

# Preparation of Cellulose Derivatives Containing Carbazole Chromophore

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**ABSTRACT:** Cellulose derivatives containing long hydrocarbon side chains and the carbazole chromophore are prepared. *N*-4'-Bromobutylcarbazole is first synthesized from carbazole and 1,4-dibromobutane. Alkylated carbazole is then reacted with cellulose acetate in dimethyl sulfoxide solution to produce cellulose ethers containing the desired chromophore. Polymers containing a mixture of alkyl side chains are also prepared by the subsequent addition of 1-bromododecane to the reaction mixture. Characterization of the resulting cellulose derivatives by FTIR spectroscopy indicates that the deacetylation of cellulose acetate and the subsequent etherification are both complete. In addition, the incorporation of the carbazole chromophore is clearly shown by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy. Polymers of different carbazole content, ranging from 2.9 to 1.1 chromophores per anhydroglucose repeat unit, are obtained by varying the reaction conditions. Substitution is found to be controlled primarily by the quantity of alkylating agent introduced while variation of the reaction time has little effect. This method is used to prepare (dodecyl) $_y$ (*N*-4'-carbazolylbutyl) $_x$ cellulose, (decyl) $_y$ (*N*-4'-carbazolylbutyl) $_x$ cellulose, and (butyl) $_y$ (*N*-4'-carbazolylbutyl) $_x$ cellulose. Cellulose acetate can be replaced by (methyl)cellulose as the starting material to obtain analogous products. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2764–2772, 1999

**Key words:** cellulose derivatives; carbazole chromophore; cellulose ethers; Langmuir–Blodgett films

## INTRODUCTION

Polymer science had its beginnings with the characterization of cellulose. Current worldwide interest in cellulose chemistry and technology remains strong, and new derivatives are constantly being considered for a large variety of industrial applications.<sup>1,2</sup> Cellulose is the most widely available renewable organic raw material in the world because it is the chief constituent of nearly all forms of plant life. However, cellulose has not yet reached its potential in many areas of application. The major reason for this is that natural unmod-

ified cellulose is difficult to process because it decomposes before it melts and is insoluble in most solvents. Efforts have been made to find new solvents for converting unmodified cellulose directly into fibers, for the characterization of cellulose material, and for the production of cellulose derivatives.<sup>3</sup>

Alkyl ethers constitute an important class of cellulose derivatives. Ethers are typically more stable to chemical conditions than the other derivatives, such as esters, and thus have found many applications. Cellulose ethers are traditionally prepared by the reaction of cellulose swollen in aqueous alkali with alkyl halides or epoxides.<sup>4</sup> These heterogeneous reaction conditions result in alkyl substitution that is often irregular and incomplete. Furthermore, this method cannot be

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employed to produce alkyl ethers with side chains containing more than three carbon atoms because of the insolubility of longer chain alkylating reagents.

Convenient new synthetic methods that can be carried out under homogeneous reaction conditions are therefore of interest. Isogai et al.<sup>5</sup> compared three different nonaqueous cellulose solvents for preparing tri-*O*-benzylcellulose. The three solvents were the N<sub>2</sub>O<sub>4</sub>-dimethyl sulfoxide (DMSO), SO<sub>2</sub>-diethylamine (DEA)-DMSO, and LiCl-dimethylacetamide (DMAC) systems. These authors concluded that among the three nonaqueous cellulose solvents, the SO<sub>2</sub>-DEA-DMSO system was the best for the preparation of tri-*O*-benzylcellulose. Furthermore, by changing the amounts of sodium hydroxide used, the degree of benzyl substitution could be controlled. The SO<sub>2</sub>-DEA-DMSO solvent system was also employed as a nonaqueous solvent for the preparation of tri-*O*-allyl, tri-*O*-methallyl, and tri-*O*-2-butenylcellulose from the corresponding chlorides under milder conditions.<sup>6</sup> Isogai et al. successfully used the same solvent to prepare a large variety of tri-*O*-alkylcelluloses.<sup>7</sup>

An alternative approach for the preparation of cellulose ethers under homogeneous reaction conditions was reported by Kondo et al.<sup>8</sup> These authors employed soluble cellulose derivatives as starting materials rather than cellulose itself. In this way, fully substituted cellulose alkyl ethers were prepared from cellulose acetate in DMSO solution.<sup>9</sup> Somewhat surprisingly, the addition of a small amount of water to the reaction mixture was found to improve the efficiency of etherification.

