

Preparation of the New Derivatives of Cellulose and Oligomeric Species of Cellulose Containing Magneson II Chromophore

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ABSTRACT: Fully acetylated cellulose triacetate (CTA) was hydrolyzed in the presence of hydronium ions in a solution of acetic acid and concentrated sulfuric acid to give a hydroxyl-terminated cellulose triacetate oligomers (HCTA). By using gel permeation chromatography (GPC) analysis, the molecular weight of the isolated oligomeric product was calculated to be 3748 Da. HCTA was converted to their new derivatives having 4-(4-nitrophenylazo)-1-naphthol (magneson II) as a chromophore. Then 4'-bromobutoxy-4-(4-nitrophenylazo) naphthalene was synthesized from the reaction of 4-(4-nitrophenylazo)-1-naphthol with 1,4-dibromobutane. The

synthesized alkylated chromophore was reacted with oligomeric cellulose and cellulose itself in the solution of dimethyl sulfoxide to produce cellulose ethers containing the desired chromophore. In the last step, the isolated compounds were used for the preparation of new polymers and oligomers, which contain both of dodecane and butoxy-4-(4-nitrophenylazo)naphthalene as the alkyl side chains in their backbone. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 4034–4039, 2008

Key words: polysaccharides; degree of polymerization (DP); synthesis

INTRODUCTION

Polymer science have had its beginnings with the identification of cellulose. The practical importance of cellulose as the most abundant and a renewable source of natural polymer is well known.^{1,2} However, two areas of recent progress posing scientific problems and technical challenges may be mentioned briefly, i.e., (i) introducing many new organic solvent systems for cellulose, some of them for the transformation of cellulose into threads of regenerated cellulose; (ii) a continuous diversification of chemical products manufactured by chemical transformation of cellulose, especially for the soluble cellulose ethers used as processing aids.^{3–12} Cellulose ethers constitute an important class of cellulose derivatives because of their more stability to chemical conditions than other derivatives such as esters.¹³ Cellulose ethers also typically synthesized by reaction of alkali cellulose with alkyl halides or epoxides.¹⁴ This heterogeneous reaction conditions results to ether derivatives with three disadvantages: (i) water can react in other undesired reactions; (ii) heterogeneous conditions may prevent from penetration of reagents into the parent cellulose; and (iii) longer chain alkylating reagents are insoluble in water.^{15,16} Application of SO₂-DEA-DMSO as a non-

aqueous solvent system have been used to the preparation of a wide variety of tri-*O*-alkyl cellulose derivatives under mild conditions.¹⁷ Also, an alternative approach has been reported to achieve better results for the preparation of cellulose ethers under homogeneous reaction condition with employing soluble cellulose derivatives as starting materials rather than cellulose itself.¹⁸

With this procedure, new cellulosic derivatives containing various alkylated groups can be conveniently prepared.^{18–20} On the other hand, the obtained compounds, like some other natural and biocompatible compounds, have potential applications as the Langmuir–Blodgett films in the different fields and have been appreciated.^{21–27} The Langmuir–Blodgett films in comparison with the common films have some advantages such as high degree of molecular orientation, precise control of film thickness at the molecular level, control of layer architecture, high optical stability for optical processes, and building up noncentrosymmetric structures for second-order nonlinear optics.^{28–30} Based on hairy-rod concept, several types of macromolecules namely rigid-rod-like polymers, could decorate with flexible alkyl side chains, has been used to construct stable and homogeneous ultrathin films by the Langmuir–Blodgett technique. Among these macromolecules, the incompletely alkylated cellulose derivatives, which contain free hydroxyl functions, are one of the most suitable candidates to construct regular ultrathin multilayers by Langmuir–Blodgett technique with respect to their practical applications.^{31,32} It has been shown

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TABLE I
Reaction Conditions Employed for the Preparation of Copolymers of (Dodecyl)
[4'-butoxy-4-(4-nitrophenylazo)naphthalene] CTA and (Dodecyl)
[4'-butoxy-4-(4-nitrophenylazo)naphthalene] HCTA

Sample	Step 1 (R-Br) ^a	T ₁ (h)	t ₁ (°C)	Step 2 (R-Br)	T ₂ (h)	t ₂ (°C)
a*	3.95 (3.3)	23	70	13 (20)	60	90
b*	3.95 (3.3)	23	70	13.5 (20)	40	80

^a The mol ratio of R-Br (3.95) to the three substitution sites (3.3).

