

Research Article

The Composition-Tunable Polydiacetylenic Complex Films: Conformational Change upon Thermal Stimulation and Preferential Interaction with Specific Small Molecules

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Polydiacetylenic complex films were prepared using 10,12-pentacosadiynoic acid (PCDA) and para-xylenediamine (*p*XDA) upon acid-base interactions. The thermochromatic reversibility of the complex films was modulated by changing the mixed molar ratio (3:1, 2:1, and 1:1) of the two molecules. The corresponding conformational changes of the complex films were studied by ex situ FTIR analysis upon thermal stimulation for the first time. In addition, the binding specificities of α -, β -, and γ -cyclodextrins (CDs) with the films were studied, where the α -CDs can induce stronger red fluorescent emission of the films. These fundamental results may be useful for platforms that use these polydiacetylenic complex films as optoelectronic devices or chemical/biological sensors.

1. Introduction

Conjugated polymers are well-known sensing materials because of the changes in their electronic absorption and photon emission responding to environmental perturbations [1, 2]. Based on this property, a variety of conjugated polymers, such as polythiophene [3–5], polyaniline [6, 7], polypyrrole [8], polyacetylene [9], and polydiacetylene (PDA) [10–12], have been investigated as sensing materials. Though all of these conjugated polymers can be used as sensing materials, PDA is of significant interest due to its facile fabrication method for photopolymerization of well-ordered diacetylene (DA) monomers [13].

Another unique property of PDA materials is their color change from blue to red, where the red phase of the PDA is fluorescent while the blue phase is not [14, 15], in response

to various stimuli, including temperature [16, 17], organic solvent [18, 19], mechanical stress [20, 21], and ligand-receptor interactions [22, 23]. The phase change from blue to red is due to the release of side-chain strain. The partial distortion of conjugated p-orbital arrays shortens the effective π -conjugated length, which changes the electronic states and the optical properties [24–26]. The blue-to-red color change of PDA is generally not reversed after removing the external stimuli, though a few examples of reversible chromism in specially designed PDA materials have been reported to date [16, 27]. Recently, we synthesized PDA complex films using two organic molecules at different ratios, 10,12-pentacosadiynoic acid (PCDA) and para-xylenediamine (*p*XDA) [28]. These complex films were formed by acid-base interactions between the carboxylic acid groups of PCDA and the amino groups of *p*XDA as well as proton transfer from the carboxylic

acid to the amino group. These polydiacetylenic complex films are phase-reversible upon thermal stimulation. Their modulated reversibility is related to the intermolecular π - π stacking. However, a detailed analysis has not been carried out yet to study the phase-reversing mechanism and related conformational changes of the complex films.

Here, the influence of conformational changes on the thermochromism of the complex films has been studied during phase transition and reversing using *ex situ* FTIR spectroscopic analysis to reveal the detailed interactions among the bimolecules. In addition, as part of our continuing efforts to develop polydiacetylenic complex films, we studied cyclodextrins- (CDs-) induced color transitions and the fluorescent properties of the films.

2. Experimental

2.1. Fabrication of the Polydiacetylenic Complex Films. A detailed fabrication method for polydiacetylenic complex films has been described in previous reports [28, 29]. Firstly, PCDA and *p*XDA were dissolved in tetrahydrofuran (THF) at a concentration of 1.5×10^{-2} M, respectively. Then different molar ratios (3:1, 2:1, and 1:1) of the mixture solution were used to form thin films by spin-coating on a calcium fluoride (CaF_2) substrate. The resulting white films on CaF_2 substrates were photopolymerized at 254 nm for 2 min to form polymeric PDA complex films in blue phase. Red phase PDA complex films were obtained from the blue phase PDA complex films by applying thermal stimuli.

