Preparation, Characterization, and Optical Properties of a Chitosan–Anthraldehyde Crosslinkable Film

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ABSTRACT: A novel chitosan–anthraldehyde derivative film was prepared by the reaction of 79% deacetylated chitosan with 9-anthraldehyde with a hydrogel by a solution casting method. The prepared chitosan derivative film was confirmed by ultraviolet–visible absorption spectroscopy of the absorption peak at 266 nm due to the presence of an anthracene ring. The crosslinking reaction showed significant changes in the Fourier transform infrared spectrum of the chitosan derivative film. The characteristic peak of CH=N stretching bands at 1610 cm^{-1} confirmed the formation of a Schiff base after the reaction of chitosan with 9-anthraldehyde. The film was evaluated by X-ray diffraction, scanning electron microscopy, photoluminescence spectroscopy, and second harmonic generation (SHG). The nature of the crystallinity of the chitosan derivative from X-ray diffraction analysis confirmed that the film may have had nonlinear optical properties. The chitosan derivative showed a redshifted emission maximum because of the electron-rich polymer main chain. No reabsorption of the second harmonic signal and no resonance enhancements were noticed during the SHG study; this indicated that the chitosan derivative possessed SHG ability. Overall, the chitosan derivative film opens new perspectives for optical material for biomedical applications. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 3056–3062, 2010

Key words: biomaterials; biopolymers; NLO; synthesis

INTRODUCTION

Polymer materials that have specific properties, such as optical activity, in particular, the ability to participate in energy- or electron-transfer processes, have become increasingly important in recent years.[1,2] Thus far, most studies have been carried out with synthetic polymers.[3] The good optical and mechanical properties of a Schiff base polymer can be controlled optically; this has aroused considerable interest.[4] At first, inorganic materials were mainly studied, and they were found to be difficult to process and fabricate, to possess only marginal optical nonlinearity, and to be expensive. Because of these disadvantages of inorganic materials, research efforts in nonlinear optical materials have been focused on organic materials. Among them, organic polymeric materials have advantages with regard to the ease of structure modification, good processability into thin films, large susceptibility, high laser damage thresholds, faster response times, and so on.[5–10] The crosslinked type of polymers exhibits an even greater stability of optical activity than the host–guest system, but a significant optical loss occurs as a result of limited uniformity in the crosslinking reaction. Organic biopolymers containing chromophoric groups for optical properties may be an interesting addition to biomedical applications. However, there is a growing interest in natural polymers for practical applications, in particular, in biotechnology and environmental protection.[11,12] A unique feature of natural polymers compared with synthetic ones is their ability to undergo biodegradation.[13] Among various natural polymers, one of the most obvious choices for these applications is polysaccharide, the most abundant polymer in biosphere.

Chitosan, a linear β-(1,4)-D-glucosamine, is a biocompatible, nontoxic compound mainly obtained by the deacetylation of chitin, a natural structural component present, for instance, in crustaceans. Because of its special biological, chemical, and physical properties, chitosan and its derivatives have applications in many industrial, biomedical, optical, agriculture, and environmental protection fields because of its biodegradability, biocompatibility, and bioactivities.[14–21] It is not completely deacetylated though, so it is a copolymer of acetamide and amine groups, with a pK_a between 6.3 and 7.0; it is soluble in acidic media and may be processable as a film, gel, or polyelectrolyte. The most accepted approach for the improvement of the thermal stability of chitosan is

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the chemical modification of the structure by the introduction of thermally stable heterocyclic polymers such as polyazomethine.[22–24] So the incorporation of an anthracene moiety onto chitosan may provide fluorescence-labeled chitosan, and it may produce a combination of optical properties into biomolecules that may lead to the application of visible light to conduct the efficient degradation of a wide range of unwanted human tissue cells.

