Preparation and properties of polydiacetylene based temperature sensors

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Abstract: Polydiacetylene vesicles with different concentrations were prepared, which have a good temperature-induced discoloration effect. As the temperature rises, the appearance colors appear blue-violet, purple, rose-red, watermelon-red and orange-red. The UV-Vis spectrophotometer was used to study the thermochromism process of the corresponding polydiacetylene molecules. As the temperature increased, the maximum absorption peak at 650 nm gradually decreased, the maximum absorption peak at 550 nm gradually increased, consistent with the appearance of color change. In addition, the blue-phase polydiacetylene molecule is not fluorescent, while the orange-red polydiacetylene molecule is fluorescent, and the fluorescence emission peak is at 560 nm. Fourier transform infrared spectroscopy was used to investigate the temperature-induced discoloration properties of polydiacetylene molecules. The possible reason was that with the increase of temperature, the perturbation of polydiacetylene molecules caused the distortion of the side chain structure, resulting the conformation transition of ene-yne conjugates. As the bone structure changes, the effective conjugation length becomes shorter, which in turn changes the color of the polydiacetylene molecule.

1. Introduction

Diacetylene compound is a conjugated compound that does not exist as a single substance in nature and needs to be separated and purified from some natural substances[1]. In addition, diacetylene monomers undergo topochemical polymerization under ultraviolet light or gamma rays to form polydiacetylene[2]. The polymerization process requires no catalyst or initiator, which ensures the purity of polydiacetylene to a large extent. The premise of topological chemical polymerization of diacetylene molecules is accurate assembly, and this kind of assembly method is diverse[3-4]. (2) assembly of polydiacetylene liposome[5]; (3) assembly of polydiacetylene nanofibers[6]; (4) assembly of polydiacetylene composite material[7]. The special properties of diacetylene determine the research value in the field of chemistry and biology.

Polydiacetylene is a typical conjugated polymers with the π conjugated main chain structure of alkene alkyne alternation. When affected by external environment stimulation, the delocalized electron motion state of polydiacetylene changes, which will cause a strong color change of polydiacetylene molecules. The obvious color change can be seen by the naked eyes during the experiment, which is reflected in the transition of the system color from blue to orange red. Because this color change is easy to be observed by the naked eyes, it has superior optical and electrical properties, and is widely used in the sensing field: (1) polydiacetylene chemical sensor,
which can be roughly divided into polydiacetylene temperature sensor, polydiacetylene pH sensor, polydiacetylene ion identification sensor, polydiacetylene gas sensor and polydiacetylene organic molecular sensor[8-10]; (2) polydiacetylene biosensor, which can be roughly divided into polydiacetylene pathogen microbial sensor and polydiacetylene biomolecular sensor[11]. The outstanding characteristics of these sensors are simplicity, sensitivity, high economic benefit, visible to the naked eyes and easy to distinguish, which can be applied to the field of food safety rapid detection and immune analysis[12]. Cao Chen et al. prepared a chemical sensor based on molecular recognition of melamine. This sensor is sensitive to pH, and changes in color and state will occur within a certain pH range. As pH increases, the color changes from blue to red, and the solution state changes from liquid to solid[13]. Kim et al. prepared the temperature sensor, which could produce intuitive color change under the condition of 20°C-130°C, and the color change range changed from red to yellow, which could realize the detection of a variety of substances at a higher temperature[14].

Using 10,12-pentacosadiynoic acid as raw material and polydiacetylene temperature sensor as the starting point, polydiacetylene vesicles were prepared by different assembly processes. Through the study of the temperature sensors, it is found that they can achieve a variety of discoloration under the condition of 80°C and short time. The discoloration mechanism of polydiacetylene was studied by Fourier transform infrared spectrometer. The discoloration mechanism may be that with the increase of temperature, the conformation of ene-alkyne conjugated skeleton changed, the effective conjugation length became shorter, leading the color change and fluorescence emission. The advantages of this kind of sensor are high sensitivity, good discrimination, strong stability and low price.