2.2. Characterization. The complex films were visualized with a scanning electron microscope (SEM; JEOL, JSM-5200) and a high-resolution transmission electron microscope (HR-TEM; JEOL, JEM-3010). The structure of the films was characterized by X-ray scattering (Bruker D8 DISCOVER). An FTIR spectrometer (Perkin-Elmer, Spectrum GX) was used to acquire transmission spectra for the films spin-coated on the CaF_2 substrate. A mercury cadmium tellurium (MCT) detector was cooled with liquid nitrogen. The detector collected 256 scans at a resolution of 4 cm^{-1} . A nonpolarized infrared beam was used. The *ex situ* transmission spectra were obtained after the samples underwent a heating-and-cooling cycle. The temperature was controlled to reach 65°C , room temperature (RT), 85°C , RT, 105°C , RT, 125°C , RT, 145°C , RT, 165°C , and RT, in turn. The desired temperature was maintained for 10 min via a house-built temperature-controlled heating plate. The visible absorption spectra of the films were obtained using a UV-vis spectrophotometer (Agilent Technologies, HP 8453). The fluorescent images of the films were recorded using a fluorescence microscope (Olympus, BX51).

3. Results and Discussion

3.1. SEM, TEM, and XRD of Films. For morphological analysis, we employed SEM and HR-TEM. As shown in the SEM (Figures 1(a)–1(c)) and the magnified HR-TEM (Figures 1(d)–1(f)) images, all the complex films were composed

of relative uniform patches ranging over several hundred nanometers. X-ray diffraction analysis confirmed the formation of highly ordered lamellar crystal structures with an intense (100) reflection as shown in Figure 1(g). The crystal plane distance of the complex films was of 4.7 nm. The other crystal planes are shown in the magnified X-ray diffraction patterns (see SI in Supplementary Material available online at <https://doi.org/10.1155/2017/5983106>).

3.2. FTIR Spectroscopic Analysis. In our previous work, we studied the visible color changes of polydiacetylenic complex films upon consecutive heating-and-cooling cycles for thermal reversibility analysis [28]. *Ex situ* FTIR analysis of the films was carried out in the transmission mode here to gain insight into the thermally promoted colorimetric reversibility of the three kinds of complex films. Figure 2 shows the *ex situ* FTIR spectra of the case of 2:1 (stoichiometric) film. The peaks observed at 1692 , 1644 , 1528 , 1460 , and 1408 cm^{-1} correspond to the C=O stretching, NH_3^+ asymmetric deformation, COO^- asymmetric, CH_2 scissoring, and COO^- symmetric stretching bands, respectively. Initially, at RT, there was no C=O stretching band but rather COO^- asymmetric and symmetric stretching bands. This means that there is complete acid-base complexation between the carboxylic acid group of PCDA molecules and the amino group of *p*XDA molecules [29]. This complexation between the two molecules plays an important role in the conformational change upon thermochromism. By heating and cooling the CaF_2 substrate, we observed the FTIR spectra at RT. No significant changes were observed in the FTIR spectra after the complex films underwent 65°C -RT, 85°C -RT, and 105°C -RT cycles. During the heating process, the films turned deep blue (65°C), purple (85°C), and red (105°C). They all return to the initial blue color after cooling to RT (see SI). The color change due to heating is likely polymer side-chain reordering. This decreases the polymer effective conjugation length. However, in this system, π - π stacking between the *p*XDA molecules makes the conformational structure of PDA return to the initial form. However, after undergoing 125°C -RT cycle, the peak of the C=O stretching band from the carboxylic acid group was observed at 1692 cm^{-1} and the intensities of NH_3^+ asymmetric deformation and COO^- asymmetric and symmetric stretching bands decreased. This means that some complexation in the complex films was destroyed, and some PDA molecules were isolated from the *p*XDA molecules. This was followed by 145°C -RT and 165°C -RT cycles, and the intensity of the C=O stretching band gradually increased. The intensities of the NH_3^+ asymmetric deformation and COO^- asymmetric and symmetric stretching bands continuously decreased. As shown in the photographs, the colors of the films turned purple and red sequentially after cooling (see SI). Meanwhile, we can observe that the peak of C=O stretching band broadens, and the shoulder peak at 1712 cm^{-1} corresponds to the C=O stretching of red phase PDA molecules [30].

