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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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Online publication date: 10 July 2003

To cite this Article Yang, Suizhou , Wu, Xiaodong , Wang, Xianyan , Samuelson, Lynne A. , Cholli, Ashok L. and Kumar, Jayant(2003) 'Synthesis and Characterization of Fluorescent Cellulose', *Journal of Macromolecular Science, Part A*, 40: 12, 1275 – 1282

To link to this Article: DOI: 10.1081/MA-120025307

URL: <http://dx.doi.org/10.1081/MA-120025307>

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Synthesis and Characterization of Fluorescent Cellulose[#]

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ABSTRACT

A new cellulose based fluorescent polymer has been successfully synthesized by esterification of 1-pyrenebutyric acid and cellulose. This polymer was characterized by solid state ¹³C cross-polarization/magic angle spinning (CP/MAS) nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR), ultra-violet-visible (UV-VIS) and fluorescence spectroscopic techniques. Spectroscopic results show that the pyrene chromophores have been covalently linked to cellulose. The quenching of fluorescence of by dinitrotoluene (DNT) follows the Stern–Volmer relationship. This suggests the potential use of this polymer in sensor and other applications.

Key Words: Cellulose; Fluorescence; Esterification; Quenching.

INTRODUCTION

Cellulose, naturally occurring in most plants, some algae, and bacteria, is a ubiquitous and renewable biopolymer and has provided needs of humans for thousands of years. It has

[#]Dedicated to the memory of Professor Sukant K. Tripathy.

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been used in a variety of ways in everyday life, such as textiles, papermaking, food processing, packaging, building materials, and pharmaceuticals. Its derivatives are also used to meet the increasing needs of consumers. Cellulose can also be used in its derivative forms in a wide variety of application. The linking of fluorophores to cellulose will provide potential applications.

Cellulose is a linear polymer in which the anhydroglucose units alternate up and down and are joined together by β -1,4-glycosidic bonds. Every glucose unit contains three hydroxyl groups, one primary alcohol, and two secondary alcohols. These hydroxyl groups could be the coupling sites of the fluorescence chromophores. In this paper, we report a one-pot synthesis of fluorescent cellulose (F-cellulose) by covalently linking of fluorescence chromophores to the cellulose.

EXPERIMENTAL

Reagents and Materials

Cellulose with a molecular weight ca. 5.8×10^8 was obtained from Aldrich Company. 1-Pyrenebutyric acid, *N,N'*-carbonyldiimidazole (CDI), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and anhydrous *N,N*-dimethyl formamide (DMF) were supplied by Fisher Scientific Company and used as received.

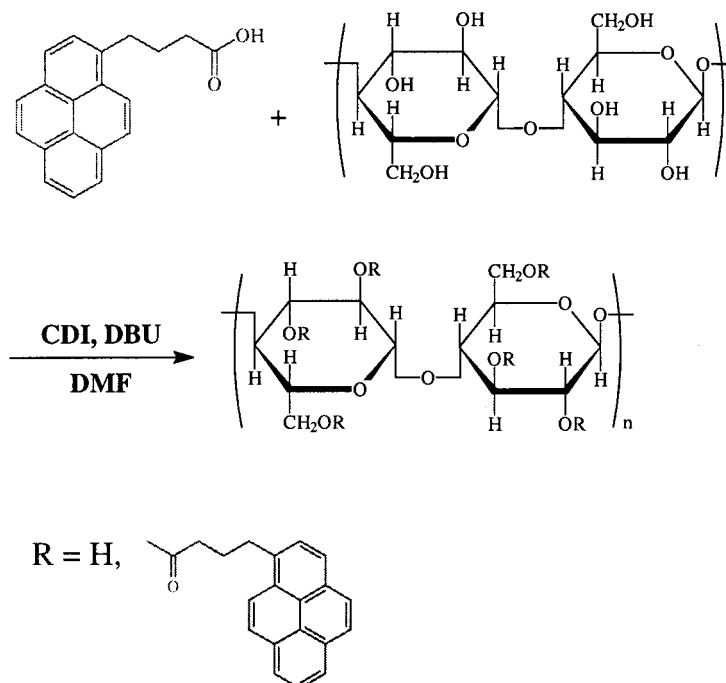
Synthesis of Cellulose with Fluorescence Cellulose

