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Synthesis and solvent-sensitive fluorescence properties of a novel surface-functionalized chitosan film: potential materials for reversible information storage

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Abstract

Pyrenesulfonylchloride (PSC) was prepared and convalently bound to glutaraldehyde (Glu) crosslinked chitosan (CS) films by a post modification method. The monomer emission of pyrene (Py) immobilized on the CS films was weak both at dry and wet state if super-pure water was used to wet the films. However, upon addition of salts or replacing the super-pure water with tap water the monomer emission increased dramatically whereas the change in the excimer emission was hardly observed. Furthermore, the increasing process could last as long as 7 h. In contrast, the emission returned to the original intensity at once when the films were washed with super-pure water three to four times. The process could be repeated for at least five times. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Pyrenesulfonylchloride; CS films; Monomer emission

1. Introduction

Modification of polysaccharides may yield commercially interesting materials as is shown by the wide application of cellulose and starch derivatives in various industries. Chitosan(CS) is a well-known biocompatible and biodegradable natural polysaccharide with low toxicity [1]. It is normally produced by deacetylation of chitin, which is recovered from crustacean shells (crabs, crawfish, etc.) [2]. CS-based materials, such as hydrogels, fibres, films, etc., have found increasing use in a variety of applications ranging from, e.g. purification of drinking water to immobilization of enzymes, cells, drugs and functional coordination compounds [3–6].

Surface modification is important both theoretically and technologically. It is often used to modify the properties of polymers like permeability, biocompatibility and surface hydrophilicity or hydrophobicity. In the current work, pyrene was employed to modify CS films in order to prepare, initially, a chemical sensor for solvent polarity. This is because the steady-state emission spectra of pyrene and its derivatives have fine vibronic bands and the ratio of the intensity of peak 3 to that of peak 1 is very sensitive to the microenvironmental polarity of the pyrene species [7–8]. However, the sensitivity of pyrene functionalized CS films to solvent polarity is not as good as expected due to lack of the fine structure in the monomer emission as also due to poor compatibility of the films to organic solvents. Unexpectedly, quite a surprising phenomenon was observed in that the fluorescence emission of the pyrene functionalized CS films was very dependent upon both the ionic strength of the medium and the time for which the films were immersed in the medium. It is also surprising that the fluorescence emission returned to the original intensity immediately when the films were washed with super-pure water three to four times. Clearly, the pyrene functionalized CS films may be novel materials for reversible information storage. This paper reports the details of the preparation and the preliminary investigation results of the properties of the films.

2. Experimental

2.1. Materials

Pyrene (ACROS-96%) was purified by recrystalization from ethanol and then extracted with Soxhlet's extractor by ethanol. CS was prepared and purified as described before [4]. The degree of deacetylation was determined to be 100±3 mol% by FT-IR and pH titration [9,10]. The viscosity

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average molecular weight of CS was 1.9×10^5 [6]. Sodium nitrate, calcium nitrate and aluminium nitrate were from Xi'an Chemicals and of analytical grade. Urea (analytical grade from Xi'an Chemicals) was recrystalized twice from a mixture of ethanol and water (1:1, v:v). The purity of urea was checked by measuring the absorbency of its 5 mol l^{-1} solution in a 1-cm cell at 260 nm. The absorbency was less than 0.1 indicating that the urea solution was free of heavy metals, cyanate and biurate [11].Water used throughout (except tap water) was purified by successive de-ionization and double distillation.

2.2. Preparation of chitosan films

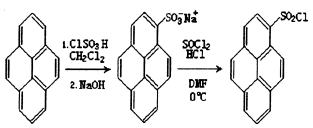
A CS solution of 1 wt.% was prepared by dissolving 0.1 g of CS in 10 ml of acetic acid (0.25 mol l^{-1}) solution. To ensure complete dissolution, the mixture was stirred overnight at room temperature, then filtered with a glass funnel and finally mixed with 100 μl of formaldehyde solution (37–40%) just before use. The mixture was thoroughly degassed under vacuum. The degassed solution (500 μl) was then poured into one of the inside surfaces of a 1 cm quartz cell placed horizontally in a 50°C clean oven. The cell was covered with a beaker. The crosslinking reaction and the evaporation of the solvent was allowed to proceed for 24 h. In the end, the cell was removed from the oven and allowed to cool to room temperature in a dessicator under vacuum. The cooled films were deprotonated by placing in a dilute NaOH solution (0.1 mol l^{-1}) for 10 min. Upon removal from the NaOH solution, the films were rinsed thoroughly with plenty of pure water and then dried again in the oven at 50°C for 24 h.