Figure 3 shows the *ex situ* FTIR spectra of the case of 3:1 (termed as PCDA-rich) film. Initially, the spectra show the C=O stretching band as well as the NH_3^+ asymmetric

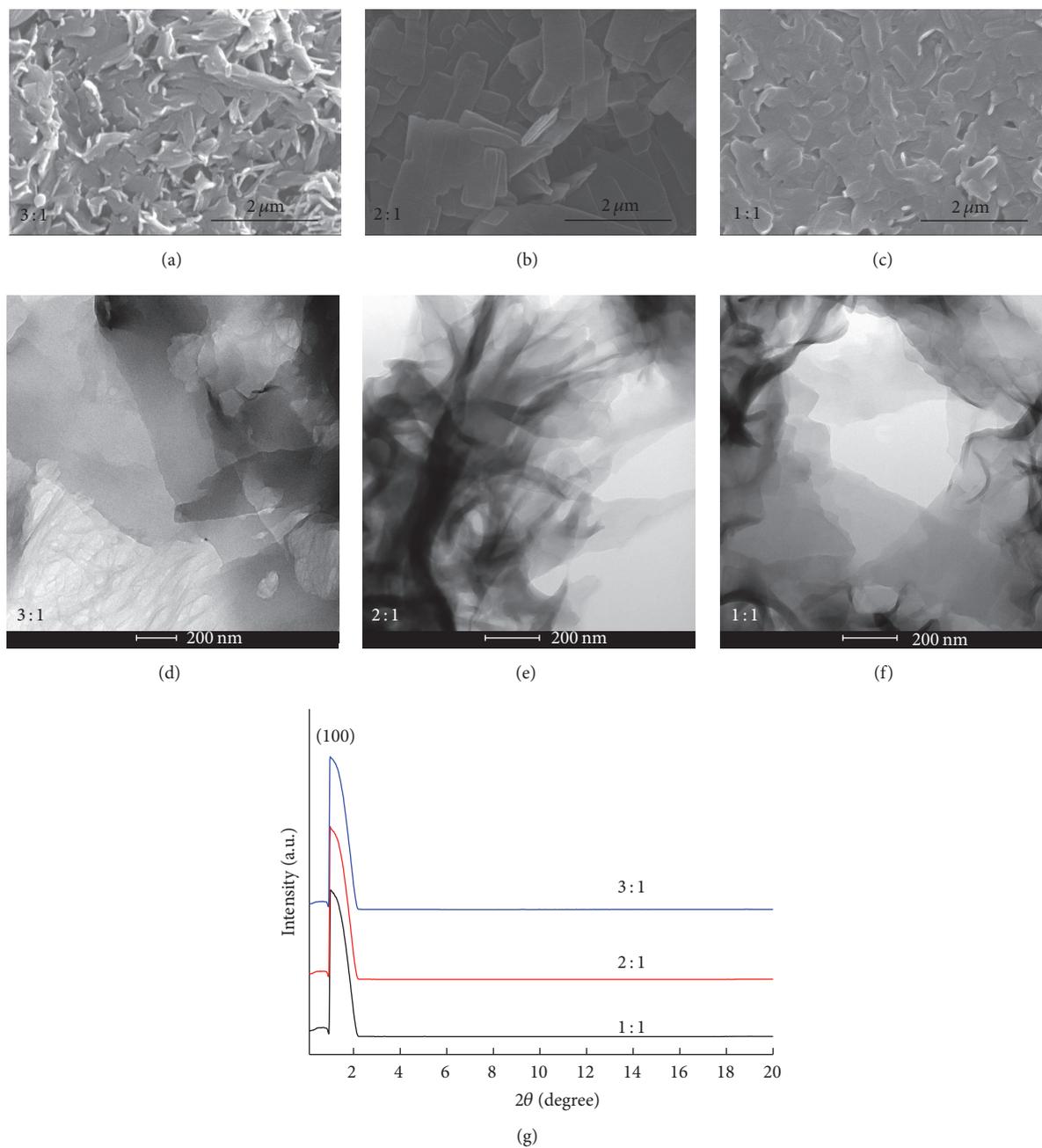


FIGURE 1: SEM (a)–(c) and HR-TEM (d)–(f) images and X-ray diffraction patterns (g) for 3:1, 2:1, and 1:1 polydiacetylenic films.