In this article, we describe a simple method to introduce a certain amount of fluorescent groups into chitosan to make them fluorescent without essentially affecting their polymer properties. This fluorescence-labeled chitosan may be used as a standard sample for the quantitative analysis of chitosan by either fluorescence. The fluorescence[25,26] labeling of chitosan can be used as an alternative to radioactive assays with the additional advantage that the chitosan can be observed directly with, for example, fluorescence microscopy and second harmonic generation (SHG). Another example[27] is the use in ultracentrifugation studies of chitosan. A chitosan derivative may also be useful for detecting chitosans in biological systems. With this view, in this study, we intended to prepare and characterize crosslinkable chitosan films with 9-anthraldehyde and evaluate their optical properties.

EXPERIMENTAL

Materials

Chitosan with a 79% degree of deacetylation was obtained as gift sample from the Central Institute of Fisheries Technology (Cochin, India). 9-Anthraldehyde (Sigma–Aldrich, Bangalore, India), methanol (Merck, Mumbai, India), and glacial acetic acid (Merck) were used as received. Deionized water, with a conductivity of 20 μS/cm, was generated in the laboratory.

Preparation of the chitosan–anthraldehyde derivative film

Chitosan derivative films were prepared by a solution casting method. In a 100-mL beaker, 500 mg of chitosan in 25 mL of 1% (v/v) aqueous acetic acid was prepared, stirred, and filtered to remove the undissolved matter. Then, we added the crosslinker, a 9-anthraldehyde solution, dropwise to the chitosan solution with vigorous stirring. A bubble-free solution was spread over a clean glass plate to a desired thickness and dried under atmospheric conditions at room temperature for about 24 h. Finally, the resulting crosslinked chitosan derivative films were carefully detached from the glass plates.

Characterization

Spectroscopy analysis

Fourier transform infrared (FTIR) spectra were recorded on an ABB FTLA FTIR/attenuated total reflection spectrophotometer (Zurich, Switzerland). Ultraviolet–visible (UV–vis) absorption spectra were measured on a PerkinElmer (USA) LS 35 spectrophotometer. The samples were dissolved in ethanol and 1% acetic acid and placed in an ultraviolet cell at room temperature, and scanning was done in the wavelength range 200–800 nm.

X-ray diffraction analysis

The X-ray diffraction pattern of the hydrogel film was recorded on X-ray diffractometer (D/Max2500VB2+/Pc, Rigaku, Japan) with Cu Kα characteristic radiation (wavelength = 0.154 nm) at a voltage of 40 kV and a current of 50 mA. The scanning rate was 3°/min, and the scanning scope of 2θ was from 2 to 50° at room temperature (25°C).

Morphology study

The morphology of the chitosan–anthraldehyde derivative films was analyzed with a Leica Cambridge S360 scanning electron microscope (USA) at an accelerating voltage of 15 kV.

Photoluminescence spectroscopy

The photoluminescence spectra were recorded on a PerkinElmer LS 55 fluorescence spectrometer.

SHG measurements

SHG activity was measured by the spin-coating technique. A Q-switched Nd:YAG laser (Surelite-III, Continuum, Sichuan, China) at 1064 nm was used as the pump beam. The delay between the flash lamp pump and Q-switch trigger was kept at a very large value of 450 ns to decrease the pulse energy (38 mJ) and increase the pulse width (20 ns). A diverging lens of focal length 30 cm was used to increase the beam diameter to fit the sample diameter of 13 mm. We used a 90° configuration scheme. The scattered second harmonic radiation was collected by a lens of focal length of 30 mm in imaging mode. A photomultiplier tube (PMT; IP21, EMI Electronics, Ltd.) with gain of 10^6 was used. The response of the PMT was such that the SHG pulse was traced to be 40 ns in a 500-MHz oscilloscope (model 3054B, Tektronix). The experimental setup used for our measurement is shown in Figure 1.