2.3. Surface functionalization of the CS films

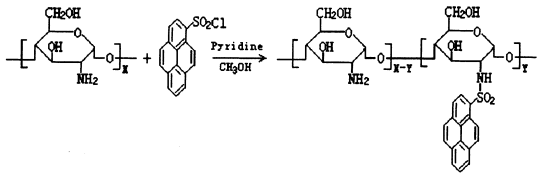
The procedure used for synthesis of pyrenesulfonylchloride (PSC) is illustrated in Scheme 1.A literature method was employed for the preparation [12]. The intermediate sodium pyrenesulfonate and the product, PSC were characterized by elemental analysis and FTIR spectroscopy. The results were in good agreement with those reported in the literature.

2.4. Preparation of pyrene functionalized CS films

A suitable amount of PSC (57 mg) was dissolved in methanol (200 ml). To the solution, 2 ml pyridine was added with stirring. The cell coated with CS films was immersed in the PSC solution at room temperature for 72 h. The cell was removed from the solution and rinsed with



Scheme 1. Synthesis of pyrenesulfonylchloride (PSC).



Scheme 2. Immobilization of pyrene onto the surface of CS films.

plenty of dichloromethane to remove free PSC. The cell was then put into a Soxhlet's extractor and extracted with dichloromethane for at least 4 h to ensure that there was no nonconvalently bound PSC in the films. The surface modification reaction may proceed as that described in Scheme 2.

After purification, the cell with surface functionalized films was dried at room temperature in a clean and draught-free place. The absence of the purifying solvent in the product films was verified by the absence of the strong C–Cl stretches observed in dichloromethane in IR spectroscopy.

2.5. Analytical methods

All fluorescence spectra were recorded on a Perkin-Elmer LS 50B luminescence spectrometer with a front face method. For monitoring the changes in the fluorescence spectrum, an automatic monitoring with preset time interval method was employed. The emission was deducted to 1% of the real intensity to allow monitoring for as long as possible.

Pressed KBr disks for PSC and sodium pyrenesulfonate and the films for CS and PSC-CS were used for the transmission infrared spectroscopy measurement. All the FTIR measurements were conducted on a EQUINOX55 FTIR spectrometer at room temperature at a resolution of 2 cm^{-1}.

3. Results and discussion

3.1. Surface functionalization and characterization

Syntheses of PSC and the intermediate, sodium pyrenesulfonate were straightforward. However, the immobilization of PSC onto the surface of the CS films proved more problematic due to poor compatibility of the two components. Therefore, a suitable solvent, for example, methanol should be employed as the reaction medium because this kind of solvent can dissolve PSC and at the same time swell the CS films. It was only in the swollen state that the amino groups in the films were available for functionalization. Extraction with ethanol proved to be a successful and very efficient method for the purification of the PSC-CS films. The surface functionalized films prepared in this way were characterized by IR spectroscopy.

In Fig. 1, the FTIR spectrum of PSC, CS and PSC-CS are denoted as (a), (b) and (c), respectively. Basically, the profile of (c) is characterized by that of CS (b) indicating that CS

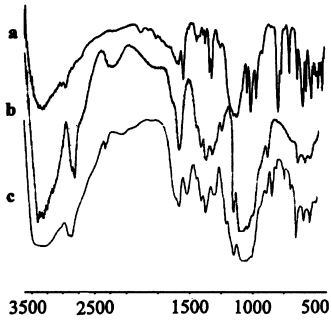


Fig. 1. Infrared spectra of PSC (a), CS (b) and PSC-CS (c).

is the main component of C. Appearance of a series of new sharp peaks, such as 855, 757, and 521 cm^{-1}, etc. which are the characteristics of (a), in (c) is a strong evidence for the successful immobilization of PSC onto CS films.

3.2. Ground state association and excimer formation

Excimer formation is due to the interaction of an excited pyrene species with a pyrene molecule in its ground state [13]. The interaction is both orientation and distance dependent. The required inter-planar distance for a perfect sandwich-like structure is about 3.5 Å [14]. Excimer formation in the PSC-CS films was detected by the presence of a broad structureless band centered at 480 nm (cf. Fig. 2).