* 7 mL DMSO added after 30 h of second alkylation reaction; **a**: CTA and **b**: HCTA.

that a different class of cellulose derivatives, such as cellulose alkyl ethers with degrees of substitution (DS) near to 3, form monolayers at the air/water interface that can be transferred onto solid substrates.^{32,33} For this purpose, it is necessary to vary the hydrophobicity of the multilayers or to induce the functional groups into the polymer film, which is the subject of this report. Regarding the fact that the realization of nonlinear optics utilities requires the incorporation of appropriate active chromophores into the systems possessing mechanical properties, here, we report the preparation and characterization of such materials to produce alkylated cellulose derivatives consisting of magnesium II chromophore.

EXPERIMENTAL

Materials

Cellulose triacetate (CTA) was purchased from Fluka (M_w , 72,000–74,000) and was dried at 105°C for 3 h in air before use. 1-Bromododecane (Merck) and 4-(4-nitrophenylazo)-1-naphthol (Merck) were used without further purification.

Characterization

¹H NMR spectra were recorded on a Bruker-NMR 400 MHz spectrometer, IR spectra were recorded on a Shimadzu model FTIR 8101N spectrometer, gel permeation chromatography (GPC) analyses were performed using a GPC Waters 150°C with polystyrene (PSt) as the standard (column, ultra styragel 10⁴, 10⁵, and 10⁶ Å; detector, RI; flow rate 1.0 mL/min; column temperature 30°C), viscosimetry was performed using Oswald viscometer, Perkin-Elmer differential scanning calorimeter (DSC) was used to determine the thermal transitions of the polymers and scanning rate was 10°C/min.

Depolymerization of CTA

Twenty grams of CTA (inherent viscosity 6.37 dL/g in DMF, at 25°C) was depolymerized using 200 g hot glacial acetic acid solution (99.9%). A quantity of

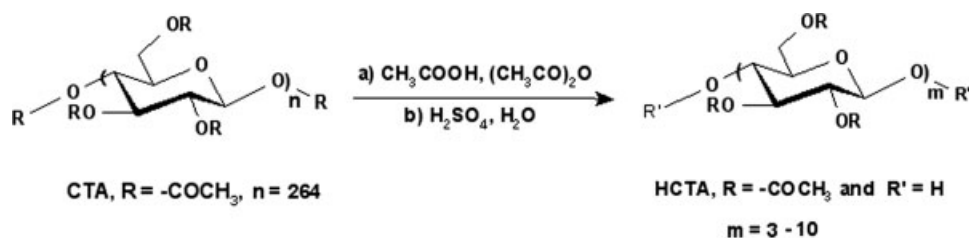
3.3 mL acetic anhydride was added to the solution of CTA and 1.0 mL concentrated sulfuric acid was gradually added as catalyst in 2 min. Also, 1.2 mL water was added to the solution and stirred at 80°C for 7 h and cooled to 35°C. The catalyst was neutralized by adding 15 mL of a 21% aqueous solution of Mg(AcO)₂ to the reaction. The resulted product was worked-up with the addition of excess diethyl ether in which milky precipitate was formed. The precipitate was washed with ethanol (10 mL) and then with water (10 mL). The obtained white powder was soluble in dichloromethane, mp 161.97°C; Yield 89%. Inherent viscosity was measured 1.92 dL/g in DMF as solvent at 25°C.