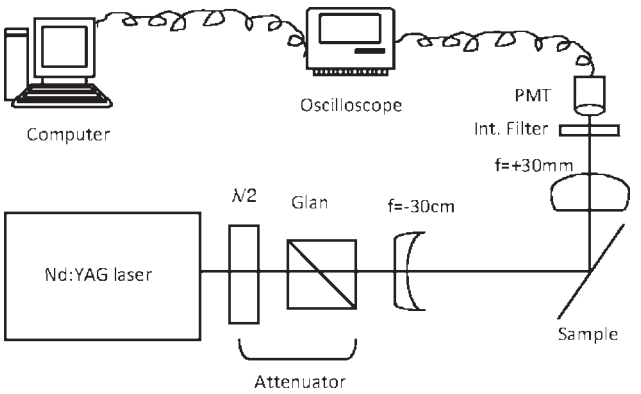


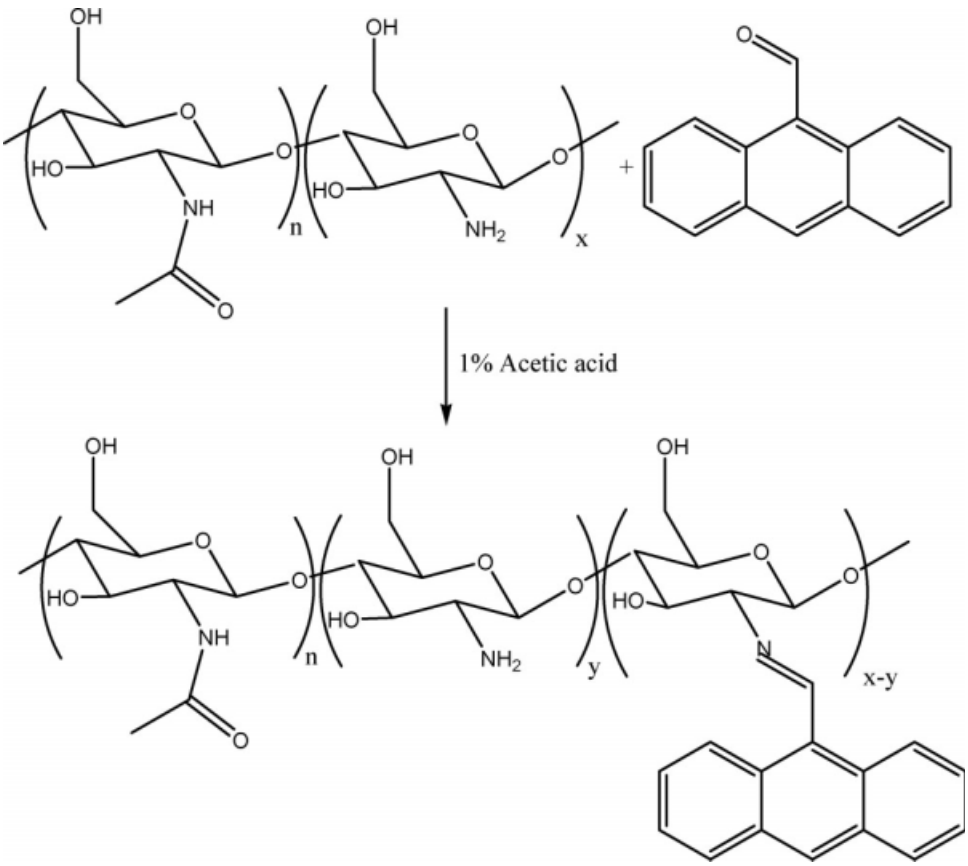
Figure 1 Experimental setup for the SHG measurements.

RESULTS AND DISCUSSION

The choice of chitosan as the film-promoting macromolecular structure stemmed from two considerations, namely, the fact that previous work showed the very good aptitude of this modified polysaccharide to give strong thin membranes[26] and the presence of primary amino groups in most of its repeat units. The formation of a Schiff base between the NH_2 functions of chitosan and the 9-anthraldehyde function borne by the chitosan–anthraldehyde derivative hydrogel was prepared (Scheme 1), and the film was drawn in a solution casting method. The chitosan–anthraldehyde derivative film was confirmed by UV–vis absorption spectroscopy and FTIR study.