deformation, COO^- asymmetric and symmetric stretching bands, and CH_2 scissoring. These observations indicate the coexistence of complexed and noncomplexed PDA molecules. Hence, after undergoing the 65°C -RT cycle, the intensity of C=O stretching band decreased and shifts to 1712 cm^{-1} due to the noncomplexed PDA molecules. There are also some red phases in the film (see SI). Following the next 85°C -RT, 125°C -RT, and 125°C -RT cycles, the peak at 1712 cm^{-1} gradually increased, and this was accompanied by

increase of the red phase in the film. After 145°C -RT and 165°C -RT cycles, the intensity of the C=O stretching band at 1692 cm^{-1} slightly increases accompanied by the intensity of the NH_3^+ asymmetric deformation and the COO^- asymmetric and symmetric stretching bands decrease. The phenomenon of 3:1 film is similar to the case of 2:1 film from the 145°C -RT cycle.

Finally, the 1:1 complex film showed the strongest reversibility upon thermal stimulation. The ex situ FTIR spectra of

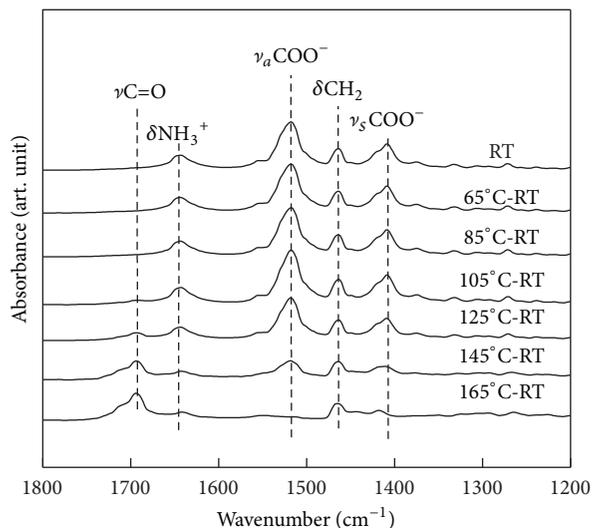


FIGURE 2: Ex situ FTIR spectra of a 2:1 polydiacetylenic film upon thermal stimulus.

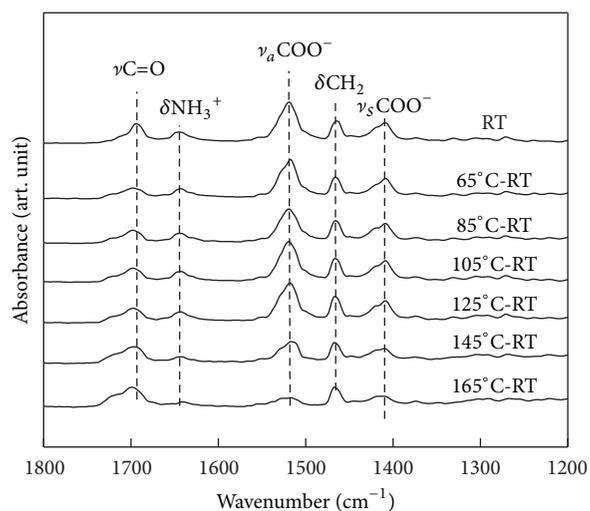


FIGURE 3: Ex situ FTIR spectra of a 3:1 polydiacetylenic film upon thermal stimulus.

the 1:1 (termed as *p*XDA-rich) film upon thermal stimulation are shown in Figure 4. Due to enlarged reversibility window for 2:1 and 3:1 films, there are no evident changes in the spectra until the 125°C-RT cycle; that is, the film remains blue (see SI). After the film undergoes the 145°C-RT cycle, the intensities of the NH_3^+ asymmetric deformation and COO^- asymmetric and symmetric stretching bands decrease. The C=O stretching band at 1692 cm^{-1} appears, and the color of the film remains. Ultimately, after the 165°C-RT cycle, the film turns red, and the intensity of the NH_3^+ asymmetric deformation disappeared similar to the COO^- asymmetric and symmetric stretching bands. We consider the increased π - π stacking to be due to high amount of *p*XDA molecules, which results in the strongest thermochromism reversibility.

