv) its inertness towards guest molecules.

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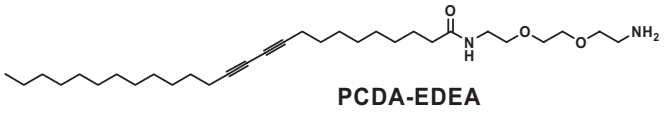
## 2. Results and Discussion

### 2.1. PDA Vesicles

The amine-terminated diacetylene monomer 10,12-pentacosadiynoic acid–2,2′-(ethylenedioxy)bis(ethylamine) (PCDA-EDEA, shown below) was prepared following the method described in the literature.[14c] The diacetylene monomer was subjected to the standard procedures for the formation of PDA vesicles in either deionized water or in *N*-(2-hydroxyethyl)-piperazine-*N*′-2-ethanesulfonic acid (HEPES) buffer (5 mM, pH 8.0).




PCDA-EDEA

A typical deep-blue-colored solution was obtained when a sonicated suspension containing monomeric diacetylene was irradiated with 254 nm UV light. Figure 1 shows the visible spectra of a diacetylene-containing deionized solution. As can be seen from the spectra, the absorption at 640 nm gradually increases and reaches a maximum after ca. 8 min irradiation.

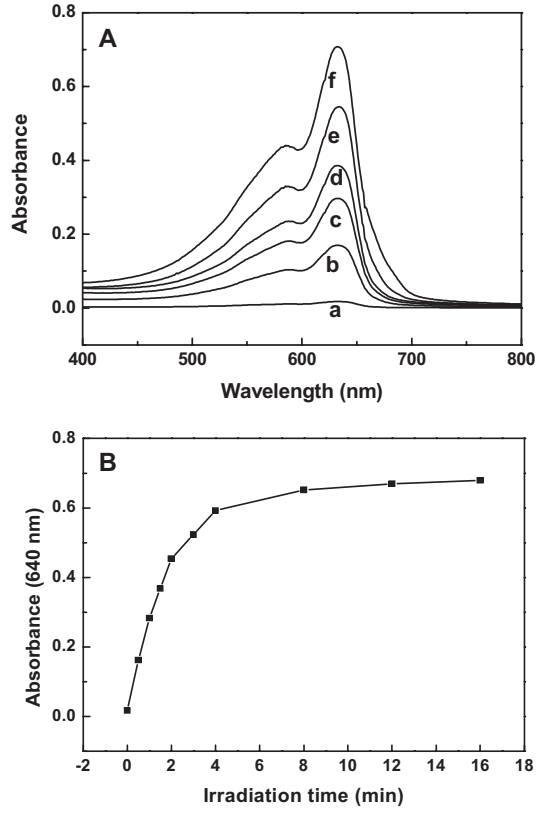



**Figure 1.** A) Visible absorption spectra of a molecularly assembled diacetylene suspension irradiated with UV light for a) 0, b) 0.5, c) 1, d) 2, e) 4, and f) 12 min. B) Plot of the absorption at 640 nm as a function of irradiation time.

Scanning electron microscopy (SEM) images of the PDA vesicles, prepared with PCDA-EDEA, are shown in Figure 2. The polymerized diacetylene vesicles are nearly spherical with sub-100 nm diameters.

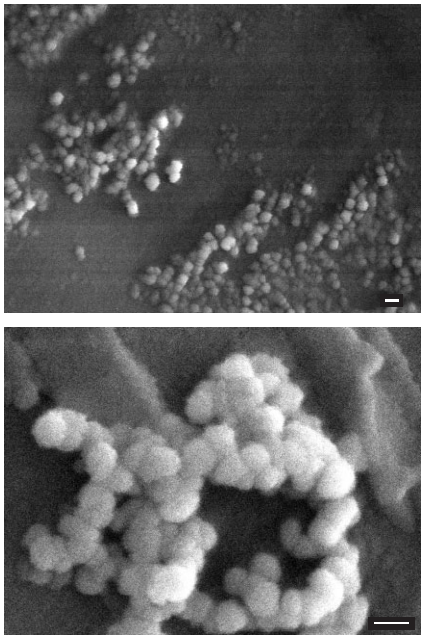


**Figure 2.** SEM images of PDA vesicles prepared from PCDA-EDEA. Scale bars = 100 nm.

In order to investigate the blue-to-red color transition upon thermal treatment, a PDA solution prepared with PCDA-EDEA was heated to 60 °C while monitoring color changes by UV-vis spectroscopy (Fig. 3). Heating the solution from room temperature to 60 °C produced a color change from blue to red. As expected, the absorption at 640 nm decreased, and the absorption at 500 and 550 nm simultaneously increased, upon heating (Fig. 3A). Plots of the absorption at 640 and 550 nm as a function of temperature indicate that the color change is complete at around 60 °C (Fig. 3B). The heat-induced red-to-blue color change was found to be an irreversible process.

