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Synthesis of 5-dimethylaminonaphthalene-1-sulfonyl carboxymethyl chitosane

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ABSTRACT

Deacetylated carboxymethyl chitosane (CM-chitosane) can react with dansyl chloride [5-Dimethylaminonaphthalene-1-sulfonyl chloride], affording 5-Dimethylaminonaphthalene-1-sulfonyl CM-chitosane. This reaction takes places under dilute sodium hydroxide in water/methanol solvent system to afford fluorescent dansylated CM-chitosane in good yield. The fluorescent property of the polymer is well established by different methods such as spectrofluorimetry, visualization under uv-lamp, preparation of fluorescent strips of filter paper by dipping it into the polymer solution and similar methods. Spectroscopic data such as H-NMR, FT-IR and UV-Visible are well correspond with the bond formation of the CM-chitosane to the dansyl group.

KEYWORDS

Chitosan;
CM-chitosane;
Spectrofluorimetry;
Dansyl chloride.

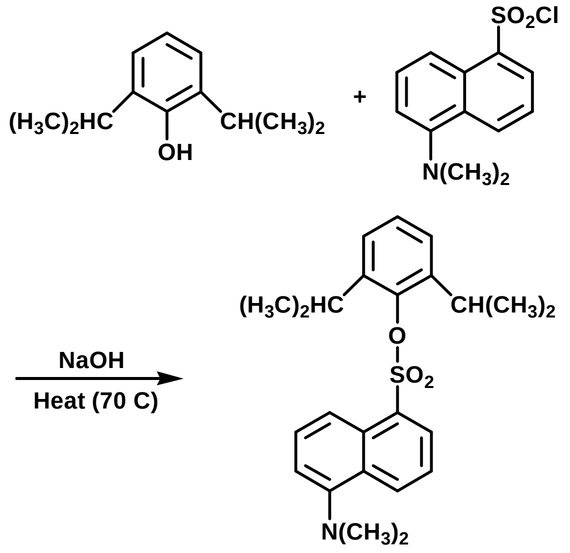
INTRODUCTION

The development of fluorescent labels for organic molecules is of great practical importance in chemical, biological, and pharmaceutical sciences[1–4].

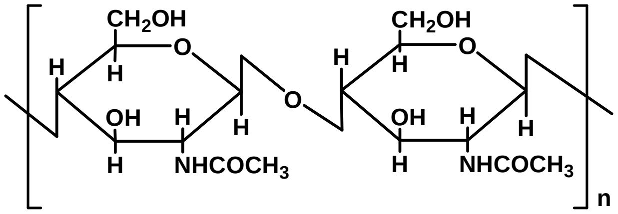
Research on fluorescent polymers has become an interesting area due to their wide applications as luminescent substrates in various industries. The assembling of many fluorophores onto a polymer chain affords the polymer high brightness under conventional microscopy.

Conjugated fluorescent organic polymers are showing great potential in a variety of exciting applications. They have been investigated as emissive layers of electroluminescent devices that have potential to be the next generation of flat panel displays. They have shown promise as indicators in field tests for chemical warfare agents.

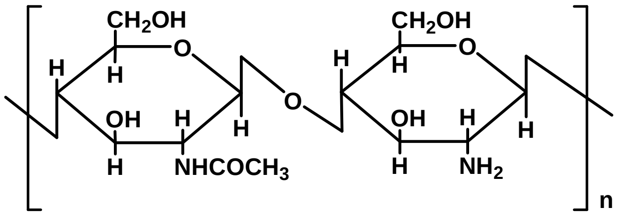
In general, there are two ways to synthesis such polymers. One of them is the polymerization of a polymerizable fluorescent monomer with some common monomers; the other is the chemical modification of polymers by fluorescent molecules or fluorescent oligomers. In recent years, considerable effort has been devoted to dansyl group is one of the most attractive chormophores due to its strong fluorescence, relatively long emission wavelength and easy derivation. Fluorescent labeling of amine functional groups using dansyl chloride, and in sodium carbonate buffer, allowed the detection of microgram amounts of analytes.[5] Dansyl chloride can also react with phenolic compounds. Sensitive detection of phenolic compounds has been studied for different applications[6,7].



The biopolymer chitosan is obtained from the partial deacetylation reaction of the chitin in concentrated alkaline solutions[8-10]. Chitosan also chemically known as (1-4)-[2-amino-2-deoxy-â-D-glucan] .