Fluorescent cellulose was synthesized through the ester formation of cellulose and 1-pyrenebutyric acid using a one-pot method^[1] (Sch. 1). Cellulose (0.50 g, 3.1 mmol glucopyranose units), 1-pyrenebutyric acid (0.9 g, 3.1 mmol), and DBU (0.48 g, 3.1 mmol) were added into 50 mL of anhydrous DMF in a 250 mL flask that was cooled in the ice bath. *N,N'*-Carbonyldiimidazole (0.5 g, 3.1 mmol) was then added to this mixture. After stirring for one week at room temperature under nitrogen atmosphere, the mixture was then added into 150 mL of methanol and the precipitated material was isolated by centrifuge. The polymer was purified by repeated dissolution and precipitation with DMF and methanol, respectively. Finally, it was washed with 10% hydrochloric acid, water, aqueous 10% potassium carbonate, and methanol, and was dried in vacuum at 60°C. The degree of substitution (DS) is about 0.1 per anhydroglucose unit. It is determined based on the molar extinction coefficient of 1-pyrenebutyric acid ($\lambda_{\max} = 341 \text{ nm}$, $\epsilon_{\max} = 2.77 \times 10^4$) in DMF dilute solution.

Characterization

The solid-state ^{13}C cross-polarization/magic angle spinning (CP/MAS) nuclear magnetic resonance (NMR) spectra were obtained on a Bruker DRX 300 MHz NMR spectrometer operating at a frequency 75.46 MHz. Contact time of 2 ms and proton $\pi/2$ pulse width of 4.7 μs was used; 2048 data points were collected with a recycle time of 3 s at MAS of 10 KHz. A total number of 15,000 free induction decays (FIDs) were co-added from the sample packed in a 4 mm rotor. All the data were collected at room temperature.





Scheme 1. Synthesis of fluorescent cellulose.

The UV-VIS absorption spectra were recorded using a Perkin-Elmer Lambda 9 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 1720 FTIR spectrometer. The KBr pellets were prepared by using thermally treated KBr powder for all samples. Fluorescence spectra measurements were performed using Perkin-Elmer LS55 Luminescence spectrometer.

RESULTS AND DISCUSSION

Figure 1 shows the ^{13}C CP/MAS NMR spectra of cellulose, F-cellulose, and 1-pyrenebutyric acid (F-Dye). The assignments of solid-state ^{13}C NMR resonance peaks for cellulose were based on the work of Atalla and Vanderhart^[2,3] and our previous work.^[4] The sharp peak at 65.4 ppm in the top spectrum is attributed to C6, the primary alcohol groups. The resonances for the ring carbons C2, C3, and C5 appear in the 70–80 ppm chemical shift range. The resonance peak at 89.2 ppm corresponds to the carbon C4. The most down field peak, at 105.5 ppm, is assigned to C1, the anomeric carbon. In the case of cellulose, the resonances for crystalline and amorphous domains are observed in the solid state ^{13}C NMR spectrum.^[2,3] Normally, the resonances due to crystalline domains appear as narrow peaks, and broad peaks for amorphous domains.^[2,3] The shoulder peaks for the C6 and C4 carbons (63.2 and 84.6 ppm) are associated with the amorphous regions of the cellulose. The ^{13}C CP/MAS spectrum of 1-pyrenebutyric acid (F-dye) is shown in the