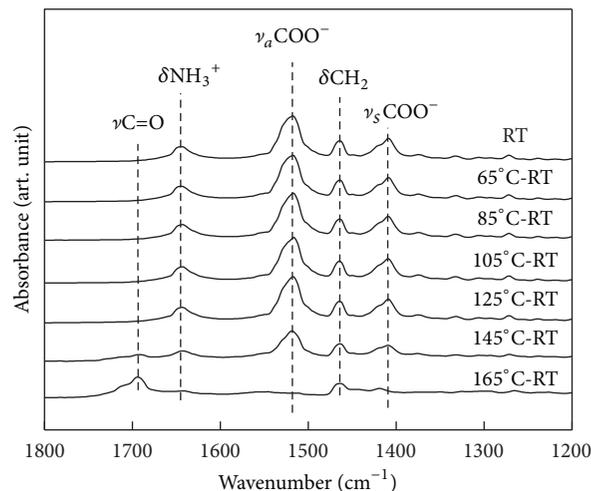


FIGURE 4: Ex situ FTIR spectra of a 1:1 polydiacetylenic film upon thermal stimulus.

We used FTIR to confirm the structural change of the films upon thermal stimulation as a function of molar ratio.

3.3. Interaction with CD Molecules. CDs are well known for their ability to form inclusion complexes with a variety of substrates [31]. In addition, different binding specificities of α -, β -, and γ -CDs make these small molecules attractive model systems for studying ligand-receptor interactions. There have also been some reports about vesicles or Langmuir-Schaefer film type PDA materials that interact with CDs. Here, the optical changes of the 2:1 complex film upon interaction with different sizes of CDs were studied for the first time. The 2:1 complex film was incubated in an appropriate concentration of α -, β -, and γ -CDs solution for 20 min. The color changes of each film were monitored by UV-visible spectroscopy (Figure 5). Initially, the film shows a typical blue color corresponding to an absorption maximum wavelength of 640 nm on UV-vis spectra. After incubation in 1 mM of α -CDs solution, the absorption maximum peak remains at 640 nm. However, the absorption maximum peak shifted to 540 nm after incubation with 5 mM and 10 mM α -CDs solution as shown in Figure 5(a). Compared with α -CDs, neither β -CDs nor γ -CDs induced an absorption peak shift in the PDA films. As the concentration increases to 10 mM, both β -CDs and γ -CDs showed a small peak at 540 nm (Figures 5(b) and 5(c)). A well-defined equation was used to quantify the colorimetric response (CR) [32]. Figure 5(d) shows that the CR values of the complex film caused by α -, β -, and γ -CDs are 9.1% (1 mM), 61.9% (5 mM), and 75.1% (10 mM), respectively. All of the CR values caused by β - and γ -CDs are below 20%. We also observed the fluorescent images of the same films (Figure 6). The films incubated in 5 and 10 mM α -CDs solutions emit a strong red fluorescent signal. However, the films incubated in β - and γ -CDs solutions only emit pale fluorescent signals. This suggests a shape match between the CDs and PDA-*p*XDA molecules. The α -CDs respond to the