FTIR spectra

The FTIR spectra of the chitosan film and chitosan–anthraldehyde derivative films are shown in Figure 2. In chitosan [Fig. 2(a)], a broad —OH stretch absorption band between 3500 and 3100 cm^{-1} and the aliphatic C—H stretch between 2990 and 2850 cm^{-1} appeared. As the —OH stretch band and the aliphatic C—H stretch band were aligned, they appeared as a broad band from 3500 and 2850 cm^{-1} in the spectrum. The other major absorption band between 1220 and 1020 cm^{-1} represented the free primary amino group ($—NH_2$) at the C_2 position. The peak at 1647 cm^{-1} represents the acetylated amino group of chitin, which indicated that the sample was not fully deacetylated. The peak at 1384 cm^{-1} represented the —C—O stretching of a primary alcoholic group ($—CH_2—OH$). In the chitosan–anthraldehyde derivative [Fig. 2(b)], OH stretching band at 3550 cm^{-1} and CH=N stretching bands at



Scheme 1 Preparation of the chitosan–anthraldehyde derivative film with a hydrogel.

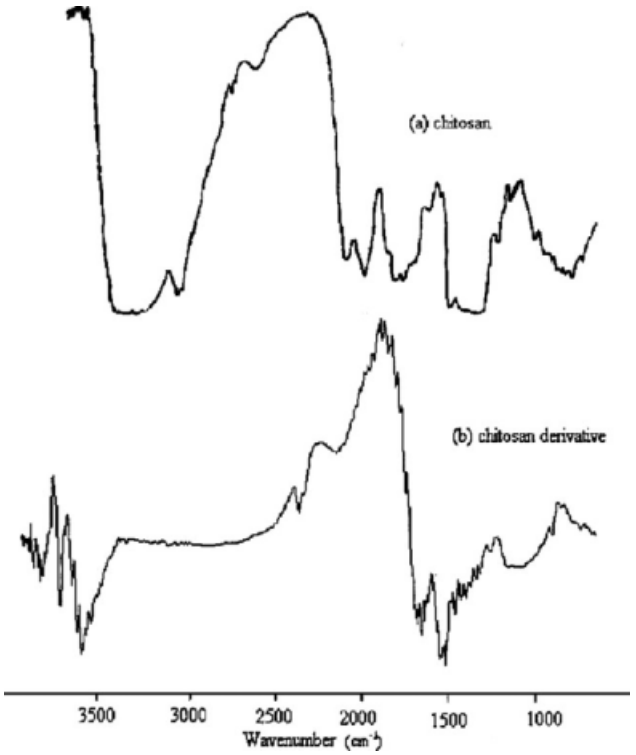


Figure 2 FTIR spectra of (a) chitosan and (b) the chitosan–anthraldehyde derivative film.

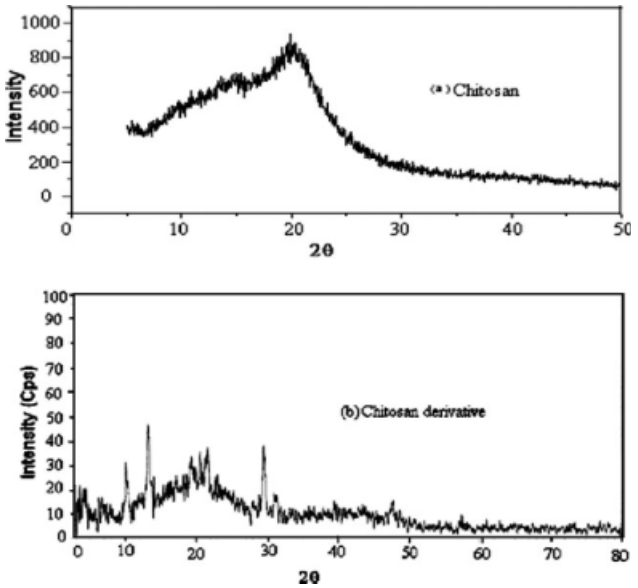


Figure 3 X-ray diffraction spectra of (a) chitosan and (b) the chitosan derivative.