2. Reagents and instruments
Anhydrous ethanol; Polyvinyl alcohol; 10,12-pentacosadiynoic acid. Fluorescence spectrophotometer (F-2700, hitachi high-tech company); UV-Vis spectrophotometer (UV-1750, shimazu company, Japan); Fourier transform infrared spectrometer (Nicolet-iS5, semel technologies co., LTD.).

3. Experimental methods

3.1 Preparation of polydiacetylene vesicles
10,12-pentacosadiynoic acid ethanol solutions of different concentrations (0.001 mol/L, 0.005 mol/L, 0.01 mol/L) were prepared, and appropriate amount of deionized water was added to the samples after evaporation to obtain the corresponding prepolymer of the vesicle solution.

The resulting propolymer solution was sonicated for 15 min at 60°C. Following sonication, the solution was cooled at 4°C for 12 hours. Polydiacetylene vesicles are prepared by radiation under UV light.

4. Results and discussion

4.1 The effect of ultraviolet radiation time on the polymerization degree of polydiacetylene vesicle
The prepared diacetylene vesicles were placed in the UV analyzer and treated with the UV lamp for 1 minute, 2 minutes and 3 minutes respectively. As the irradiation time increases, the degree of polymerization increases (Figure 1).
4.2 Effects of temperature on polydiacetylene vesicles

4.2.1 Chromogenic state of polydiacetylene vesicles at different temperatures. The obtained polydiacetylene vesicles with three different concentrations (0.001 mol/L, 0.005 mol/L and 0.01 mol/L) were put into an electric thermostatic blast drying oven for heating. The thermochromic reaction of polydiacetylene vesicles was investigated at different temperatures (40℃, 50℃, 60℃, 70℃ and >80℃). It can be observed that with the increase of temperature, the color of the polydiacetylene vesicle changes from blue to orange-red, and goes through dark blue, blue-purple, purple, rose-red and watermelon red in the middle. When the temperature is >80℃, the color remains orange-red, and the discoloration process of each concentration is shown in Table 1.

Table 1. Color development of polydiacetylene vesicles with three different concentrations at different temperatures.

| Concentration | Room temperature | 40℃ | 50℃ | 60℃ | 70℃ | 80℃ |
|---------------|------------------|-----|-----|-----|-----|-----|
| 0.001 mol/L   | Blue             | Purple | Mei red | Mei red | Mei red | Orange red |
| 0.005 mol/L   | Blue             | Dark blue | Dark blue | Dark blue | Watermelon red | Orange red |
| 0.01 mol/L    | Blue             | Dark blue | Purple | Mei red | Mei red | Orange red |

4.2.2 Visible spectral analysis of Polydiacetylene vesicles at different temperatures. The ordered polyacetylene monomers undergo topological chemical polymerization under the guidance of ultraviolet light, forming hyperconjugates, which greatly reduces the π-π* electronic transition ability, making polyacetylene molecules have strong absorption in the visible light area, and the maximum absorption peak is about 650nm. With the temperature rising, the corresponding maximum absorption peak of polyacetylene molecules gradually moves to 550nm[15]. Polydiacetylene molecules with different concentrations have the same change trend with temperature. Figure 2 shows the visible spectral analysis of 0.001 mol/L polydiacetylene vesicles under different temperature stimulation.
4.2.3 Colorimetric response analysis of Polydiacetylene vesicles. In order to quantitatively describe the color response of polydiacetylene that changes from blue to orange, CR value of colorimetric response was defined through its absorption spectrum data[16]. The value represents the degree to which the color of polydiacetylene changes from blue to red in the process of color response. The larger CR value is, the color of polyacetylene tends to be red. The calculation formula is referenced from the literature[17-18].

Table 2. Colorimetric response values of Polydiacetylene at different temperatures (room temperature, 40℃, 50℃, 60℃, 70℃, 80℃) of 0.005 mol/L.

|                | CR_{rt} | CR_{40℃} | CR_{50℃} | CR_{60℃} | CR_{70℃} | CR_{80℃} |
|----------------|---------|-----------|-----------|-----------|-----------|-----------|
| 0.005 mol/L    | 0       | 1.7%      | 11.5%     | 22.5%     | 42.5%     | 49.3%     |

4.3 Investigation of temperature response time of Polydiacetylene vesicles

The obtained three polydiacetylene vesicles with different concentrations were put into an electric thermostatic blast drying box for heating. The response time of thermochromic reaction of polydiacetylene vesicles was explored at different temperatures (40℃, 50℃, 60℃, 70℃ and >80℃). Can be observed when at a certain temperature, explore different times (2 min, 6 min, 10 min) polydiacetylene vesicle color from blue to other color, dark blue, violet, purple, mei red, watermelon red, when the temperature > 80℃ color orange red unchanged, the concentration process as shown in Table 3.