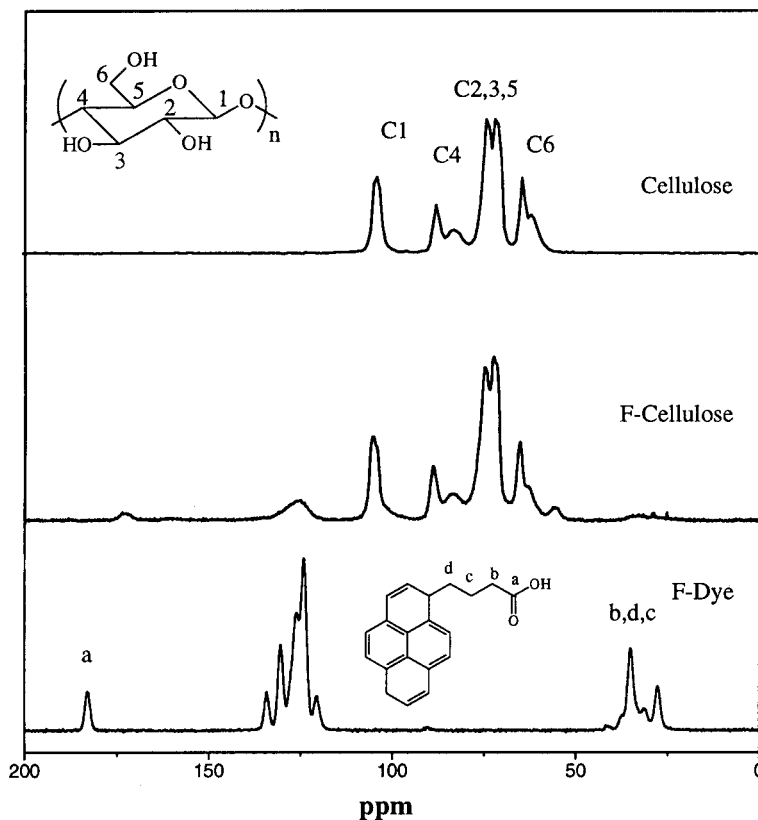


Figure 1. ^{13}C CP/MAS spectra of cellulose, F-cellulose, and 1-pyrenebutyric acid (F-dye).

bottom of Fig. 1. The peaks around 116–136 ppm are attributed to aromatic carbons in pyrene ring. The methene carbons, b, d and c, appear in the 22–40 ppm range. The most downfield peak at 182.9 ppm is attributed to carbonyl carbon of the carboxylic acid. In the ^{13}C CP/MAS NMR spectrum of F-cellulose, the peaks appearing in 116–136 ppm are attributed to pyrene carbons that are linked to the cellulose. The broad peaks in 22–40 ppm are attributed to the methene carbons in the fluorescence chromophore. As a result of the esterification, the carbonyl carbon of the ester appears at 172.7 ppm, a 10 ppm upfield shift from the carbonyl carbon of 1-pyrenebutyric acid. In addition, another broad peak appears at 55.9 ppm, which is associated with the carbons of alcohol (C6) after the formation of an ester bond. The relative intensity of the amorphous peak, C6, is decreased compared to its crystalline peak. Thus, the solid state ^{13}C NMR indicates that the primary coupling of F-dye is at the primary alcohol (C6). It also suggests the coupling may also take place at C2 and C3 carbons, since the relative intensities of resonances for C2, C3, and C5 in 70–80 ppm region are also changed after esterification (middle spectrum). The analyses of solid-state NMR data suggest that the pyrene chromophores are covalently linked to cellulose.

