Preparation and Properties of Solvent-induced Discoloration Polydiacetylene Sensors

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Abstract: Polydiacetylene (PDA) films were prepared from 10, 12-pentacosadiynoic acid monomers by 1, 4-addition polymerization. The PDA sensors had different discoloration properties for different solvents. With the increase of time, the appearance color of the sensor changed from blue to red. The fluorescence properties of the films were studied by fluorescence spectra. There was no fluorescence phenomenon in blue-phase PDA, but there was fluorescence phenomenon in red-phase PDA film. The fluorescence signal peak appeared at 570 nm. In addition, the PDA polyvinyl alcohol (PVA) film and PDA test paper were prepared with PVA and filter paper as substrates, and their properties were studied. The PDA test paper shows a better tendency to change color from blue to red to the solvent, and the discoloration can complete in 1 s.

1. Introduction
Diacetylene is a highly unsaturated hydrocarbon and a class of compounds with conjugated carbon-carbon triple bond, which exists widely in nature[1]. Diacetylene shows some significant biological activities, such as anti-inflammatory, antibacterial, anti-cancer, etc[2-7]. Diacetylene groups can be used in π-conjugated alkynyl polymers[8] and macrocyclic hydrocarbon polymers[9]. Under the treatment of ultraviolet light, γ-ray or plasma, the self-assembled diacetylene monomers would undergo topological chemical polymerization to form polydiacetylene (PDA) with π-conjugated main chain structure of alkene alkyn alternation[10].

Conjugated polymers have the ability of light capture, which can be used to amplify the sensing signal of fluorescence, and are widely used in the field of optoelectronics and sensing materials. Conjugated polymers are polymers with large delocalized π bonds in molecules[11-13]. PDA is a kind of conjugated polymer with special properties. PDA molecules usually have maximum absorption values near 620 nm and 550 nm, corresponding to the blue phase (620 nm) and red phase (550 nm) visible to the naked eye, respectively[14, 15]. The discoloration of PDA is caused by many external factors, such as temperature, pH, mechanical stress, biomolecule interaction and organic solvents[16-18]. The optical properties of PDA mainly come from its conjugated main chain. The blue PDA is unstable and would change from blue to red when stimulated by the outside world[19-21]. Chance[22] believes that when PDA is stimulated, the structure of the side chain will produce tension so that the skeleton is deformed, that is, the plane type changes to non-plane type, which leads to the change of color. Kim[23] believes that the release of the side chain stress leads to the partial deformation of the π-orbit or the rotation of the conjugate skeleton, which leads to the decrease of the effective
conjugate length and the change of color. It is worth noting that unlike the blue PDA, the red PDA would emit fluorescence at a certain excitation wavelength, so there are many PDA biosensors based on its fluorescence response.

PDA sensors have the advantages of convenient detection, good sensitivity and low cost, which makes many researchers carry out research and development. At present, it is known that there are four kinds of sensors: PDA vesicle, PDA film, liposome and composite sensor. Zhang and colleagues[24] designed a microarray sensor embedded in polydimethylsiloxane to detect volatile organic compounds. Wacharasindhu and colleagues[25] used the drop coating method to disperse PDA on the surface of the filter paper, and the sensor had a good color change in organic compound vapors. However, there are still some problems in such sensors, such as low sensitivity, long response time and so on. In other words, the current PDA sensor still needs to be further improved in terms of its sensitivity and response time.

In this paper, PDA films were prepared by evaporation-induced self-assembly process. This polydiacetylene film is sensitive to tetrahydrofuran (THF), N-dimethylformamide (DMF), dichloromethane and chloroform, and can change color within 1 s.

2. Reagents and instruments
10, 12-pentacosadiynoic acid, absolute ethanol, methanol, n-hexane, dichloromethane, chloroform, THF and DMF. Fluorescence spectrophotometer (F-2700, hitachi high-tech company); UV-Vis spectrophotometer (UV-1750, shimazu company, Japan).

3. Experimental methods
3.1. Preparation of PDA film
10, 12-pentacosadiynoic acid (1.1238 g) ethanol (300 mL) was filtered to remove the polymerized portion to get a colorless or yellowish transparent solution. The 10, 12-pentacosadiynoic acid solution was evaporated and concentrated in the oven, and the concentrated solution should be sealed and kept away from light. An appropriate amount of 10, 12-pentacosadiynoic acid solution was dropped on the glass slide and evaporated to dryness in the dark to obtain a colorless film-like diacetylene. The blue PDA film was obtained by polymerization at the wavelength of 254 nm for 30 s.

3.2. Preparation of PDA test paper
The filter paper strips (1 cm × 5 cm) on the glass slides were wet with the 10, 12-pentacosadiynoic acid solution, and evaporated to dryness in the dark. The color of the filter paper strips changed from colorless to blue under ultraviolet radiation at 254 nm for 30 s.