In this article we report on the adaptation of this method for the preparation of cellulose derivatives containing the carbazole chromophore. A variety of cellulose ethers have been shown to be suitable materials for the fabrication of ultrathin films by the Langmuir–Blodgett technique.<sup>10,11</sup> In general, stable monolayers can be spread at the air–water interface and successfully transferred to a variety of solid substrates. The potential applications of Langmuir–Blodgett films in fields such as integrated optics and solid-state electronics have long been appreciated. The realization of these applications, however, requires the incorporation of appropriate active chromophores into systems possessing the mechanical properties and stability necessary for the fabrication of actual devices. This article reports on the synthesis and characterization of such materials. Further-

more, the synthetic approach employed allows for the systematic variation of parameters such as the average number of chromophores per anhydroglucose unit and the length of the hydrocarbon side chains. These characteristics, in turn, influence the properties of Langmuir–Blodgett films prepared from these new cellulose derivatives.<sup>12</sup>

## EXPERIMENTAL

### Materials

Methylcellulose (Aldrich, viscosity 15 cp, 2% in water) and cellulose acetate (Aldrich, MW 30,000, acetyl content 39.8%) were dried at 105°C for 3 h in air before use. DMSO (Aldrich) was dried over 3-Å molecular sieves. Carbazole, 1,4-dibromobutane, 1-bromododecane, and benzyltriethylammonium chloride were commercially obtained (Aldrich) and used without further purification.

### Preparation of *N*-4'-Bromobutylcarbazole

*N*-4'-Bromobutylcarbazole was prepared by modification of a previously reported method for the *N*-alkylation of carbazole.<sup>13</sup> A mixture containing carbazole (500 mg, 3 mmol), benzene (1.5 mL), benzyltriethylammonium chloride (25 mg), and aqueous 50% sodium hydroxide (1.5 mL) was prepared. A molar excess (10-fold relative to carbazole) of 1,4-dibromobutane was added, and the mixture was stirred at 40°C for 1 h. The benzene was removed by evaporation and the residue extracted with chloroform. The chloroform layer was washed with water and dried over Na<sub>2</sub>SO<sub>4</sub> overnight. The chloroform was evaporated and excess dibromobutane removed by heating to 80°C under a vacuum. The raw product was recrystallized from benzene.

### Preparation of Cellulose Ethers Containing Carbazole

Cellulose derivatives containing carbazole were prepared by adapting a known method for the synthesis of cellulose alkyl ethers.<sup>9</sup> Cellulose acetate (500 mg) was dissolved in a mixture of DMSO (30 mL) and water (0.5 mL) under nitrogen. After stirring at room temperature for 1 h, finely powered NaOH was added (12.5 molar excess relative to the three substitution sites per anhydroglucose ring). The solution was stirred for an additional hour, then heated to 50°C before the introduction of *N*-4'-bromobutyl carbazole. The

reaction was allowed to proceed for time  $T_1$ , then heated to 70°C before the second alkylating agent, 1-bromododecane, was added. The reaction was allowed to continue for an additional time  $T_2$ . Seven samples of the general type (dodecyl) $_y$ (*N*-4'-carbazolylbutyl) $_x$ cellulose were prepared by varying the reaction times  $T_1$  and  $T_2$  and the amounts of alkylating reagents. The exact conditions are summarized in Table I. Products were isolated by precipitation in 200 mL of distilled water followed by extraction with methylene chloride. The products were purified by repeated dissolution and precipitation in the solvent/nonsolvent pair  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ . Final purification was achieved by gel permeation chromatography (GPC) on Lipophilic Sephadex (Sigma) in  $\text{CHCl}_3$  or  $\text{CH}_2\text{Cl}_2$ . The preparative column was 95 cm in length and had a diameter of 4 cm. A Waters R401 differential refractometer served as the detector. Sample concentrations of about 20 mg/mL were employed and each injection was 2 mL. The flow rate was kept constant at 2 mL/min. Under these conditions the polymeric product appeared as the first peak after about 30–50 min. Additional peaks appearing at longer elution times corresponded to small molecule reagents present in excess, notably 1-bromododecane.