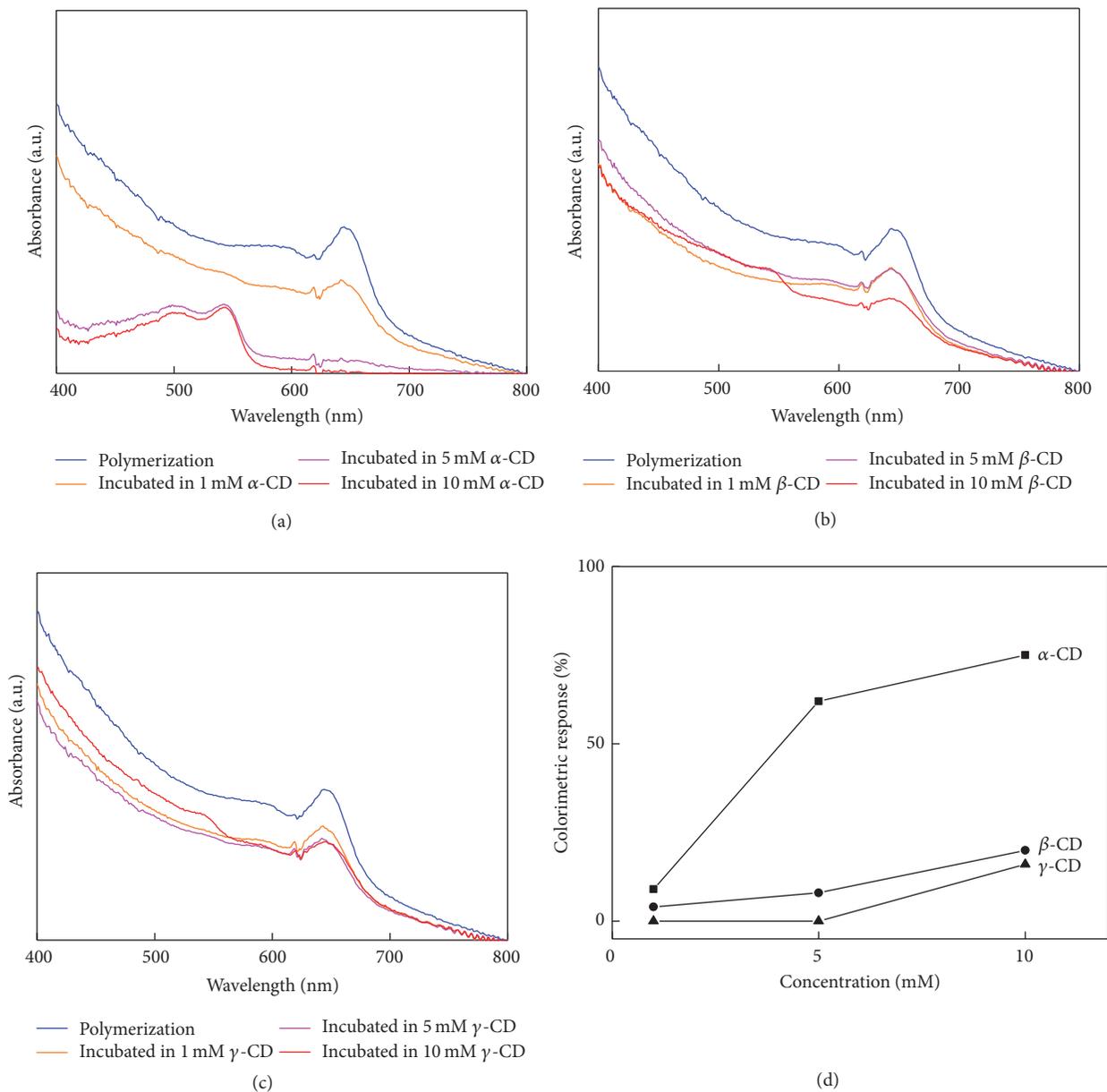


FIGURE 5: UV-visible absorption spectra of the films after 20 min incubation with various concentrations of α - (a), β - (b), and γ -CDs (c) and the corresponding colorimetric response (CR) analysis (d).

best shape match and induce an irreversible phase transition of the complex films.