Preparation of 4'-bromobutoxy-4-(4-nitrophenylazo)naphthalene

A solution containing 4-(4-nitrophenylazo)-1-naphthol (1 g, 3.4 mmol), dichloromethane 100 mL, benzyltriethylammonium chloride 800 mg, and aqueous sodium hydroxide 50% (50 mL) was prepared. Then about 10-fold excess molar relative to chromophore from 1,4-dibromobutane was added and the mixture was stirred at 40°C for 1 h. The dichloromethane was removed by evaporation, and the residue was extracted by chloroform. The chloroform layer was washed with water and dried over Na₂SO₄ overnight. Then chloroform was evaporated and excess dibromobutane was removed by heating at 80°C under the vacuum. Purification of crude compound accomplished using column chromatography, using *n*-hexane/dichloromethane (2/1 : v/v) as eluent. The desired compound was obtained in solid form, mp 136°C, synthesized by 66% yield.

Preparation of cellulose and oligomeric species of cellulose ethers containing magnesium II

A modified method reported in literature was employed.³⁴ CTA (250 mg, 0.003 mmol) was dissolved in a solution of DMSO 30 mL and water 0.5 mL under nitrogen. After stirring at room temperature for 1 h, the powder NaOH was added (12.5M excess relative to the three substitution sites per glucose unit). The solution was stirred for an additional



Scheme 1 Depolymerization reaction of CTA in acidic conditions.

hour and then heated to $t_1^\circ\text{C}$ (see Table I) before the introduction of 4'-bromobutoxy-4-(4-nitrophenylazo)-naphthalene. The reaction was allowed to proceed for time T_1 and then heated to $t_2^\circ\text{C}$ before adding the second alkylating agent, 1-bromododecane. The reaction was allowed to continue for an additional hours T_2 and in the end compound (dodecyl) [4'-butoxy-4-(4-nitrophenylazo)naphthalene] CTA was obtained. (Dodecyl) [4'-butoxy-4-(4-nitrophenylazo)-naphthalene] hydroxyl-terminated cellulose triacetate oligomers (HCTA) was prepared from HCTA (250 mg, 0.66 mmol) in the same way, but with varying the reaction conditions, temperature, and the amounts of alkylating reagents. The exact reaction conditions summarized in Table I. The resulted products were isolated by precipitation in 80 mL of cold water and followed by extraction with methylene chloride. The crude product was purified by repeated dissolution and precipitation in the solvent/nonsolvent pair of $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$. Yield about 90%.

RESULTS AND DISCUSSION

Depolymerization and characterization of CTA

Among the blocking groups upon the C_2 -, C_3 -, and C_6 -hydroxyls of the anhydroglucose units, the acetyl group is obviously one of the choice because of its easily removing. However, it is important to mention that the acetyl blocking groups in the backbone of CTA are not inadvertently removed during the depolymerization reaction of primary CTA. The resistance of acetyl groups in hydrolyzing reaction condition is relatively good and prevents from occurring the additional blocking reactions. Actually, the attempts to minimize the unwanted reactions has been made with applying weak acidic condition to achieve the highest yield of the difunctional CTA blocks. The DS of oligomeric blocks should be close to 3 as much as possible (Scheme 1).

The molecular weights of CTA before hydrolyzing and after hydrolyzing (HCTA) were measured using GPC instrument. It was indicated that M_n (number-average molecular weight) of 73,000, while in the same condition the oligomeric cellulose (HCTA), M_n

is 3748 with polydispersity 1.4 (CTA, $n = 264$ gives HCTA, $m = 3-10$; n and m are the anhydroglucose units numbers) (Fig. 1).

The GPC chromatogram of HCTA (Fig. 1) indicates a relatively narrow molecular weight distributions. The DSC spectrum (Fig. 2) depicts that the T_g of the HCTA oligomer is 59.44°C .

The FTIR spectrum showed the expected relatively strong hydroxyl stretching absorption at 3508 cm^{-1} due to the hydroxyl-terminated end groups and a strong carbonyl absorption at 1757 cm^{-1} for the acetyl groups of obtained HTCA.