The FTIR spectra of cellulose, F-cellulose and 1-pyrenebutyric acid (F-dye) are shown in Fig. 2. As a result of the reaction, the characteristic peaks arising from the F-cellulose



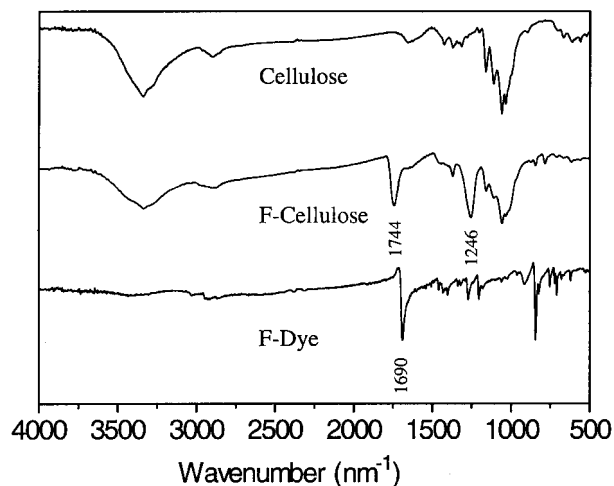


Figure 2. Fourier transform infrared spectra of cellulose, F-cellulose, and 1-pyrenebutyric acid (F-dye).

can be easily identified in its spectrum if compared with the spectra of cellulose and F-dye. In the spectrum of the F-dye, the characteristic absorption band at 1690 cm^{-1} is attributed to the C=O stretching of carboxylic acid. After esterification, the band attributed to C=O stretching appears at 1744 cm^{-1} in the spectrum of F-cellulose. Correspondingly, a strong vibration band at 1246 cm^{-1} is associated with C—O—C stretching of the ester. These observations, along with solid state NMR data, strongly suggest the ester formation as a result of coupling of 1-pyrenebutyric acid and cellulose.

Figure 3 shows the UV-VIS and fluorescence emission (excitation 341 nm) spectra of 1-pyrenebutyric acid (F-Dye) and F-cellulose. In the UV-VIS spectrum, F-Dye has strong absorbance at 325 nm and

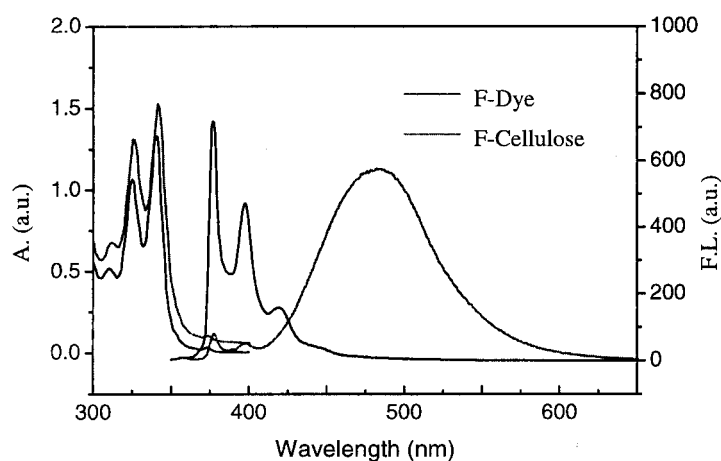


Figure 3. UV-VIS and fluorescence emission (excitation 341 nm) spectra of 1-pyrenebutyric acid (F-dye) and F-cellulose in DMF.



341 nm, and F-cellulose exhibits a similar UV-VIS spectrum as of 1-pyrenebutyric acid. For the fluorescence emission spectrum with an excitation wavelength at 341 nm, 1-pyrenebutyric acid shows strong peaks at 377 and 398 nm with a shoulder at 420 nm. However, the F-cellulose features a broad peak with maximum emission at 482 nm and two small peaks at 377 and 398 nm. This change in fluorescence may be due to the formation of the pyrene excimer. Cellulose and F-cellulose samples are shown in Fig. 4. Sample A is cellulose, and sample B is F-cellulose. The sample B under UV irradiation shows a blue fluorescence.