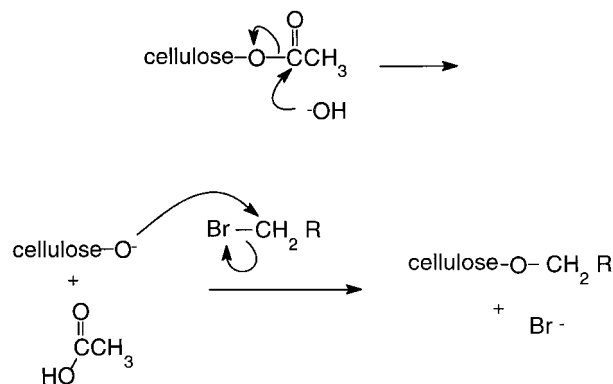
### Characterization

Products were characterized with a Nicolet 550 FTIR and a Bruker 300-MHz NMR spectrometer. IR measurements were made on cast films and

**Table I** Reaction Conditions Employed for Preparation of Polymers of General Type (dodecyl) $_y$ (*N*-4'-carbazolylbutyl) $_x$ Cellulose

Sample	Equiv R-Br Step 1	$T_1$ (h)	Equiv R-Br Step 2	$T_2$ (h)
a	8.8 (A)	22	2.2 (A)	5
b	4.4 (A)	5	9.0 (B)	22
c	2.2 (A)	20	12.8 (B)	7
d	2.2 (A)	15	12.8 (B)	12
e	2.2 (A)	10	12.8 (B)	17
f	2.2 (A)	5	12.8 (B)	22
g	2.2 (B)	5	12.8 (B)	22

$T_1$  and  $T_2$  are the reaction times for the two alkylation steps as defined in Scheme 2. The quantity of alkylating agent (R-Br) added in each step is given as molar equivalents relative to the three substitution sites on the anhydroglucose ring. The alkylating agents are also identified as A, (*N*-4'-bromobutyl)carbazole, or B, 4-bromododecane.

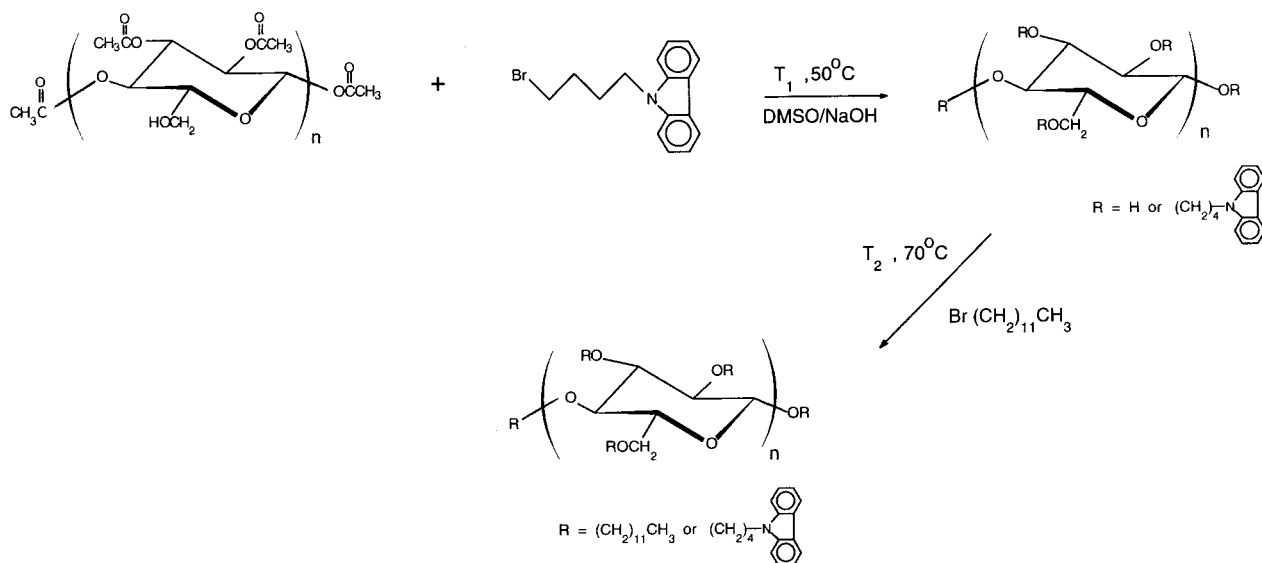


**Scheme 1** Base catalyzed deacetylation of cellulose acetate and subsequent alkylation to yield cellulose ethers.

NMR spectra were recorded in  $\text{CDCl}_3$  solution. Molecular weights were determined by GPC with a Wyatt Optilab 903 refractometer and a Waters model 590 pump. GPC columns were supplied by Shodex and calibration curves were obtained for polystyrene standards (Pressure Chemicals).