Reference to the figure reveals that the fluorescence emission from the PSC-CS films was characterized by an excimer emission both in dry and wet state (cf. 6 and 7 in Fig. 2). However, monomer emission increased significantly with wetting of the films, which may be attributed to the swelling of the CS films. It can be imagined that the distance between neighboring pyrene species increases with the swelling of the films. As a result, some pyrene species would have lost their possibility to interact with the neighboring species and thereby the ratio of monomer emission to excimer emission (I_{376}/I_{480}) would increase with the wetting of the PSC-CS films. This is clearly demonstrated by comparison of spectrum 6 and 7 shown in Fig. 2. Fundamental differences between the excitation spectrum of the PSC-CS films (4 in Fig. 2) in the wet state analyzed at 376 nm and that (3 in Fig. 2) measured at 515 nm are obvious. Clearly, compared with the measurement at 376 nm, the one measured at 515 nm is broad and significantly red shifted indicating that the broad structureless emission (7 in Fig. 2) centered at 480 nm is a mixture of normal excimer emission and that emitted from the excited state of the ground state dimers. A similar conclusion applies to the broad band emission (6 in Fig. 2) from the dry films. Furthermore, with the exception of normal excimers and ground state dimers which may adopt nearly perfect sandwich-like structures, there are some distorted or twisted or partially overlapped ground state dimers and excimers (the second excimer), of which the emission is centered at 425 nm (cf. 5 in Fig. 2). The corresponding excitation spectrum is centered at 290 nm (cf. 2 in Fig. 2), which is about 50 nm blue shifted when compared with 1 or 3 in the figure.

Considering the discussions above, it may be concluded that the fluorescence emission from the PSC-CS films at longer wavelengths may originate from both the excimer emission and the excited state of the ground state dimers. Any alteration to the ground state association will alter the emission properties of the functionalized films. In addition, the high density of the pyrene species immobilized on the CS films can be responsible for the twisted ground state dimers and partially overlapped excimers.

3.3. Sensitivity to solvent

As mentioned earlier, the monomer emission increases with wetting of the dry PSC-CS films. Normally, the emission reaches equilibrium within a few seconds (<1 min) if super-pure water was used for the wetting. However, if tap water was used instead, the monomer emission increased continually whereas the excimer emission remained constant within the experimental error. As examples, Fig. 3 shows a few spectra from the PSC-CS/tap water system recorded at different times after addition of tap water. Generally speaking, the increasing process can last as long as 7 h. To monitor the process longer, a deduction of 99% of the emission was adopted. Considering the fact that some minerals exist in tap water, sodium nitrate, calcium nitrate and aluminium nitrate were employed to test the sensitivity of the fluorescence of the films to different ions. The results are shown

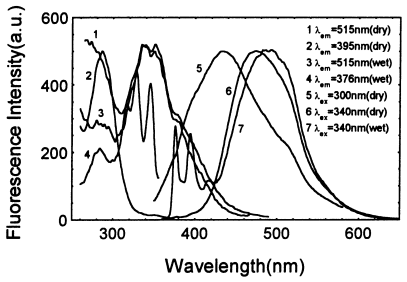


Fig. 2. Fluorescence emission and excitation spectra of the PSC-CS films recorded at various conditions (normalized at the maximum of each spectrum).

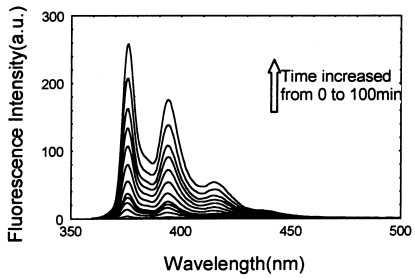


Fig. 3. Fluorescence emission spectra of PSC-CS films immersed in tap water measured every 8 min.

