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## Synthesis Of Fluorescent Polyacrylamide Based On Dansyl Chloride [5-Dimethylaminonaphthalene-1-Sulfonyl Chloride]

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### ABSTRACT

During the past decades, research on fluorescent polymers has become an interesting area due to their versatile applications as luminescent probes in various fields. The assembling of many fluorophores onto a polymer chain affords the polymer high brightness under conventional microscope. In general, there are two ways to synthesize such fluorophore-enriched 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. Fluorescent polymers with different polarity and functionalization are synthesized for various applications. We found that polyacrylamide can react by a nucleophilic substitution mechanism with dansyl chloride [5-Dimethylaminonaphthalene-1-sulfonyl chloride]. This reaction takes place under dilute sodium hydroxide in water/methanol or dimethylsulfoxide solvent system to afford fluorescent dansylated polyacrylamide in good yield. The fluorescent property of the polymer is well established by different methods such as spectrophotometry, visualization under uv-lamp, preparation of fluorescent strips of filter paper by dipping into the polymer solution and other methods. Spectroscopic data such as H-NMR, FT-IR and UV-Visible are well correspond with the bond formation of the polymer amide nitrogen to the dansyl moiety. © 2007 Trade Science Inc. - INDIA

### INTRODUCTION

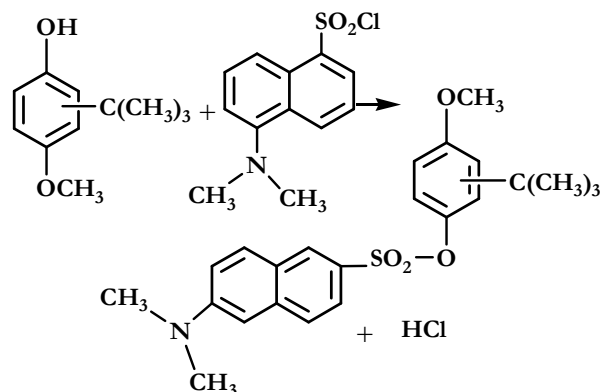
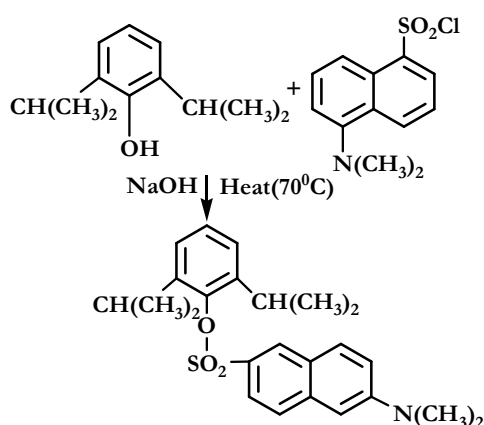
The development of fluorescent sensors for organic molecules is of great practical importance in chemical, biological, and pharmaceutical sciences<sup>[1-4]</sup>. Recently, many very sensitive fluorescent sensors have been developed for peptides<sup>[5]</sup>, metal ions<sup>[6-9]</sup>, saccharides<sup>[10-12]</sup>, and others. 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. Recognition and sensing of heavy and transition metal ions via artificial receptors are of current interest in supramolecular chemistry because of their significant importance in chemical, biological, and environmental assays<sup>[13]</sup>. Of particular interest in this regard are fluorescent sensors, because they have both high sensitivity and ease of signal transduction<sup>[14]</sup>. A practical fluorescent sensor for targeting ions of specific importance should at least have the following properties: simplicity, high selectivity,

strong signal output, wide conditions of coordination and recognition in aqueous environments<sup>[14a]</sup>. Fluorescent sensors can be classified into two major groups: chemo sensors and biosensors according to the originality of the responsive moieties for analytes<sup>[15]</sup>. These sensors can also be divided into three classes based on their difference in ion sequestering pathways<sup>[16]</sup>. Class I are “fluorogenic” chelating agents (e.g. oxine), class II are fluoroionophores with separate fluorophore and ionophore linked with or without a spacer and class III are fluorescent sensors based on resonance energy transfer (RET, also called electronic energy transfer, EET) which is also frequently termed fluorescence resonance energy transfer (FRET)<sup>[17]</sup>.

In recent years, considerable effort has been devoted to dansyl group is one of the most attractive chromophores due to its strong fluorescence, relatively long emission wavelength and easy derivation. Fluorescent labeling of amine functional groups using dansyl chloride (DNS-Cl), and in sodium carbonate buffer, allowed the detection of 1  $\mu$ g amounts of analytes<sup>[18]</sup>. The methodology presented allows dansylation of primary, secondary, and tertiary amine groups at a temperature of 25°C. The dansylation of tertiary amines involves a chemical reaction which removes one substituent (or branch) of the amine group. A one molar working concentration of Na<sub>2</sub>CO<sub>3</sub> is used, and is at pH 11.0. Dansyl chloride can also react with phenolic compounds. Sensitive detection of phenolic compounds has been studied for different applications<sup>[19,20]</sup>.