3.3. Color changing pattern drawing
The glass rod was dipped in the 10, 12-pentacosadiynoic acid solution to write the "Li Yan Cheng" pattern on a blank paper. After dried, the paper was polymerized under the irradiation of ultraviolet lamp. It could be clearly seen that the part written on the white paper changed to blue. The THF solvent was sprayed in the blue area, and the pattern changed from blue to red. The color-changing pattern was completed, as shown in Fig. 1.

Fig. 1. The pattern after polymerization and the pattern after color change

4. Results and discussion
4.1. Effect and analysis of solvent on PDA film
The PDA film has different discoloration reaction, response time and sensitivity to different solvents. The PDA film changes its color after contacting with DMF, THF, chloroform and dichloromethane for 0.5 s, indicating that the colorimetric response is quite fast. The discoloration time is shown in Table 1.

| Reagent              | Dosage [mL] | Initial discoloration time [s] | Final discoloration time [s] |
|----------------------|-------------|-------------------------------|-------------------------------|
| N-dimethylformamide  | 4           | 0.5                           | 0.5                           |
| Tetrahydrofuran      | 4           | 0.5                           | 0.5                           |
| Chloroform           | 4           | 0.5                           | 0.5                           |
| Dichloromethane      | 4           | 0.5                           | 0.5                           |
| Absolute ethanol     | 4           | 1                             | 3                             |
| Methanol             | 4           | 2                             | 5                             |
| n-hexane             | 4           | 5                             | 75                            |

The photos of the discoloration of the PDA films (0.0025 g) mixed with different solvents (0.2 mL) for 60 s are shown in Fig. 2. The film responded best to DMF and THF, but poorer to methanol and n-hexane.

4.2. Colorimetric response analysis of PDA films

The visible spectra of the PDA film in absolute ethanol (Fig. 3) show that the blue phase has a strong absorption peak at the wavelength of 640 nm, and the intensity of the absorption peak decreases with the increase of time, while the intensity of the absorption peak at the wavelength of 540 nm of the red phase increases with time. The visible spectra of the PDA films in n-hexane, methanol, dichlorohexane, DMF, chloroform and THF show similar results.
intensity of the red phase peak increases with time, and the degree of the transition to red deepens with time.

| CR       | 30 [s]   | 10 [min] | 30 [min] | 60 [min] |
|----------|----------|----------|----------|----------|
| n-hexane | 27.28%   | 32.64%   | 38.67%   | 44.86%   |
| Absolute ethanol | 36.46% | 43.68%   | 62.68%   | 67.16%   |
| Methanol | 46.39%   | 54.15%   | 56.94%   | 58.76%   |
| Dichloromethane | 67.27% | 67.88%   | 69.85%   | 73.83%   |
| DMF      | 72.42%   | 74.65%   | 76.12%   | 76.85%   |
| Chloroform | 75.52% | 76.68%   | 81.52%   | 83.09%   |
| THF      | 81.00%   | 85.13%   | 89.76%   | 93.41%   |

4.3. Fluorescence analysis

In the process of stimulus response of PDA, as shown in Fig. 4, fluorescent signal would also appear. There was a fluorescence emission peak at 570 nm for red phase, while there was no fluorescence emission peak for blue phase, which indicated that red PDA had fluorescence, while blue phase had no fluorescence. Therefore, some PDA sensors are built based on the fluorescence response. PDA has the advantages of natural dual signal detection, leading to the potential application value in the field of biochemical sensing.

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4.4. Analysis of the test results of PDA PVA film

After 48 hours, the PDA PVA film in methanol turned red, while the films in other solvents remained unchanged (Fig. 5). It can be explained that solvent molecules cannot effectively enter the PVA film and react with PDA, which does not distort the conjugated system of PDA, resulting in no discoloration. Methanol molecules rarely enter the PVA, so the color change of PDA PVA film is slow.

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4.5. Performance and analysis of PDA test strip

The results of studying the response of the obtained filter paper strips to different solvents show that the effects of DMF, THF, dichloromethane and chloroform are stronger, and the blue test strips turn red immediately after contacting with the solvents. The order of the discoloration time is TTHF < Tchloroform < TDMF < Tdichloromethane < Tmethanol < Tethanol < Tn-hexane. It can be observed from the photos (Fig. 6) that the discoloration effect of DMF and THF is the best, while that of methanol and n-hexane is poor.
5. Conclusions
The discoloration reaction of PDA sensors to different solvents was studied by making sensors on different substrates. The experimental results show that PDA film and test paper have discoloration effect from blue to red for different solvents. The visible spectrum analysis of the PDA film shows that the signal peak of the blue phase appears at 640 nm and the signal peak of the red phase appears at 540 nm. With the increase of time, it can be seen that the intensity of blue phase peak decreases and the intensity of red phase peak increases. From the fluorescence spectra, it can be seen that the blue PDA has no fluorescence, and the red PDA has fluorescence, and the position of the fluorescence peak is at 570 nm.

Therefore, the functional PDA sensor can be used as a portable sensor for organic solvents. Red-phase PDA has strong fluorescence, which will have important research value and wide application prospect in the preparation and development of fluorescence sensors in the future.

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