### 2.2. PDA-Embedded PVA Films

Embedment of PDA supramolecules in PVA films was carried out by a mixing–drying process. A typical method and photographs of a resultant PDA solution and a PDA-embedded PVA film are shown in Figure 4. A diacetylene vesicle solution prepared with PCDA-EDEA was irradiated with 254 nm UV light to induce polymerization. The resultant blue-colored solution (ca. 1 mM, 5 mL) containing PDA vesicles was mixed with an aqueous 10 % PVA solution (5 mL; 1:1, vol %), then cast into a Petri dish (diameter 6.5 cm) and dried at 30 °C for two days (or at room temperature for five days). The blue-colored film was then peeled from the dish.

In Figure 5A is shown an example of a typical blue-colored, transparent PDA-embedded PVA film (thickness: ca. 180 μm)

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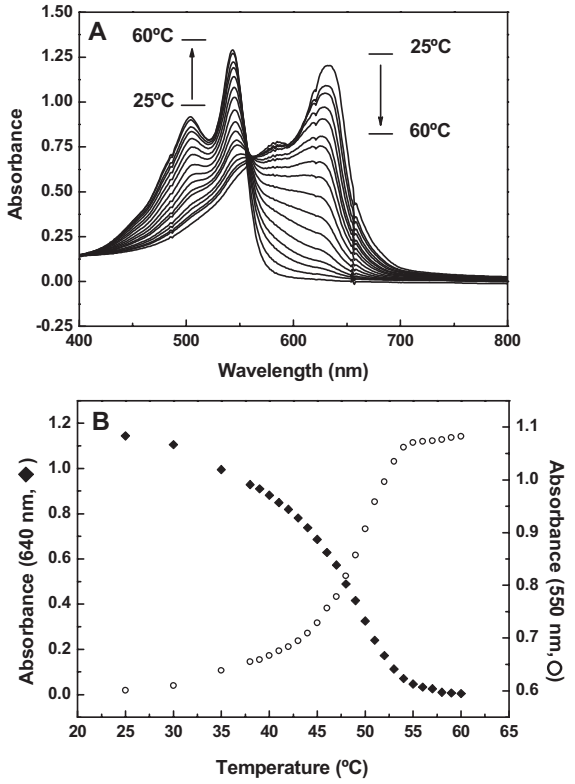


**Figure 3.** A) Visible spectral changes and B) absorbance at 550 and 640 nm as a function of temperature of a PDA solution prepared with PCDA-EDEA in deionized water upon heating.

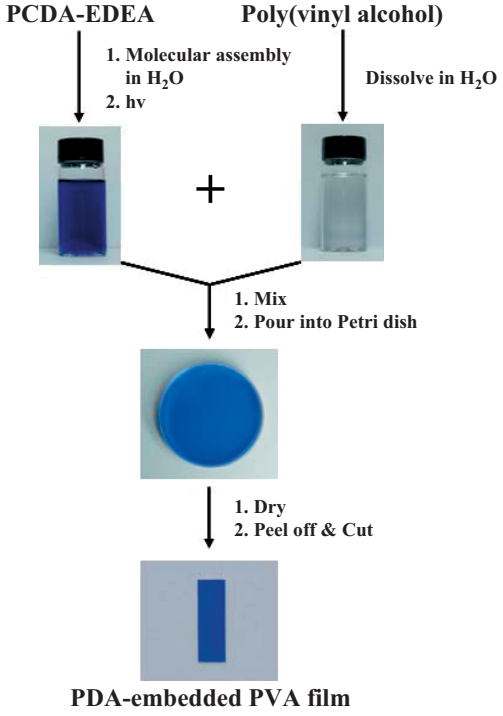


**Figure 4.** Fabrication of PDA-embedded PVA films.

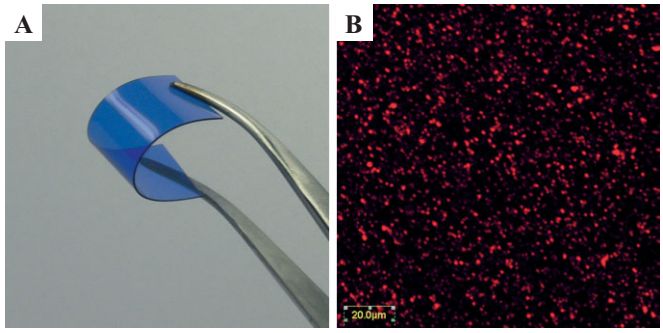


**Figure 5.** A) A photograph of a flexible PVA film containing PDA vesicles; B) a confocal fluorescence microscopy image of the film after heating.