### Reaction of propofol with dansyl chloride



And the use of dansyl chloride in the spectrofluorimetric determination of the synthetic antioxidant in foodstuffs is good examples<sup>[21]</sup>.

In the present study we use dansyl chloride polyacrylamide. We found that polyacrylamide can react by a nucleophilic substitution mechanism with dansyl chloride [5-dimethylaminonaphthalene 1-sulfonyl chloride] this reaction take place under two different mild conditions: A-dilute sodium hydroxide in water/methanol solvent system  $\beta$ -triethylamine-DMSO system these reactions afford fluorescent dansylated polyacrylamide in good yields. The fluorescent property of the product well established by different methods such as spectrofluorimetry, visualization under uv-lamp and similar methods. Spectroscopic methods were used for establishing the structure of the fluorescent polymer product. The results show bond formation between the amide NH<sub>2</sub> and dansyl group.

The maximum emission wavelength of the product was appeared in 454-455nm while the excitation wavelength of the product occur at 330-340nm. the high stocks shift (105-115nm) of the product (dansylated polyacrylamide) make it a suitable fluorophore for different applications.

### EXPERIMENTAL

Polyacrylamide was purchased from Merck chemical company or synthesized by known procedures in our laboratory. Dansyl chloride was purchased from merck chemical company. H-NMR spectra was run by a 500 MHz Bruker DRX system. FT-IR spectra was run by a Bruker Tensor-27 system. Spectrofluorimetric investigations were performed by a Shimadzu

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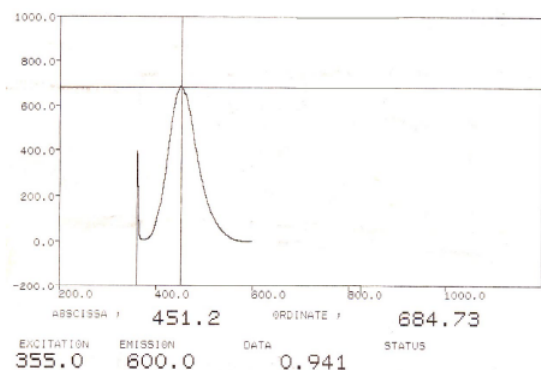


Figure 1 : spectrofluorimetry spectra of dansylated polyacrylamide

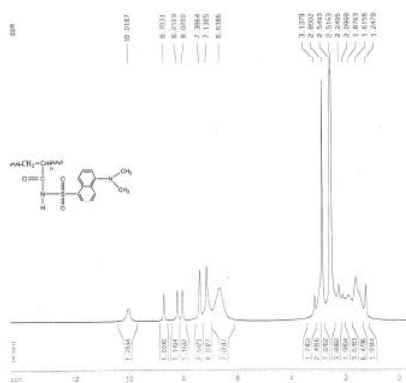


Figure 2 : <sup>1</sup>H-NMR spectra of dansylated polyacrylamide

3100 instrument.

### Preparation of fluorescent polyacrylamide

0.45gr of polyacrylamide, 10ml distilled water, 2.5ml 1.2% sodium hydroxide was added into a 100ml two necked round bottomed flask equipped with a magnetic stirrer and reflux condenser. 0.055gr dansyl chloride in 5ml methanol was added to the mixture from the side neck of the balloon. The mixture was well stirred under reflux condition for 1.5h. At the end of the reaction time, the mixture was cooled to room temperature and extracted with diethyl ether to remove any unreacted dansyl chloride from the mixture. The aqueous layer was dried by evaporation of the water. The product was washed by aliquots of distilled water several times and dried in a dark place overnight. The pure fluorescent polyacrylamide was obtained.

### RESULT AND DISCUSSION

In a proposed nucleophilic substitution mecha-

nism the sodium hydroxide will abstract the amide hydrogen of Polyacrylamide and the nucleophilic -NH<sup>-</sup> will attack to the -SO<sub>2</sub>- group of dansyl chloride. As a result the -SO<sub>2</sub>-NH- bond will form between the polymer and dansyl group. Substitution of 5-N,N dimethyl naphthalene sulfonyl group (dansyl) on the polyacrylamide was well done and established by the NMR spectra of the product (figure 2). The fluorescent properties of the polymer was measured by determination of its maximum emission wavelength which occurred at 451nm (figure 1). It shows very good fluorescent emission under uv lamp.

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