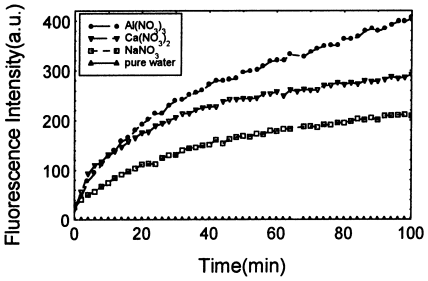


Fig. 4. Monomer emission intensity of PSC-CS films in aqueous solution as a function of time for various salts (0.041 mol l^{-1}).

in Fig. 4. It can be noted that for the systems with different salts (same molar concentration), again, monomer emission increases with elongation of time and, the greater the valence of the cations, the more pronounced is the increase. This difference has been attributed tentatively to the difference in the ionic strength of the three systems. To confirm this argument, various concentrations of sodium nitrate were employed to test the sensitivity. The results are shown in Fig. 5.

Reference to the figure reveals that the greater the ionic strength of the medium, the greater the increase suggesting that ionic strength rather than the ionic nature is mainly responsible for the changes in the fluorescence emission of the PSC-CS films. It is not difficult to understand that the distance between neighboring pyrene species depends upon the swelling ratio of the CS films. Furthermore, for the systems with no specific interactions between the ionic species and the CS films, the greater the swelling ratio the weaker the excimer emission and the more intense the monomer emission. However, for the current study, the swelling ratio of the CS films in pure water is greater than that in a salt medium. Therefore, it is not clear what the nature of the sensitivity is at this moment.

However, the statement that a decrease in excimer emission may enhance the monomer emission was proved by urea effect studies. Urea is a well-known hydrophobic interaction breaker. It is widely used as a modifier of the aqueous solvent to study hydrophobic interactions in protein and micelle solutions [15,16]. As expected, addition

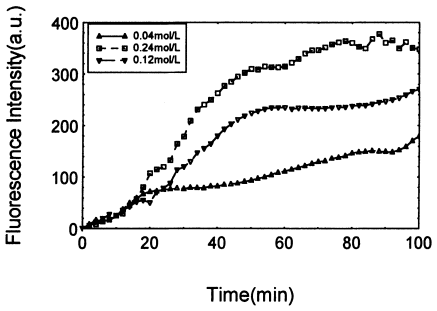


Fig. 5. Monomer emission intensity of PSC-CS films in various ionic strength media as a function of time ($NaNO_3$).

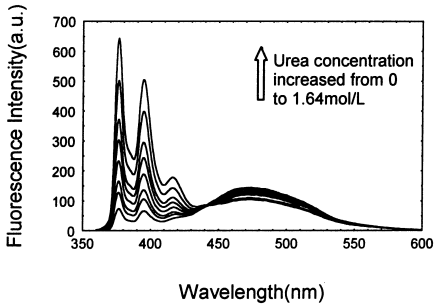


Fig. 6. Fluorescence emission intensity of PSC-CS films in urea solution as a function of urea concentration (0; 0.31; 0.59; 0.83; 1.05; 1.25; 1.43; 1.64 mol l^{-1}).

of urea inhibits the ground state association between the neighboring pyrene species on the CS films, and thereby emission from the monomer increases dramatically (cf. Fig. 6). With reference to the figure, it is revealed that there is an isochromatic point in the emission. Clearly, the monomer emission increases along with the decrease in the excimer emission. Considering this observation and those described earlier, it may be concluded that pyrene species immobilized on the CS films exist mainly in two states; isolated monomers and ground state dimers.

3.4. Reversibility of the sensitive process

The fluorescence intensity at 373 nm of the emission from the films immersed in a sodium nitrate solution was monitored as a function of time. After 50 min, the films were washed with super-pure water three to four times and the fluorescence intensity was measured. The sodium nitrate solution was used instead of pure water and the fluorescence intensity was monitored as a function of time again. The process was repeated five times. The result is shown in Fig. 7. Clearly, the sensitivity of the films to salt solution is reversible and return to the base line is fast even though the increasing process is very slow. It is hoped that the findings might be useful for reversible information storage.

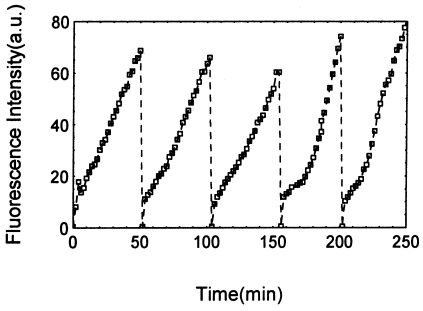


Fig. 7. Monomer emission intensity of PSC-CS films alternatively in tap water and super-pure water as a function of time.

Acknowledgements

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