formed in this manner. Depending on the amount of mixture solutions and size of the dish used, the thickness of the PVA film can be readily manipulated. Figure 5B shows a confocal fluorescence microscopy image of PVA films with embedded PDA vesicles. The sample for this fluorescence image was obtained by spin-casting a PDA-containing PVA solution on a glass substrate, followed by heating at 100 °C for 10 s. The heating process results in the generation of a red fluorescent material, since PDA in its blue-phase is non-fluorescent.[11] The fluorescence image clearly demonstrates that the PDA vesicles are well-dispersed in the PVA film.

The thermal stability of the PVA films was monitored by thermogravimetric analysis (TGA; Fig. 6). TGA thermograms before and after UV irradiation were obtained with PVA films containing diacetylene monomer. As can be seen in Figure 6, no significant difference was observed between the two states. The initial drop in weight at around 100 °C is presumably due to the loss of water molecules. The water content was observed to be ca. 5 % for both samples.

The stress-induced color change of the PVA films embedded with PDA vesicles was investigated in the next phase of our studies. For this purpose, a PDA-embedded PVA film was heated, in order to study the thermochromic behavior of a PDA-embedded PVA film. As demonstrated by the results shown in Figure 7A, the film undergoes a blue-to-red color

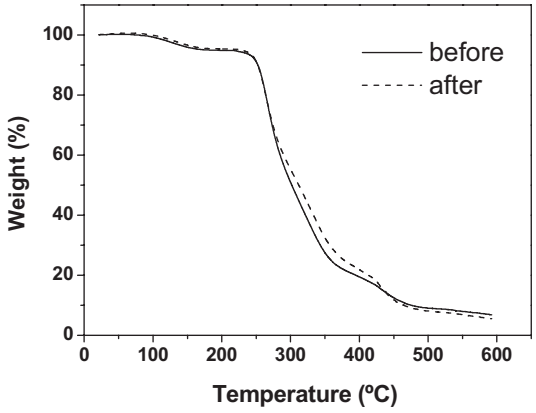


**Figure 6.** TGA thermograms of a PVA film containing diacetylene vesicles before and after 20 s of 254 nm UV irradiation.

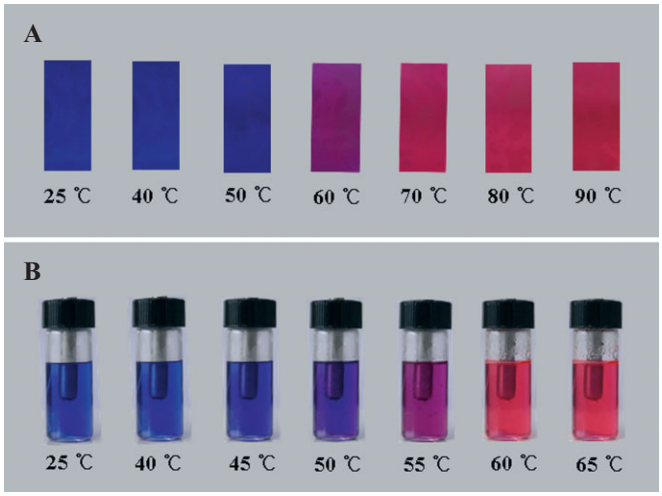


**Figure 7.** Photographs of A) the PDA-embedded PVA film and B) the PDA vesicle solution during heating process.

transition in response to thermal stress. The blue-colored PVA film at 25 °C becomes purple at 60 °C, and eventually changes to red above 70 °C. As compared to a solution of PDA vesicles (Fig. 7B), the film requires a higher temperature (ca. 10 °C) to promote a complete color transition to red. This is an expected result considering the retarded mobility of PDA molecules in the film. With this exception, the color-changing properties of a PDA-embedded PVA film and a PDA solution are similar. Also, the mixing and drying process used to construct the PDA-embedded PVA film did not impose sufficient thermal stress to promote a premature color transition.