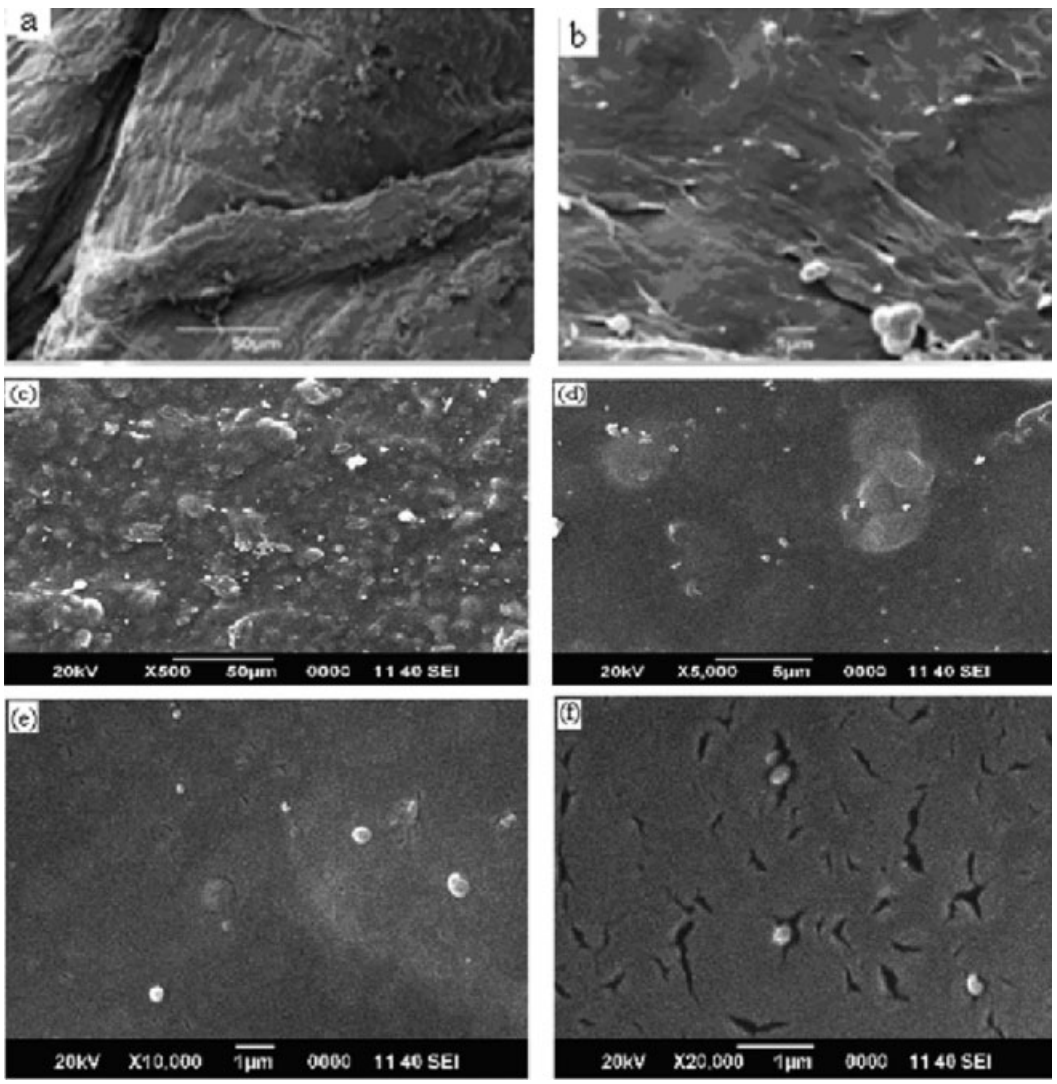


Figure 4 Scanning electron microscopy images of (a,b) the native chitosan and (c–f) the chitosan–anthraldehyde derivative.