## RESULTS AND DISCUSSION

Kondo and Gray showed that highly substituted cellulose ethers can be prepared in homogeneous solution by the reaction of bromoalkanes with cellulose acetate in  $\text{NaOH}/\text{DMSO}$  solution.<sup>9</sup> The reaction consists of a base catalyzed deacetylation to generate the cellulose alkoxide ion, which in turn reacts with the alkyl halide to produce ethers as shown in Scheme 1. In the present work, mixed cellulose ethers containing the carbazole chromophore were prepared by a two-step alkylation procedure outlined in Scheme 2. Various reaction conditions were employed (Table I) to obtain a series of polymers (denoted a–g) of differing carbazole content. In general, partial alkylation of cellulose by *N*-4'-bromobutylcarbazole was achieved in the first step of the reaction sequence followed by the subsequent substitution of unreacted sites with 1-bromododecane. Although the reaction times of the two steps differed from one sample to another, in all cases a total reaction time of 27 h was respected. As shown in Table I, *N*-4'-bromobutylcarbazole was employed as the alkylating agent in both steps of the preparation of sample a in order to obtain (*N*-4'-carbazolylbutyl)cellulose. Similarly, only 1-bromododecane was used in the preparation of sample g to yield



**Scheme 2** Reaction scheme employed to prepare mixed ethers of the general type (dodecyl)<sub>y</sub>(*N*-4'-carbazolylbutyl)<sub>x</sub>cellulose.

(dodecyl)cellulose. Product yields from this route reach 80%.

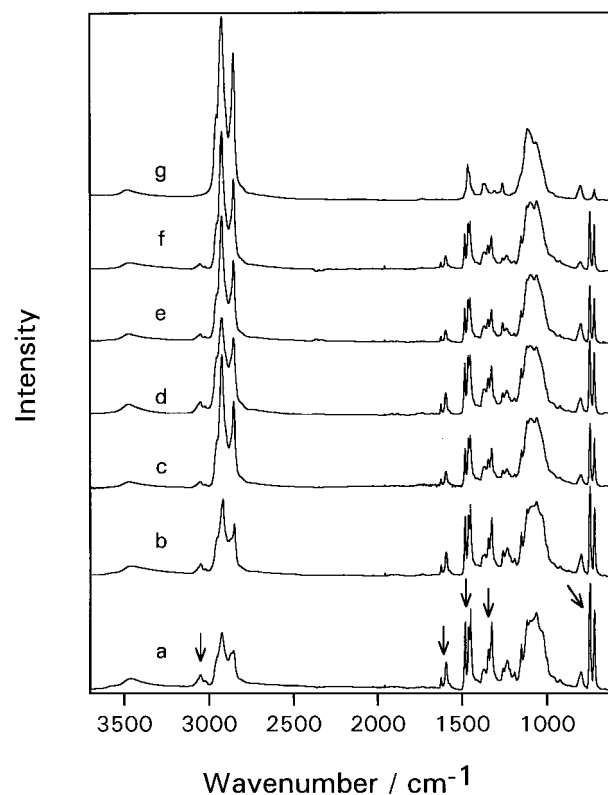
(Decyl)<sub>y</sub>(*N*-4'-carbazolylbutyl)<sub>x</sub>cellulose and (butyl)<sub>y</sub>(*N*-4'-carbazolylbutyl)<sub>x</sub>cellulose were also successfully synthesized by this method. Cellulose acetate can be replaced by methylcellulose to obtain analogous products.

### IR Spectroscopy

The FTIR spectra of the product polymers are shown in Figure 1. The absence of significant absorption at  $1746\text{ cm}^{-1}$ , which is the characteristic carbonyl frequency of cellulose acetate, demonstrates that deacetylation is complete. Furthermore, the weak intensity of the hydroxyl bands at  $3500\text{ cm}^{-1}$  indicates that relatively high degrees of alkyl substitution are achieved. In the dodecylcellulose this method is thus similar to a reaction at room temperature.<sup>10</sup> It should be noted that the spectra presented in Figure 1 were recorded for sample films cast on KBr substrates. The IR spectra of the same samples recorded in chloroform solution exhibited less intense hydroxyl bands. Therefore, a possible contribution from water cannot be neglected in the film spectra.

The presence of carbazole in samples b–g is clear from the characteristic vibrations at 1628, 1597, 1483, 1452, 1346, 1153, 749, and  $723\text{ cm}^{-1}$ . In principle it should be possible to determine the degree of carbazole substitution by comparing the intensity of these bands with one characteristic of the cellulose backbone. In practice this is not pos-

sible because of the contribution of side chain ether linkages and carbazole vibrations to the complex cellulose bands at  $1200\text{--}1000\text{ cm}^{-1}$ .