### 2.3. Patterned Color and Fluorescent Images

We next focused on the generation of patterned color and fluorescent images with PDA supramolecules embedded in PVA film. For this purpose, a photolithographic method was employed (Fig. 8). First, PVA films embedded with *unpolymerized* self-assembled diacetylene monomers were prepared em-

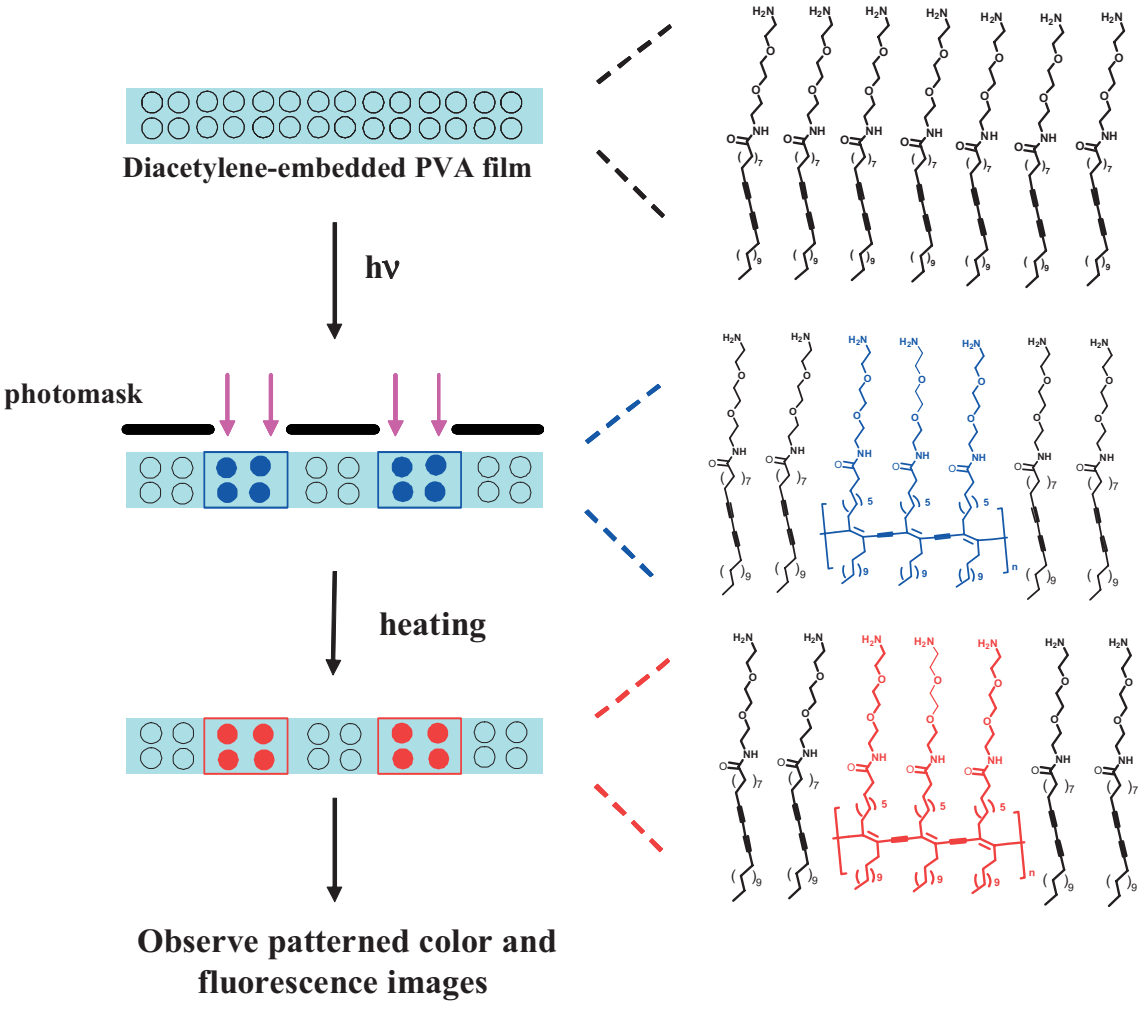


**Figure 8.** Procedures for generating patterned color and fluorescent images in PVA film.

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ploying a procedure similar to that described above. The critical issue that must be addressed in this step is that the integrity of the self-assembled diacetylene monomers should not be affected during the PVA film-making process. If PVA disrupted the structurally well-ordered nature of the diacetylene assembly, this would directly affect the next polymerization step. Then the film was irradiated with 254 nm UV light for one minute through a photomask. This process induced photopolymerization of the immobilized diacetylene vesicles in the exposed areas. The film was then heated at 120 °C for 10 s to induce the blue-to-red color change of the PDA molecules.