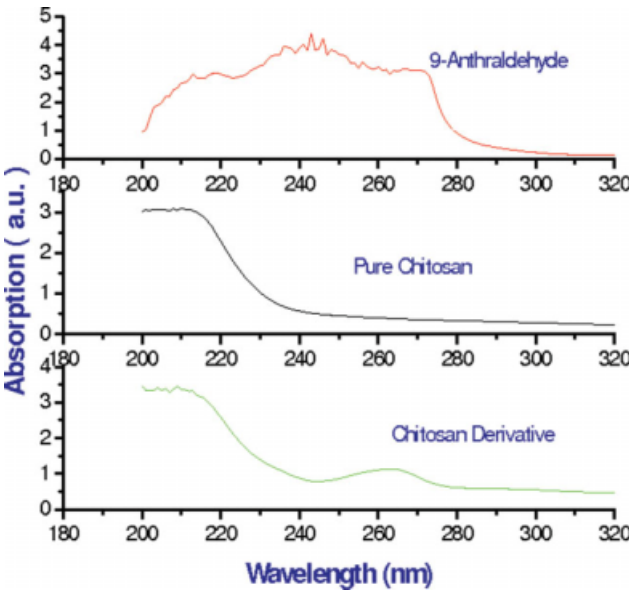


Figure 5 UV–vis absorption spectra of 9-anthraldehyde, chitosan, and the chitosan derivative. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

1610 cm^{-1} were observed. As a result of the cross-linking reaction, significant changes were observed in the FTIR spectra of the chitosan derivative film. This characteristic peak confirmed the formation of a Schiff base after the reaction of chitosan with 9-anthraldehyde.

X-ray diffraction study

The X-ray diffraction of the pure chitosan film and chitosan–anthraldehyde derivative film is shown in Figure 3(a,b). The weak diffraction peaks centered at diffraction angle (2θ) values of 10, 14, and 21° and sharp diffraction peaks at 30° were indicative of the crystalline morphology of the chitosan derivative film, shown in Figure 3(b), whereas for the pure chitosan film, shown in Figure 3(a), no diffraction peaks were observed at 2θ values of 10, 14, and 30°, but some weak diffraction peaks centered at 2θ = 20° appeared; this could have been due to the generally amorphous state of the pure chitosan film. The X-ray diffraction analysis confirmed that the chitosan derivative film may have had nonlinear optical properties.

Morphology study

Scanning electron micrographs of the native chitosan and chitosan derivative films are shown in Figure 4(a–f). Figure 4(c–f) shows the surface of chitosan derivative films to be relatively smooth,