**Figure 1** FTIR spectra of samples a–g as defined in Table I. Spectra were recorded from films cast on KBr windows.

However, it is possible to quantify the average number of carbazole groups ( $x$ ) relative to the number of dodecyl side chains ( $y$ ) from the ratio of intensities at frequencies characteristic of these two groups. For example, the absorption intensity observed at  $749\text{ cm}^{-1}$ ,  $A_{749}$ , which is assigned to aromatic out of plane C—H bending, relative to that of the symmetric  $\text{CH}_2$  stretching at  $2852\text{ cm}^{-1}$ ,  $A_{2852}$ , is given by

$$\frac{A_{749}}{A_{2852}} = \frac{x\epsilon_{749}}{(11y + 4x)\epsilon_{2852}}$$

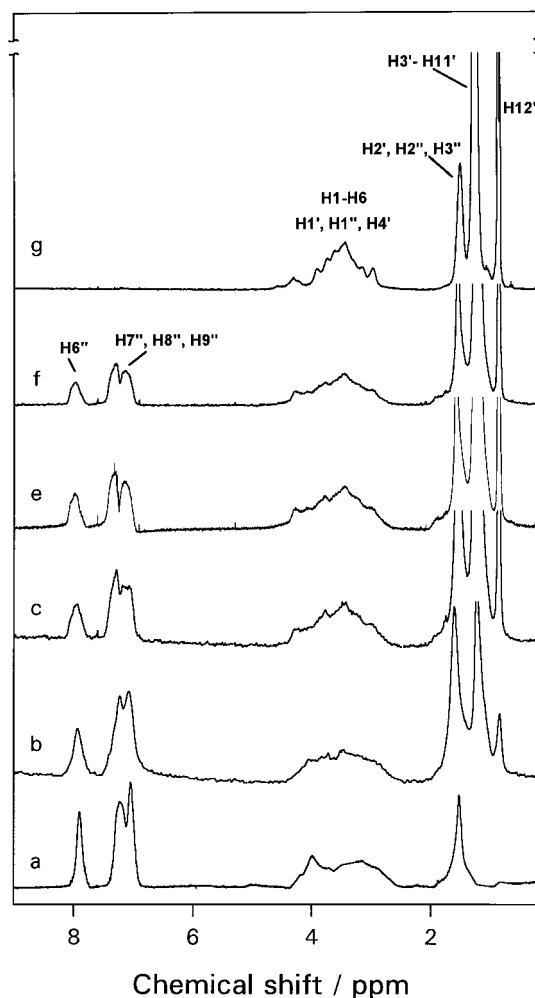
where  $\epsilon_{749}$  and  $\epsilon_{2852}$  are the absorptivities at these two wave numbers. Here it is assumed that the methylene stretching is described by a single absorption coefficient. The ratio of  $\epsilon_{749}/\epsilon_{2852}$  can be calculated from the relative intensities recorded for sample a, (*N*-4'-carbazolylbutyl)cellulose, for which  $y = 0$  because no bromododecane was introduced during the synthesis. The degree of substitution for each of the two types of side chains ( $x$  and  $y$ ) can then be calculated from the relative IR intensities if it is further assumed that  $x + y = 3$  (i.e., hydroxyl substitution is complete). While this assumption is not rigorously true, it is a reasonable simplification as indicated by the IR spectra and the NMR results discussed below. The degree of carbazole substitution ( $x$ ) calculated in this way is given in Table II. The uncertainty of  $\pm 5\%$  associated with these values corresponds to the estimated uncertainty of the spectral integrations.

### NMR Spectroscopy

The  $^1\text{H}$ -NMR spectra of the various product polymers are shown in Figure 2. The corresponding

**Table II** Degree of Carbazole Substitution (DS) Determined from  $^1\text{H}$ -NMR and FTIR Spectra of Samples a–g

Sample	Carbazole DS ( $\pm 5\%$ )	
	$^1\text{H}$ -NMR	IR
a	2.9	—
b	2.1	2.0
c	1.5	1.4
d	1.3	1.5
e	1.2	1.4
f	1.1	1.3
g	0	0



**Figure 2**  $^1\text{H}$  NMR spectra of samples a–g as defined in Table I. Spectra were recorded in  $\text{CDCl}_3$  solution.

peak assignments and relative integrated intensities are summarized in Table III. These spectra can also be used to determine the degree of substitution. However, as noted above, the evaluation of the absolute degree of substitution for either of the two types of side chains requires the quantification of a signal characteristic of the cellulose backbone. In the  $^1\text{H}$ -NMR spectra, this requirement corresponds to the integration of the resonances arising from the anhydroglucose ring protons, which are located from 4.5 to 2.4 ppm. Because of the rigidity of the cellulose backbone, these peaks are relatively broad and their quantitative integration is thus difficult. In addition, the side chain protons labeled in Figure 3 as H-1', H-1'', and H-4'' are also located in this spectral region. For these reasons, the direct determination of absolute degrees of substitution is impos-