Figure 9 shows optical (left) and fluorescence (right) microscopy images of films formed by photomasked irradiation of diacetylene-embedded PVA film. As can be seen, this process results in the clean formation of patterned blue images (Fig. 9A, left). Only the UV-exposed areas are blue, confirming that successful photoinduced polymerization of the diacetylene monomers has taken place. Thus, the diacetylene monomer assembly is maintained during the preparation of the diacetylene-embedded PVA film. This is an important observation, since it indicates that PVA as a matrix polymer does not disturb the ordered structure of assembled diacetylene molecules. Since PDA in the blue phase is non-fluorescent, no patterned fluorescence images were formed by photomasked-irradiation of diacetylene-embedded PVA film (Fig. 9A, right). As expected, heating the film at 120 °C caused the transition to red patterned images (Fig. 9B, left). The heat-treated film contains a patterned fluorescent image when viewed under a fluorescence microscope (Fig. 9B, right). This is in accord with the earlier observation that PDAs are fluorescent in the red phase.[11,12] The appearance of fluorescence upon thermal stress implies that both color and fluorescence images can be readily formed with PDAs. Interestingly, nonmasked irradiation (1 mW cm$^{-2}$, 1 min) of a film generated by photomasked irradiation followed by heat treatment afforded a new film comprised of a rigorously patterned set of red and blue images (Fig. 9C, left). As anticipated, the fluorescent pattern of the resulting film is similar to that observed before irradiation (compare Fig. 9C, right and B, right). Figure 9D shows patterned color (left) and fluorescence (right) images obtained with the independently prepared film B. We were able to obtain 5 μm width line-and-space color and fluorescent images without difficulty using this methodology.

In the final phase of this study, we investigated an issue related to the effectiveness of this technique for generating patterned images. In other words, were the patterned images generated only on the surface (or near the surface) of the film, or were they created homogeneously to the bottom of the film? To address this issue, a 400 μm thick PVA film containing molecularly assembled diacetylene monomers was prepared and the film was irradiated with 254 nm UV light. The microscopic color and fluorescence images of a cross section of the film were monitored by placing the film between two glass slides. As shown in Figure 10A, UV irradiation of the film for 2 s af-

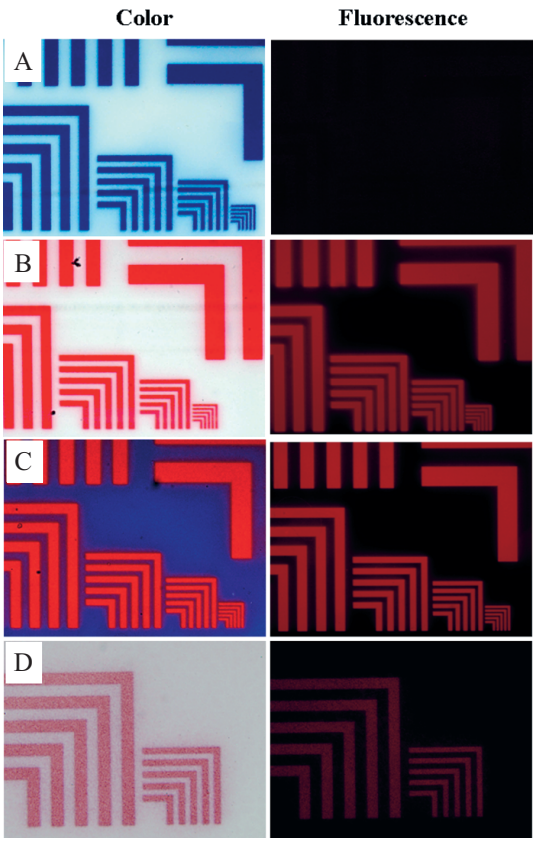


**Figure 9.** Patterned color (left) and fluorescence (right) images of the diacetylene-embedded PVA film A) after selective 254 nm UV irradiation (1 mW cm$^{-2}$) for 1 min through a photomask; B) upon heating film A at 100 °C for 10 s; C) irradiation of film B with 254 nm UV light for 1 min without using a photomask; and D) magnified images of the independently prepared film B. The narrowest linewidth shown in these images is 5 μm.