Fluorescence can be quenched by electron-deficient (i.e., electron accepting) molecules or species due to interaction with these species before fluorescing back to the ground state. Thus, the exciton will be quenched and no fluorescence is observed from the excitation of the chromophore. This quenching behavior can be used in sensor applications to detect the electron-deficient molecules. Figure 5 shows a series of fluorescence spectra of the F-cellulose polymer in DMF quenched by adding the solution of an explosive simulant, dinitrotoluene (DNT), in DMF. The intensity of the fluorescence peak decreased with increasing the concentration of DNT. As shown in Fig. 6, the quenching follows a conventional "Stern–Volmer" equation: $I_0/I = 1 + K_{sv} [Q]$,^[5] where I_0 and I are the fluorescence intensities in the absence and presence of the quencher (DNT) respectively, $[Q]$ is the quencher (DNT) concentration, and K_{sv} is the Stern–Volmer quenching constant, which defines the sensitivity to the quencher. In this case, the Stern–Volmer constant K_{sv} of the fluorescent polymer, is 2.03×10^3 .

CONCLUSION

We have successively synthesized cellulose with fluorescent properties in a one-pot synthetic procedure at room temperature. The ^{13}C CP/MAS solid state NMR and FTIR

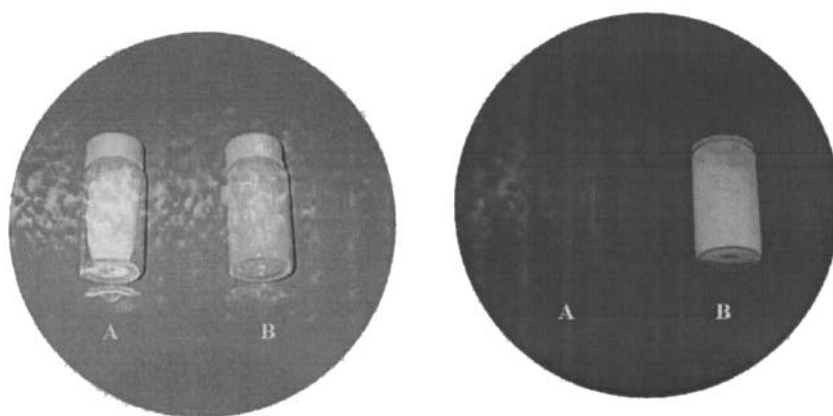


Figure 4. Cellulose (A) and F-cellulose (B) samples (left) and samples under UV irradiation (right).

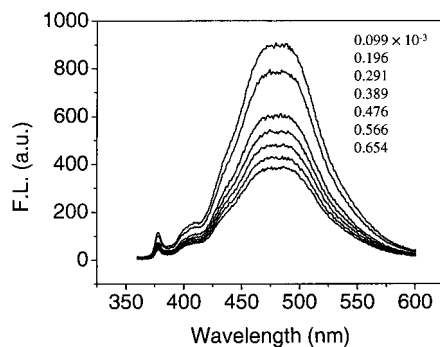


Figure 5. Fluorescence emission spectra of F-cellulose with DNT concentration in DMF.

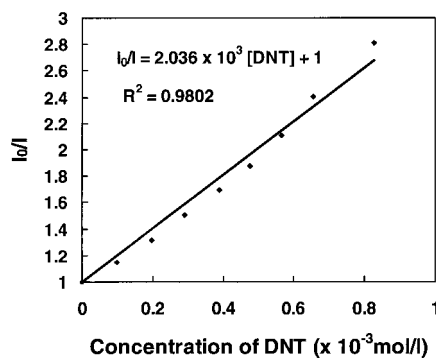


Figure 6. Stern–Volmer plot for the fluorescence quenching of F-cellulose by DNT concentration in DMF solution.

data suggested that fluorophores are covalently linked to the cellulose main chains. The fluorescence of this polymer, quenched by DNT, follows the Stern–Volmer relationship indicating its potential sensor applications.

ACKNOWLEDGMENTS

Financial support from the National Science Foundation (DMR0075170) and the Office of Naval Research (N0001490J1148) are gratefully acknowledged.

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