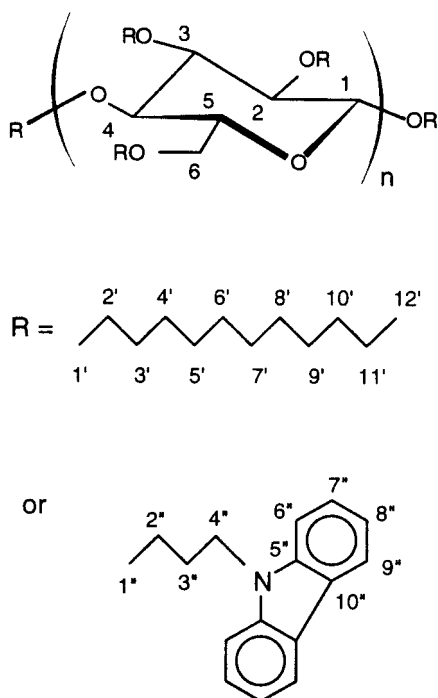


**Table III**  $^1\text{H-NMR}$  Peak Assignments and Relative Intensities for Polymers of General Type  $(\text{dodecyl})_y(\text{N-4'-carbazolylbutyl})_x\text{Cellulose}$

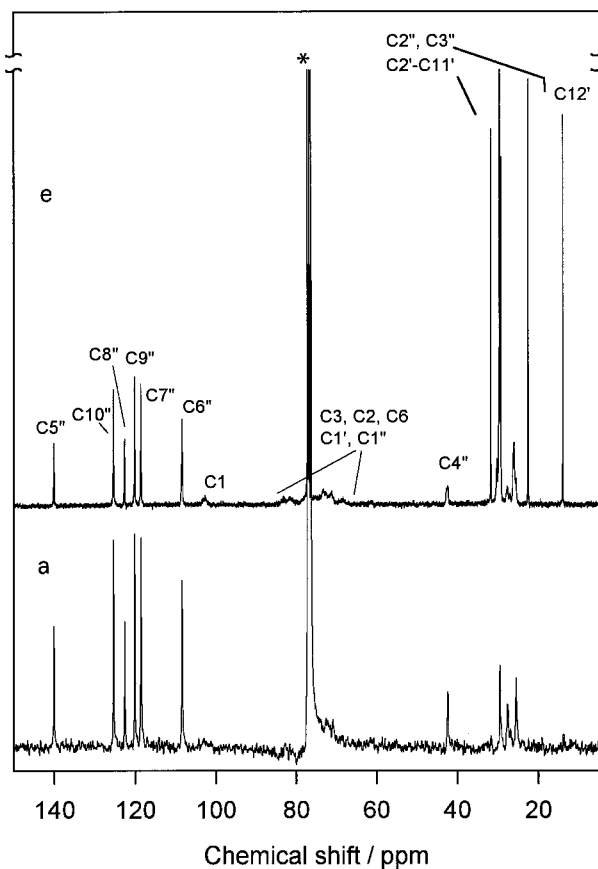
Peak Position (ppm)	Assignment	Relative Intensity (No. Protons)
7.9–7.8	H-6''	2x
7.2–7.1	H-7'', H-8'', H-9''	6x
4.5–2.4	H-1 to H-6, H-1', H-1'', H-4''	7 + 4x + 2y
1.6–1.5	H-2', H-2'', H-3''	4x + 2y
1.3–1.2	H-3' to H-11'	18y
0.88–0.85	H-12'	3y

Protons are labeled as indicated in Figure 3. The variables  $x$  and  $y$  represent the average number of carbazole moieties and dodecyl chains, respectively, per anhydroglucose unit.

sible and only relative values are calculated. However, these relative values in conjunction with the independent conclusion from IR measurements that overall substitution is complete permit the calculation of the individual degrees of substitution for the two types of side chains. The ratio of the observed intensity at 7.9–7.8 ppm (identified as the aromatic proton H-6'') to that of the dodecyl terminal methyl group at 0.88–0.85



**Figure 3** Identification of atomic positions used in the assignment of NMR signals.



**Figure 4**  $^{13}\text{C-NMR}$  spectra of samples a and e, recorded in  $\text{CDCl}_3$  solution. Solvent peaks are marked with an asterisk.

ppm readily permits the calculation of  $x/y$ . This fact combined with the assumption of complete substitution allows the degree of carbazole substitution to be evaluated. The resulting values (Table II) agree reasonably well with those determined by IR.