Preparation and characterization of 4'-bromobutoxy-4-(4-nitrophenylazo)naphthalene

To produce the cellulose and oligomeric species of cellulose derivatives containing 4-(4-nitrophenylazo)-1-naphthol (magneson II), a variety of procedures for preparation of cellulose ethers has been reported. The chromophore magneson II has some advantage for this purpose because of its proper structure and having acceptor-donor groups, aromatic rings with electric connection, which is enough stable in substitution step without any significant problems. To activate the magneson II, it was reacted with excess 1,4-dibromobutane and 4'-bromobutoxy-4-(4-nitrophenylazo)naphthalene was obtained (Scheme 2).

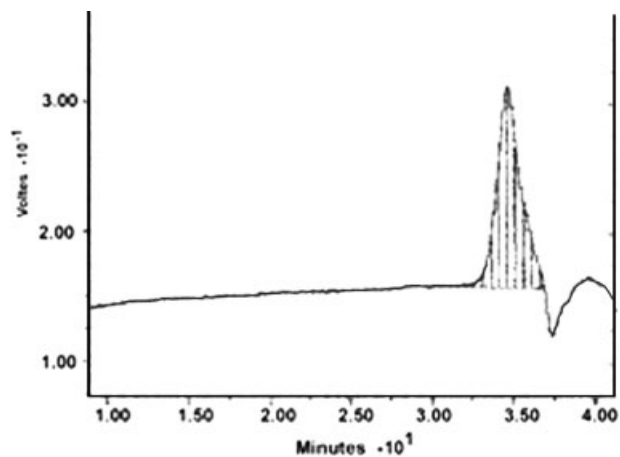


Figure 1 GPC chromatogram of HCTA.

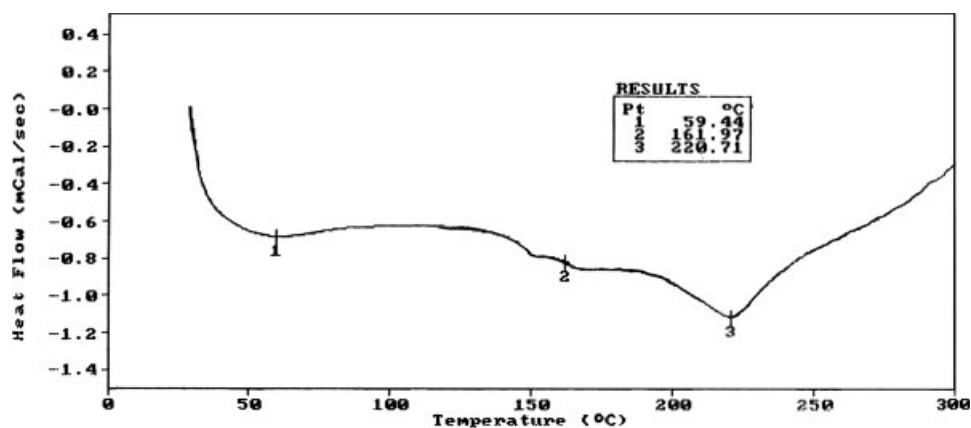


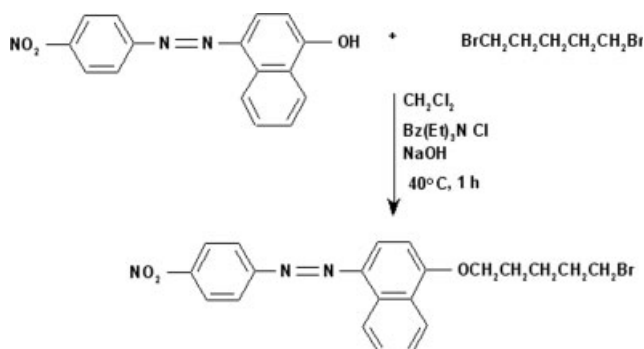
Figure 2 DSC chromatogram of HCTA.

