New generation polydiacetylenes: Thermo-optical properties as active materials of thermally actuated display devices

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Abstract
The thermo-optical characteristics of new generation fully reversible diacetylene vesicles, DCDDA-mono-mBzA and DCDDA-bis-mCPE, and their solid film compositions are covered as thermochromic display materials. Conspicuous color intensity of their solid films and blue-to-red color shift with non-fluorescent to fluorescent switching at 100°C make them promising materials for dual color thermally actuated display devices of the near future.

1. Introduction
Thermochromic displays are one of the most emerging candidates for chromatic devices. Different from the other display types, they should be considered carefully in terms of principle of actuation and structural materials. In our previous work, the preliminary results of thermochromic display on glass substrate [1] and flexible design on PES substrate [2] had been revealed. Those reports had focused on the device design, response time of the micro-pixels, and cross-talk effect between the adjacent pixels and demonstrated the feasibility of microheater-based actuation system. Heat transfer plays the main role both to increase the temperature of the micro-pixels up to thermal transition critical value and to keep this value constant at the activated pixels. Recently, a thermochromic display fabricated from dual-color thermochromic powder and embedded wiring patterns has also been demonstrated [3].

In parallel with the device design and optimization of the thermo-optical properties of the overall display device, the active material is of great importance in terms of its reversibility and temperature dependent color variations. The diversity of several diacetylene vesicles have recently been reported for bio-/chemo-sensor applications [4]. The current work investigates thermo-optical features of new generation diacetylenes, DCDDA-mono-mBzA and DCDDA-bis-mCPE, for thermal display applications. Color contrast, reversibility, and active pixel temperature of these new candidates are compared with those of the previously employed PCDA-EDEA vesicles.

2. Materials and Experimental
DCDDA-mono-mBzA and DCDDA-bis-mCPE are diacetylenic lipid monomers. The polymerization of the vesicle solutions could be achieved by UV or γ irradiation, which results in polydiacetylene (PDA). Two vesicle solutions were irradiated with 254nm UV-light (1mWcm⁻²) to have blue color polymers. The temperature dependent color variations and colorimetric reversibility of these materials after polymerization were characterized simply by heat treatment on hot plate, then heating-cooling cycle test at 100°C and finally observation of the color and quality of the solution or solid film. The solid films were prepared by mixing and curing method as described in the literature [5]. The vesicle solutions were separately mixed with 10 wt % polyvinyl alcohol (PVA) in 1:1 ratio and dispensed in a Petri dish of 6.5 cm diameter. After a curing time of 4-5 days at room temperature, a solid film was formed and the same conditions of UV irradiation and heat treatment were applied as was mentioned for solution phases.

The temperature dependent fluorescence intensity profiles of the composite films were obtained by increasing the temperature of the sample by 0.5 °C steps every 2 seconds and measuring the fluorescence peak intensity value at the end of each step (BIO-RAD C1000 Thermal Cycler). The measured
intensities were then automatically normalized to 100. The excitation peak was selected to be 535 nm and the emission maxima were detected at 556 nm.

3. Results and discussion

One of the diacetylene vesicles, PCDA-EDEA, that was employed as the active material of a glass and flexible display device was demonstrated before. The device included a substrate, multilayer serpentine type microheater array that was fabricated on the substrate, a thermal isolation layer (for glass display only) and a UV-sensitive polydiacetylene (PDA)-polyvinyl alcohol (PVA) composite film. Figure 1 depicts the color variations of polydiacetylene composite film for low and high temperature range of 55°C-75°C and 160°C-180°C, respectively.

![Image](321x472 to 545x604)

Fig. 1. (Adapted from [1]) a) Schematics and optical microscope image of a microheater, and CCD camera captured image of 4X3 pixel array. b) CCD camera captured images of activated pixels at high temperature. c) The temperature dependent color change of polydiacetylene composite film on blue and red background.

Figure 2 shows the two polymers in blue phase after polymerization with UV-light, and the final state of the color after heating-cooling cycles of 15 times. As shown in the figure, the polymer of DCDDA-mono-mBzA exhibited superior color contrast over DCDDA-bis-mCPE derived polymer. Comparing to PCDA-EDEA derived PDA, the degradation of reversibility test confirmed the stability of the new solutions even for harsh conditions of cycling between room temperature 100°C.

![Image](55x200 to 279x506)

Fig. 2. Images for polymerization and heating-cooling cycle test of a) DCDDA-mono-mBzA b) DCDDA-bis-mCPE.

The solid films were observed to have different color contrast features as was illustrated in Fig. 3. Especially DCDDA-bis-mCPE, when mixed with polyvinyl alcohol, experiences degradation in the ability of polymerization; therefore the blue color is not apparent even with 254nm UV-light irradiation of 60 minutes. Similar to its solution phase, the PVA composite film of DCDDA-mono-mBzA derived PDA preserved its color and physical morphology even after several times of heating-cooling cycles.

![Image](317x143 to 542x264)

Fig. 3. Images for polymerization and heating-cooling cycle test of a) DCDDA-mono-mBzA b) DCDDA-bis-mCPE.
During blue to red color transition, non-fluorescence to fluorescence switching property of polydiacetylenes was reported elsewhere [4]. Fluorescence spectrophotometry gives very precious information about the degree of color change during heating the samples, i.e. the transition from blue to red. The linear increase of fluorescence intensity in Fig. 4a verifies that PCDA-EDEA-derived polydiacetylene composite film has intermediate color phases between 35°C and 75°C. However, DCDDA-mono-mBzA and DCDDA-bis-mCPE did not show any color change up to 100°C, which implies that the color transition is instantaneous, i.e. no intermediate color tone exists. According to these results, new generation fully reversible DCDDA-mono-mBzA can be applied to dual-color thermal displays with pixel driving temperature not less than 100°C.

4. Summary

In this paper, we have presented thermo-optical properties of fully reversible new type polydiacetylenes as a part of our on-going research about thermochromic displays. Especially DCDDA-mono-mBzA was proved to be very promising material due to its intense blue color at polymer state. The ON-OFF states of the pixels can be identified easily because they show a sharp blue to red transition at 100°C with no intermediate color tones. In the next phase of this research, characteristics of a flexible display device with DCDDA-mono-mBzA and PVA composite will be investigated. Our work stands for the first type of thermally actuated display which was shown to be feasible also for flexible design. We expect that bringing in new materials, especially for flexible and future display types contributes to the development of novel devices which are different than the conventional ones.

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5. References