In sample g (dodecylcellulose) the ring proton region was relatively well resolved and the absolute degree of substitution, which was calculated from the intensity at 4.5–2.4 ppm relative to that of the terminal methyl signal, was found to be equal to 2.9.

The product polymers were also characterized by  $^{13}\text{C-NMR}$  spectroscopy. Representative spectra for samples a and e are shown in Figure 4 and the corresponding peak positions are summarized in Table IV. Although their quantitative analysis is limited by the large variations in the relaxation times for the different carbon atoms in the sample, these spectra are useful in confirming sample identity. Resonances characteristic of the carba-

**Table IV**  $^{13}\text{C}$ -NMR Assignments for Sample e, (dodecyl) $_{1.7}$ (*N*-4'-carbazolylbutyl) $_{1.3}$ Cellulose

Peak Position (ppm)	Assignment
140.9, 126.3, 123.9, 120.8, 119.6, 111.6	C-5'', C-10'', C-8'', C-9'', C-7'', C-6''
102.8, 83.2, 81.6, 68.4	C-1, C-3, C-2, C-6
73.3, 71.3	(C-1'', C-1')
42.6	C-4''
32–22	(C-2' to C-11', C-2'', C-3'')
14.0	C-12'

Carbon atoms are labeled as indicated in Figure 3. Resonances arising from the carbazole moiety are assigned by comparison to indole.<sup>14</sup> Carbon atoms in the cellulose backbone are identified by comparison to literature values for cellulose ethers.<sup>15,16</sup> Ambiguous assignments are shown in parentheses and are not to be attributed in the specific order in which they are given.

zole moiety<sup>14</sup> are clearly present between 100 and 150 ppm. Peaks corresponding to the carbon atoms located in the cellulose backbone are weaker and more difficult to identify. C-1, C-2, C-3, and C-6 are assigned as in Table IV from literature values for cellulose alkyl ethers.<sup>15</sup> It is important to note that C-1 appears at 102.8 ppm, a position characteristic of alkyl substitution at the neighboring C-2. When unsubstituted at position C-2, the signal for C-1 shifts to 104 ppm.<sup>16</sup> Resonances corresponding to C-4 and C-5 of the anhydroglucose ring should be situated near 76–78 ppm and are certainly obscured by the intense solvent peaks in this region. Side chain methylene carbon atoms are located below 50 ppm. The four resonances attributed to the carbon atoms of the butyl spacer can be clearly identified by comparison of the two spectra shown in Figure 4.

## GPC

The molecular weights of the products as measured by GPC relative to polystyrene standards are given in Table V. The cellulose acetate starting material gives a number average molecular weight of 21,000 by the same method. Because of the large difference in chain rigidity between the calibration standards and the polymers studied here, these values clearly do not represent the true molecular weight of the cellulose derivatives. However, these measurements do permit the comparison of molecular weights among the various samples and, most importantly, confirm that the relatively high concentration of NaOH employed in the reaction mixture does not significantly reduce the molecular weight of the derivatized polymers.

## Reaction Conditions

As summarized in Table I, the reaction time and the molar excess of alkylating reagent were both varied to obtain the desired series of polymers. The influence of reaction time can be evaluated by the comparison of samples c–f. Identical reaction conditions were employed in the preparation of these samples, except for the systematic variation of the reaction time for the first alkylation step. The resulting degree of carbazole substitution is plotted as a function of reaction time ( $T_1$ ) in Figure 5. This plot shows that, although the degree of substitution does increase with reaction times, this dependence is not strong. The degree of substitution rises from 1.1 to 1.4 upon a fourfold increase in reaction time.

The second parameter varied in the synthesis is the molar excess of the *N*-4'-bromobutylcarbazole added in the first step of the reaction. Table I indicates that samples b and f differ only in the quantity of alkylating agent employed. Samples a and c can also be compared in a similar way. The