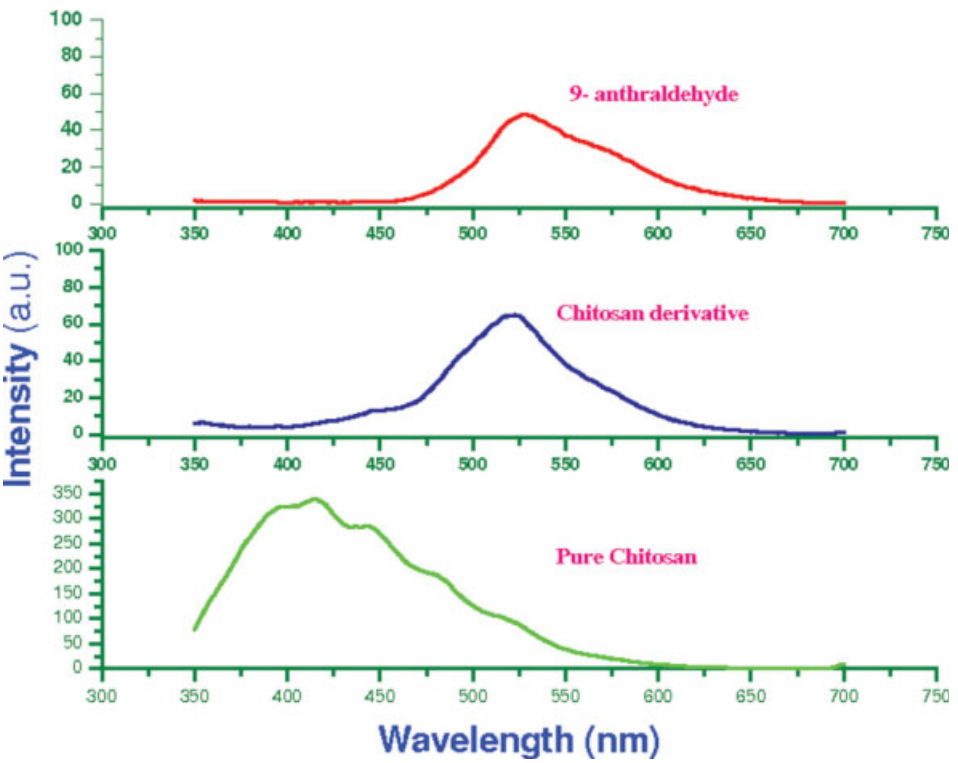


Figure 6 Photoluminescence spectra of 9-anthraldehyde, the chitosan derivative, and pure chitosan at the excitation wavelength of 325 nm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