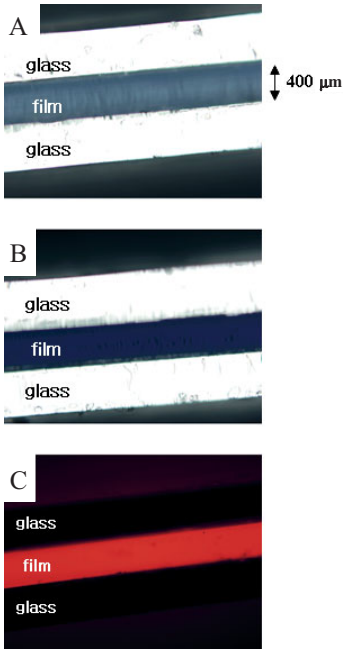


**Figure 10.** Optical microscopy images of cross sections of a 400 μm thick PVA film containing self-assembled diacetylene vesicles after irradiation with UV light for A) 2 and B) 20 s. C) Fluorescence microscopy image of film B after heating at 120 °C for 5 min.

fords a pale-blue color image, and it clearly demonstrates the polymerization occurs from the surface to the bottom of the film. Further irradiation only intensifies the blue color of the film (Fig. 10B). The fluorescence image of the film was obtained by heat treatment of film B (Fig. 10C). The homogeneously distributed fluorescence signal also supports the effectiveness of this methodology.

## 3. Conclusions

The studies discussed above demonstrate that PDA-embedded polymer films can be readily obtained by drying PDA-containing PVA solutions. The blue-colored thin polymer films formed in this manner undergo the typical PDA blue-to-red transition upon thermal stress. Thin PVA films containing monomeric diacetylene assemblies can also be prepared without loss of the molecular order of the monomers, as shown by the observation that masked UV irradiation of these films generates patterned color/fluorescent images.

## 4. Experimental

PVA (weight-average molecular weight, $M_w = 89\,000$–$98\,000$ Da ($1\ \text{Da} = 1.66 \times 10^{-27}$ kg), 99 + % hydrolyzed) was purchased from Aldrich.

### 4.1. Preparation of PDA-Vesicle Solution

The amine-terminated diacetylene monomer PCDA-EDEA, prepared as described in the literature [14c], was dissolved in chloroform in a test tube. The solvent was evaporated by a stream of $N_2$ gas, and deionized water was added to the test tube to give the desired concentration of lipid (1 mM). The resultant suspension was probe-sonicated (Fisher Sonic dismembrator model 550, 25 % power) for 15 min at ca. 80 °C. Following sonication, the solution was filtered to remove dispersed lipid aggregates using an 0.8 μm filter and cooled to 4 °C overnight. Polymerized diacetylene liposomes were prepared by 254 nm UV irradiation (1 mW cm$^{-2}$) for 5–10 min.

### 4.2. Fabrication of PDA-Embedded PVA Film

A vesicle solution (ca. 1 mM, 5 mL) containing PDA was mixed with an aqueous PVA solution (10 wt %, 5 mL) with stirring. The resultant mixture solution was cast into a Petri dish (diameter 6.5 cm) and dried at 30 °C for two days (or at room temperature for five days). During the drying process, the solutions were protected from light. The dried films were peeled from the dish and the thickness was measured using a manual thickness gauge.

### 4.3. Generation of Patterned Images

A PVA film containing diacetylene vesicles derived from molecularly assembled PCDA-EDEA monomer was prepared following the procedures described above. The diacetylene-embedded film was irradiated with 254 nm UV light (1 mW cm$^{-2}$) for 1 min through a photomask. The film was then heated to 100 °C for 10 s to induce the blue-to-red color shift of the PDA. The heat-treated film was further irradiated with 254 nm UV light (1 mW cm$^{-2}$) for 1 min without a photomask. An optical and fluorescent microscope (Olympus BX51 W/DP70) was used to observe patterned images.

### 4.4. Characterization

SEM images of PDA vesicles were recorded on a JSM-6330F FE-SEM (JEOL, Japan). A PDA vesicle solution dispersed in deionized water was dropped onto an aluminum foil substrate, then dried at 30 °C for two days. The sample was coated with platinum nanoparticles for 10 min and examined in a field-emission SEM at an accelerating voltage of 15 kV. TGA for the PVA films embedded with PDA vesicles was carried out on a TA instrument SDT 2960 simultaneous DSC-TGA system under air at heating rate of 10 °C min$^{-1}$.

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