**Table V** Weight ( $M_w$ ) and Number ( $M_n$ ) Average Molecular Weights for Samples a–g

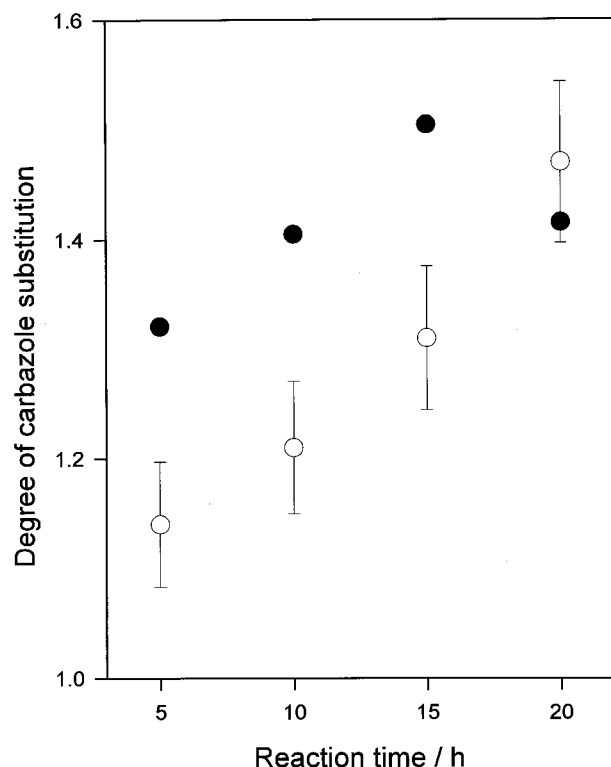
Sample	$M_w/10^5$	$M_n/10^5$	$M_w/M_n$
a	2.1	1.2	1.8
c	3.2	1.6	1.9
d	3.1	1.7	1.8
e	2.6	1.5	1.7
f	2.7	1.5	1.7
g	2.7	1.5	1.8

The polydispersity,  $M_w/M_n$ , is also given. All values were determined by GPC relative to polystyrene standards.

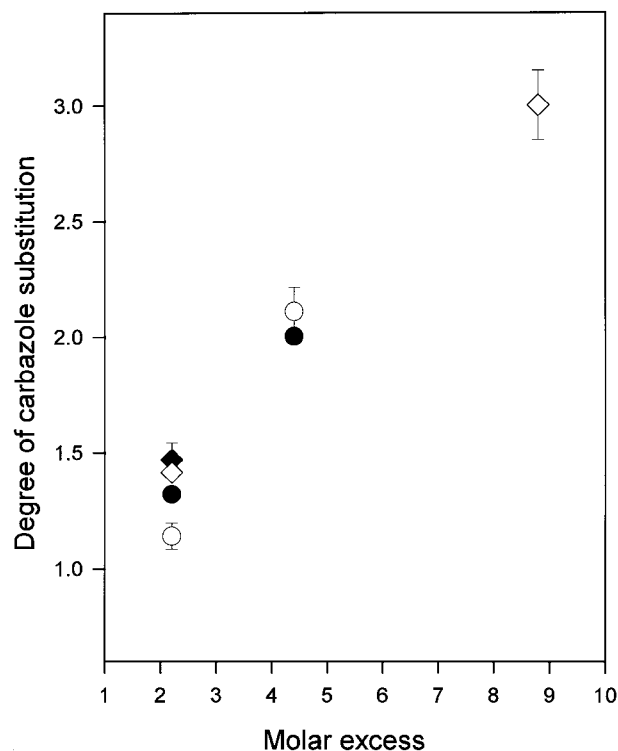
degree of carbazole substitution as a function of the molar excess of *N*-4'-bromobutylcarbazole is plotted in Figure 6 for these four samples. A striking dependence is noted. The relative unimportance of reaction time is also illustrated by the fact that the data for 5 and 20 h fall on a single curve. Thus, it is clear that the degree of substitution is controlled by the molar excess of alkylating agent rather than the reaction time.

## CONCLUSIONS

New cellulose derivatives containing the carbazole chromophore can be conveniently prepared from cellulose acetate and alkylated carbazole. Highly substituted mixed ethers are obtained by the successive introduction of two different alkylating agents. In this way, derivatives of different carbazole content, ranging from 2.9 to 1.1 chromophores per anhydroglucose repeat unit, are ob-



**Figure 5** Degree of carbazole substitution as a function of reaction time, for samples c-f. Values obtained from IR and NMR spectra are shown as filled and open circles, respectively. The error bars represent  $\pm 5\%$  and correspond to the estimated uncertainty of spectral integrations.



**Figure 6** Degree of carbazole substitution as a function of molar excess of *N*-4'-bromobutylcarbazole for samples a, c, b, and f. Values obtained from IR and NMR spectra are shown as filled and open symbols, respectively. Data for reaction times of 5 and 20 h are represented by circles and diamonds, respectively. The error bars represent  $\pm 5\%$  and correspond to the estimated uncertainty of spectral integrations.

tained. Substitution is controlled primarily by the quantity of alkylating agent introduced, and variations in the reaction time have little effect.

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