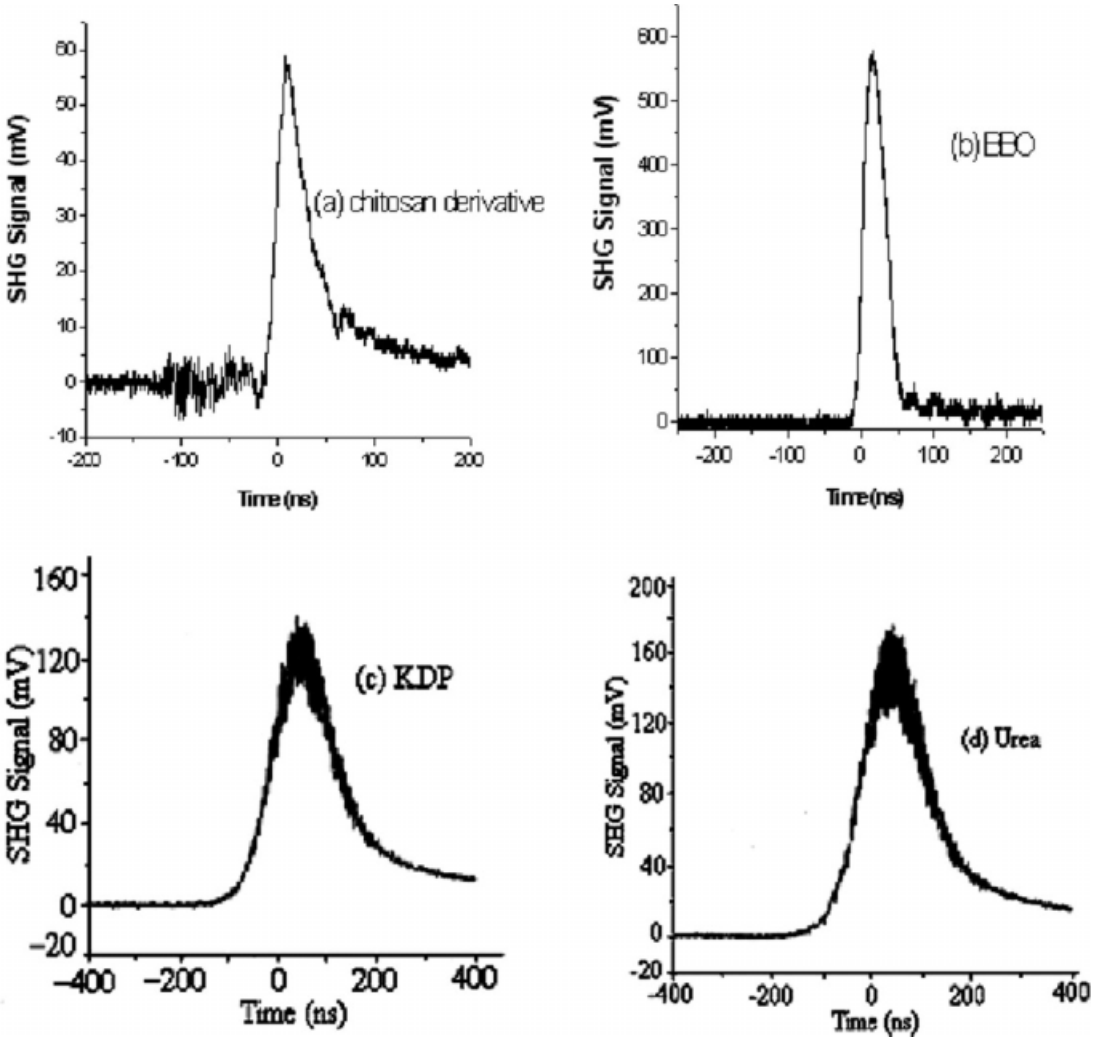


Figure 7 Oscilloscope recording of the SHG signals for (a) the chitosan–anthraldehyde derivative, (b) BBO, (c) KDP, and (d) urea.

homogeneous, and a continuous matrix without any pores or cracks with good structural integrity. It was flat and compact with very sparsely distributed small particles without any phase separation.

UV–vis absorption spectra

The UV–vis absorption spectra of the 9-anthraldehyde, pure chitosan, and chitosan–anthraldehyde derivative are shown in Figure 5. As shown in Figure 5, the absorption peak of 9-anthraldehyde in ethanol was 250 nm, and pure chitosan in 1% acetic acid was 215 nm, whereas the absorption peak of the chitosan derivative in 1% acetic acid was 266 nm because of the presence of the anthracene ring.

Photoluminescence properties

As shown in Figure 6, the emission spectra and fluorescent intensities of the 9-anthraldehyde, chitosan, and chitosan derivative were performed at an excitation wavelength of 325 nm. The photoluminescence spectra of 9-anthraldehyde had an emission peak at 527 nm, pure chitosan had an emission peak at 425 nm, and the chitosan derivative had an emission peak at 526 nm at an excitation wavelength of 325 nm. The emission spectra of the pure chitosan (emission wavelength) peak appeared at 425 nm, and the chitosan derivative emission wavelength peak appeared at 526 nm at an excitation wavelength of 325 nm. The chitosan derivative showed a redshifted emission maximum because of the electron-rich polymer main chain. The fluorescent intensity was also controlled by the conjugation length and variation of the substituents.[19,28]

SHG study

SHG is the most reliable and initial measurement for the second-order characterization of materials.

The SHG efficiency of the polymer was examined by the powder reflection technique of Kurtz and Perry.[29,30] The setup was first calibrated with known samples. We used potassium dihydrogen phosphate (KDP), urea, and β-barium borate (BBO) powder to calibrate the setup. The SHG signals, as detected by the PMT for the KDP, urea, and BBO under identical pump powers and configurations, are shown in Figure 7. No reabsorption of the second harmonic signal and no resonance enhancements were noticed during the SHG study; this indicated that the chitosan derivative possessed SHG ability (Fig. 7). It is assumed that the semicrystalline grains of a polymer exhibit a greater degree of alignment along one particular direction. The directional orientation of the polymer molecule is greatly enhanced by the donor–acceptor group of the π electron system. The centrosymmetry is necessarily broken when the preferred helicity is achieved in the supramolecular and/or self-organization, and hence, there is preference to one sense of the helix, which leads to a high SHG stability.[28,31]

CONCLUSIONS

We prepared a novel chitosan derivative hydrogel and drew a film with the solution casting method. The chitosan–anthraldehyde derivative was confirmed by FTIR and UV–vis absorption spectra and characterized by X-ray diffraction. The morphological study of the chitosan derivative was smooth and homogeneous. The photoluminescence spectra of the chitosan derivative showed a redshifted emission maximum. The chitosan–anthraldehyde derivative showed SHG. This indicated that the chitosan–anthraldehyde derivative is a very promising candidate for practical applications in the optical and biomedical fields.

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