As shown in the ^1H NMR spectrum (Fig. 3), the signals of aromatic protons are at the regions between 6.62 and 8.98 ppm with relative integration 10.7 and aliphatic protons between 2.16 and 4.33 ppm with relative integration 8.4 corresponding to 10 and 8 Hs aromatic aliphatic protons, respectively.

Preparation and characterization of cellulose and oligomeric species of cellulose ethers containing magnesium II

The reaction consists of a base-catalyzed deacetylation to generate the cellulose alkoxide ions, which in turn reacts with the alkyl halide to produce ether derivatives. Here, the cellulose ether containing 4'-bromobutoxy-4-(4-nitrophenylazo)naphthalene was prepared by a two-step alkylation procedure, which is outlined in Scheme 3.

As shown in Table I, various reaction conditions were employed to obtain a series of products (denoted with letters a and b). In general, partial alkylation of cellulose by 4'-bromobutoxy-4-(4-nitrophenylazo)naphthalene achieved in the first step of the reaction sequence followed by the subsequent



Scheme 2 Preparation of 4'-bromobutoxy-4-(4-nitrophenylazo)naphthalene.

substitution of unreacted sites with 1-bromododecane. Finally, the compounds (dodecyl) [4'-butoxy-4-(4-nitrophenylazo)naphthalene] CTA and (dodecyl) [4'-butoxy-4-(4-nitrophenylazo)naphthalene] HCTA were successfully synthesized through the same procedure, which we explained in experimental section.

The FTIR spectrum of the produced CTA derivative was shown in Figure 4. The absence of significant absorption at 1749 cm^{-1} , which is the characteristic frequency of carbonyl group in CTA and HCTA blocks, demonstrates that deacetylation was completed. Moreover, the absence or the presence of a very weak intensities of hydroxyl bands at

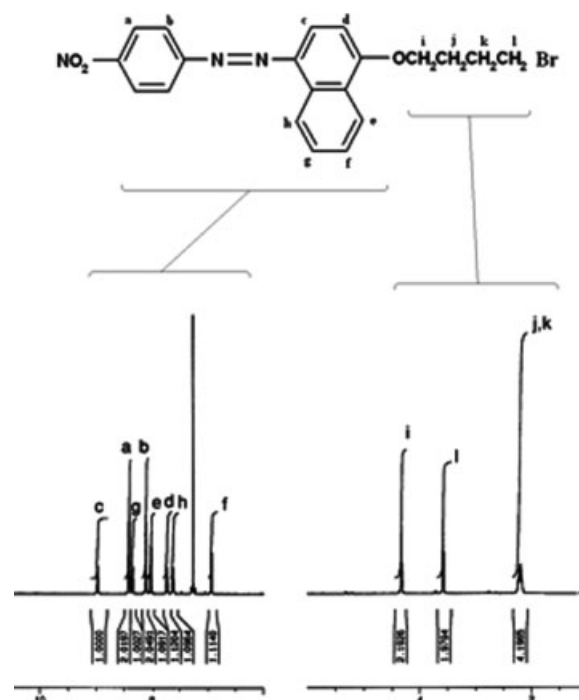
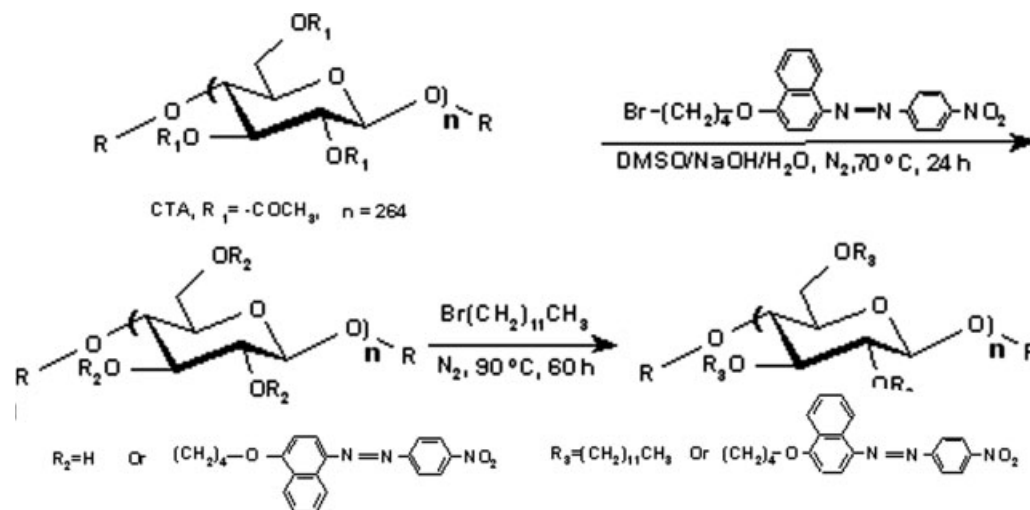