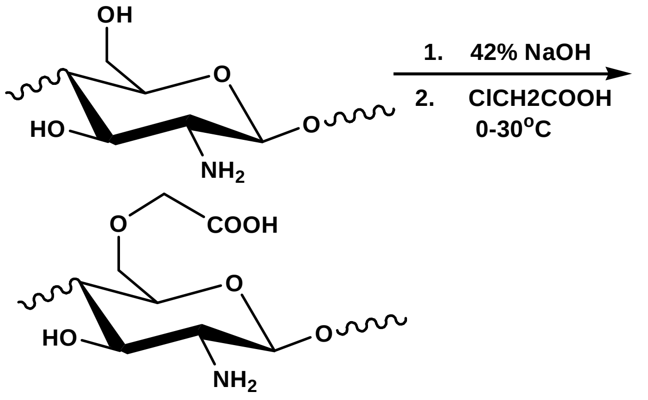


Chitin



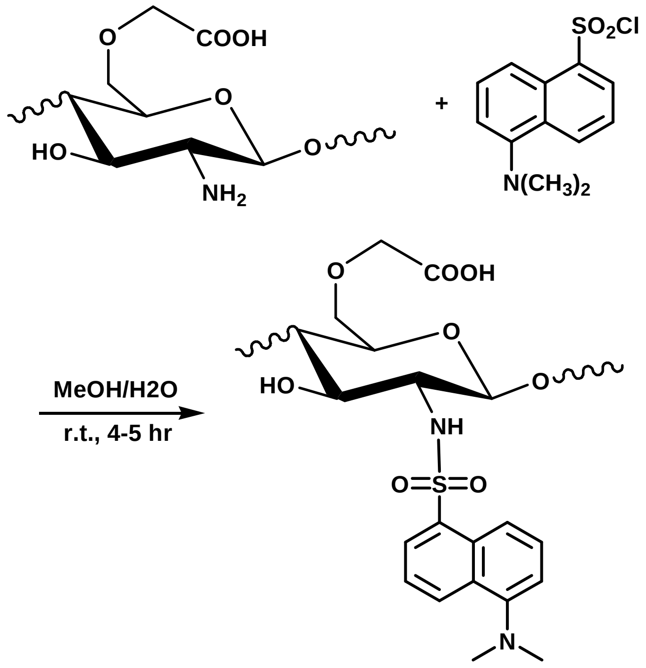
Chitosan

chitosan and chloroactic acid are used to synthesize CM-chitosane with different reaction medium- isopropanol, ethanol, glycol and n-butanol.



Every amino glucose unit contains two hydroxyl and roughly one amino groups, These groups could be the coupling sites of the fluorescence chromophores. In this paper, we report a simple method for synthesis of fluorescent CM-chitosane by covalently linking of fluorescence chromophore, 5-dimethylamino-1-naphthalene sulfonyl chloride to the CM-chitosane.

Indeed we used dansyl chloride as an active fluorescent moiety to bind chemically with the CM-chitosane. We found that CM-chitosane can bind through more reactive amino group by a nucleophilic substitution mechanism with dansyl chloride[5-dimethylaminonaphthalene 1-sulfonyl chloride].



The fluorescent property of the product well established by different methods such as spectrofolurimetry, visualization under uv-lamp and similar methods. Spectroscopic methods were used for establishing the structure of the fluorescent polymer product.

The maximum emission wavelength of the product was appeared in 482 nm while the excitation wavelength of the product occur at 315nm. The high stocks shift (167nm) of the product (dansylated CM-chitosane make it a suitable fluorophore for different applications.

EXPERIMENTAL

Chitosane fibers and dansyl chloride was purchased from Merk chemical company. N,O-carboxymethyl chitosane was prepared according to the reported procedures[11,12]. H-nmr spectra was run by a 500 MHz Brucker DRX system. FT-IR spectra was run by a Brucker Tensor-137 system. Spectrofluorimetric investigations were performed by a Shimadzu 3100 instrument.

Preparation of fluorescent fluorescent CM-chitosane

0.1 gr of CM-chitosane, 7.5ml distilled water, 2.5ml methanol was added into a100ml flask equipped with a condenser and magnetic stirrer. The mixture was stirred for 30 minutes until the mixture well dispersed. A solution of 0.01gr (0.0003 mole) dansyl chloride in 5 ml methanol was prepared and added to the mixture. The mixture was well stirred at room temperature for 4 to 5 hours. At the end of the reaction time, The heterogenic layer was filtered and the mixture was washed with 15 ml cold methanol to remove any unreacted dansyl chloride from the mixture. The solid product dried in a dark place overnight. The pure 5-Dimethylaminonaphthalene-1-sulfonyl CM-chitosane was obtained in good yield. Dansyl chloride itself has an absorption maxima at λ=355 nm and anemission around λ=500 nm whereas the product (5-Dimethylaminonaphthalene-1-sulfonyl CM-chitosane) has an absorption and emission maxima at λ=315 nm and λ=482 nm respectively.

1H-NMR :CH3 of acetyl group: 1.9 ppm(s); H-2, H3, H4, H5, H6: 3.3-4 ppm(overlapped multiples), naphthalene rings hydrogens: 7.1-8.5 ppm(overlapped mulltipels) -NMe2 protons: 2.8ppm(s)

The infrared spectrum of dansyl CM-chitosane is shown in Figure 1.

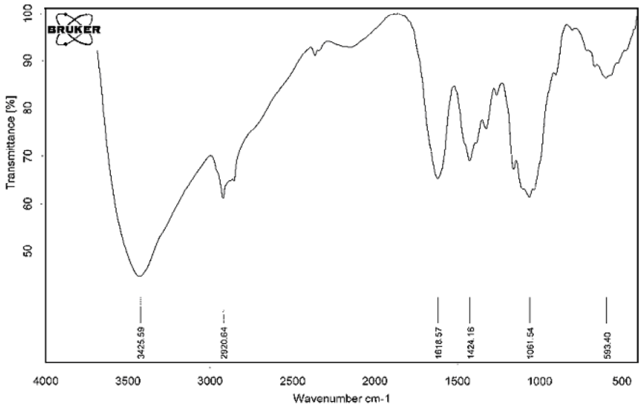


Figure 1 : Infrared spectra of dansyl CM-chitosane

RESULT AND DISSCUSION

In a proposed mechanism the nucleophilic chitosane NH2 will attack to the –SO2- group of dansyl chloride. As a result the new sulfur nitrogen bond will form . The Substitution of 5-N,N-dimethylamino naphthalene sulfonyl group (dansyl) was well accomplished on the CM-chitosane and established by the NMR spectra of the final product. The fluorescent properties of the polymer were measured by determination of its maximum emission wavelength which occurred at 482 nm. It shows very good fluorescent emission under ultraviolet radiation.

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