4. Conclusions

In summary, the composition-tunable polydiacetylenic complex films were successfully fabricated through acid-base interactions between PCDA and *p*XDA molecules. Conformational changes of the complex films upon thermal stimulation were observed by ex situ FTIR analysis. The thermochromism reversibility of the complex films was strongly dependent on the π - π stacking between the *p*XDA

molecules. We also observed the first example of a CDs-induced color transition and fluorescent emission of the complex films. These fundamental results help explain how π - π stacking dependent on conformational changes affects the reversibility window and the development of a versatile sensor platform based on polydiacetylenic complex films.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

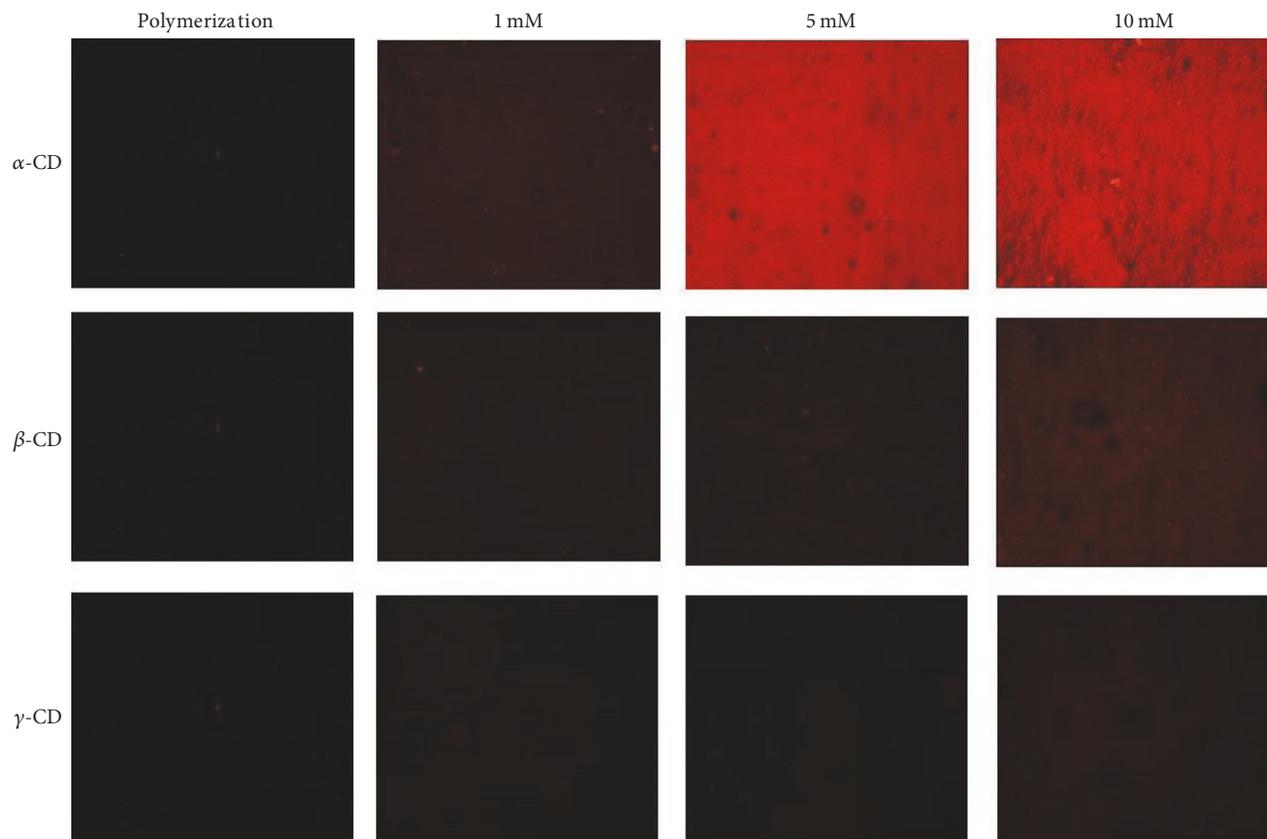


FIGURE 6: Fluorescent images of the films after 20 min incubation with various concentrations of α -, β -, and γ -CDs. The exposure time was fixed at 0.5 s.

Authors' Contributions

Chao Wang, Jin Hyuk Park, and Songwen Tan contributed equally to this work.

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