Figure 3 ^1H NMR spectrum of 4'-bromobutoxy-4-(4-nitrophenylazo)naphthalene in CDCl_3 .



Scheme 3 General reaction employed to the preparation of decorated hairy-rod amphiphiles of cellulose, oligocellulose, and its copolymers.

3300–3500 cm^{-1} for CTA-co-PEG, 2000 and HCTA-co-PEG, 2000, respectively, indicated the achievement of relatively high degrees of alkyl substitution. Also, the presence of strong double branch band at 2860 and 2930 cm^{-1} assigned to $-\text{CH}_2-$ and $-\text{CH}_3$ stretching vibrations are representative of complete etherification of copolymers. It should be noted that the spectra presented in Figure 4 were recorded from the sample films cast on KBr substrates, and probably, a contribution from water cannot be neglected in the film spectra. The presence of chromophore in samples a and b is clear from the characteristic vibrations at 2310, 1580, 1525, 1464, 1385, 1300, and 777 cm^{-1} .

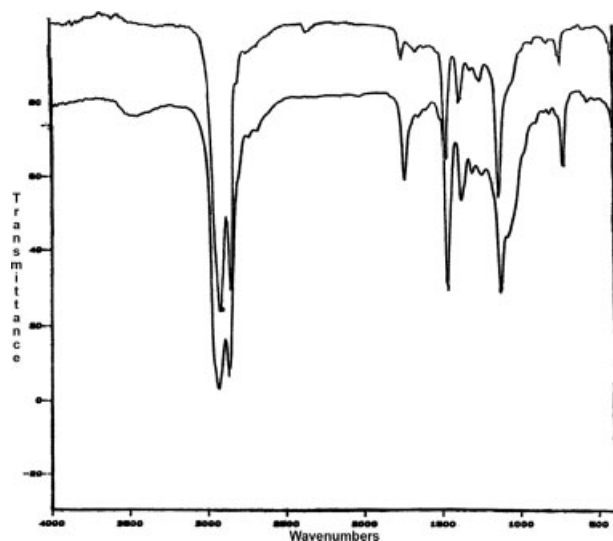


Figure 4 FTIR spectra of sample a (above) and b (below) as defined in Table I. Spectra were recorded from film cast on KBr windows.

CONCLUSIONS

New derivatives of cellulose and also oligomeric species of cellulose containing the 4-(4-nitrophenylazo)-1-naphthol chromophore were conveniently prepared from CTA and oligomeric species of CTA with 4'-bromobutoxy-4-(4-nitrophenylazo)naphthalene and dodecyl bromide. Highly substituted compounds containing different type of ether linkages were obtained with successive introduction of two different alkylating agents. The new isolated derivatives of cellulose containing magnesium II chromophore potentially could be utilized for the different applications. Our developed approach could be applied to the alkylation of other macromolecules which are soluble in DMSO such as polyvinyl acetate, polyvinyl alcohol, chitin triacetate, and amylose triacetate.

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