Table 3. 0.001 mol/L polydiacetylene vesicles responded to color changes at 40℃, 50℃, 60℃, 70℃ and 80℃ for 2 min, 6 min and 10 min, respectively.

|        | 40℃ | 50℃ | 60℃ | 70℃   | 80℃   |
|--------|-----|-----|-----|-------|-------|
| 2 min  | Blue| Blue| Purple| Mei red| Orange red|
| 6 min  | Blue| Purple| Purple| Mei red| Orange red|
| 10 min | Blue| Purple| Mei red| Mei red| Orange red|

4.4 Fluorescence analysis of vesicles

In the process of stimulus response of polydiacetylene, fluorescent signal would also appear. 520nm was chosen as the excitation wavelength to analyze the fluorescence of polyacetylene. There was a fluorescence emission peak at 560nm for orange red polyacetylene, while there was no fluorescence emission peak for blue red polyacetylene, which indicated that orange red
Polycetylene had fluorescence, while blue phase had no fluorescence[19]. This is mainly due to the fact that the atomic orbital of the lowest excited state of the blue phase molecule is intermediate symmetry (g-symmetry), and the atomic orbital of the ground state of the polydiacetylene molecule is also g symmetry, thus forming a dipole forbidden transition. The atomic orbital of the molecule in the lowest excited state of the polydiacetylene red phase is central antisymmetry (u-symmetry), which is allowed to transition in contrast to the blue phase. Therefore, the polydiacetylene red phase can produce fluorescence[20].

Due to the advantages of high sensitivity and good stability of fluorescence signal detection, the fluorescence detection of polydiacetylene molecule can make up for the inherent shortcomings of colorimetric response in analysis and detection to some extent, so that it has the advantages of natural dual signal detection in biological and chemical sensors and greatly improves the sensitivity of sensors[21].

4.5 Analysis of mechanism of polydiacetylene discoloration

Infrared spectra of PDAs of different colors are shown in Figure 4. When the temperature rises from 20°C to 80°C, the appearance color gradually changes from blue to orange-red, and the corresponding side chain hydrocarbon stretching vibration signal moves towards high wave number, from blue phase 2860 cm\(^{-1}\) and 2928 cm\(^{-1}\) to orange phase 2865 cm\(^{-1}\) and 2938 cm\(^{-1}\). Although the change in displacement is small, the reason may be that the conformation may be distorted to some extent during the color transition.

Here, the possible mechanism of thermochromic properties is proposed as follows: with the increase of temperature, the side chain disturbance of polydiacetylene leads to the change of the conformation of the ene-acetylene conjugate skeleton, and the effective conjugate length becomes shorter, thus leading to the color change of poly acetylene molecules.

![Figure 4. Infrared spectra of polydiacetylene molecules with different colors.](image)

5. Conclusion

The resulted blue-phase polydiacetylene changed into blue-purple, purple, rose-red, watermelon red and orange-red with the increase of temperature in the range of room temperature to more than 80°C. The fluorescence properties were studied by fluorescence spectrophotometer, and the results showed that the orange red copolymerized acetylene molecules had fluorescence emission peak (560 nm), while the blue copolymerized acetylene molecules had no fluorescence emission peak, indicating that the orange red copolymerized acetylene molecules had fluorescence, while the blue phase had no fluorescence. The mechanism of diacetylene discoloration is studied by Fourier transform infrared spectrometer, which may be as follows: the increase of temperature promotes the disturbance of its side chain, leading to the color transformation of the conformation distortion.
of the main chain of diacetylene.

Polydiacetylene vesicle has special optical color-changing properties and better stability compared with the vesicle system prepared by phospholipid, which provide a possibility for their application in the fields of food safety rapid detection and biological chemical sensors.

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