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Regioselective combinatorial-type synthesis, characterization, and physical properties of dendronized cellulose

Mohammad L. Hassan[a], Charles N. Moorefield[c], Kishore Kotta[b], George R. Newkome[b,c,*]

[a]*Cellulose and Paper Department, National Research Center, Dokki, Cairo 12622, Egypt*
[b]*Departments of Polymer Science and Chemistry, The University of Akron, Akron, OH 44325-4717, USA*
[c]*The Maurice Morton Institute of Polymer Science, The University of Akron, Akron, OH 44325-4717, USA*

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Abstract

Novel regioselective, homo-(**4**–**6**) and heterogeneous (**7**–**10**) dendronized cellulose derivatives have been prepared by the reaction of cellulose in a *N*,*N*-dimethylacetamide (DMAc)/LiCl solvent system with diverse dendrons (**1**–**3**) possessing an isocyanate focal group. The dendronized cellulose derivatives were characterized using Fourier transform infrared (FTIR), ^{13}C NMR, thermogravimetric analysis (TGA), and dynamic mechanical thermal analysis (DMTA). These polyfunctionally coated cellulose-based materials showed diverse solubility characteristics in organic solvents ranging from DMAc to methyl alcohol.

Keywords: Cellulose; Dendritic; Combinatorial

1. Introduction

Cellulose is a polydisperse, linear homopolymer consisting of regio- and enantio-selective β-1,4-glycosidic linked D-glucose units. It contains three reactive hydroxyl groups at the C-2, C-3, and C-6 positions, which are, in general, accessible to typical conversions of primary and secondary alcoholic groups. Hydrogen bonding between these hydroxyl groups leads to various supramolecular, semicrystalline cellulose structures [1,2]; thus, crystallinity and H-bonding associations have a strong influence on its ultimate chemical reactivity and solubility characteristics [3]. As a consequence of its inherent polyfunctional structure, naked cellulose is insoluble in water as well as common organic solvents.

New cellulose derivatives with supramolecular architectures are of increasing interest due to their various applications [4], such as in ultra-thin coatings [5–10], host–guest systems [11–14], biosensors [15–17], liquid crystalline polymers [18–22], and biomaterials [17,23–34]. Regioselective functionalization of cellulose, i.e. the introduction of either a substituent or more than one substituent onto the cellulose chain at specific hydroxyl group(s), has attracted ever-increasing attention because of its potential to prepare precisely modified cellulose materials possessing new properties differing from those derived from simple statistical substitution. The properties of cellulose derivatives not only depend on the nature of the attachments but also on their position and distribution pattern along the cellulose chain [35–49].

Dendrimers and hyperbranched polymers [50] have, in general, a three-dimensional molecular architecture and properties different from those of their linear counterparts. These unusual properties result from their highly branched structure, generally globular shape, multiplicity of chain ends, controlled molecular weight, versatility in modification of terminal groups, and potential for interaction with the immediate environment. Dendrimers are prepared by an iterative, multi-step procedure resulting in either a macromolecule (i.e. a unimolecular specie [51,52]) or a family of macromolecules with a very narrow molecular weight distribution. The resulting 1→2 or 1→3 branching structure is typically symmetric with discernible layers (or generations); the number of terminal functional groups

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* Corresponding author. Address: Departments of Polymer Science and Chemistry, The University of Akron, Akron, OH 44325-4717, USA.

E-mail address: newkome@uakron.edu (G.R. Newkome).

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increases exponentially with increasing generations. On the other hand, hyperbranched polymers are typically prepared from AB$_x$ monomers ($x>1$) in a 'one-step' procedure to give highly branched polymers possessing a less defined structure when compared to the more perfect dendrimers. These highly functionalized branched materials have found use in numerous applications such as host–guest chemistry [53], carbohydrate chemistry [54], metallodendrimers [55], catalysis [56–58], surface chemistry, non-linear optics [59], biomedical application in gene and drug delivery systems [60,61], and nanoscale electronic devices [62].

There is an increasing interest in attaching either these dendritic macromolecules or their dendron components to other materials, e.g. the attachment of benzyl- or *tert*-butyl-terminated dendrons to silica surfaces resulting in new immobilized materials designed for enhanced separations in high resolution capillary gas chromatography and capillary microextraction [63–65]. Also, dendrons containing 2,6-di(acylamino)pyridinyl moieties that are capable of 'internal' molecular recognition were covalently bonded to an agarose matrix [66]. Chemical modifications of silica [67–70], carbon [68], and chitosan [71,72] with polyamidoamine hyperbranched constructs possessing different generations have also been reported. Formation of layered thin films and bioactive films either physically adsorbed [73, 74], or covalently grafted [75–78] on various substrates using different hyperbranched polymers, has been evaluated. To the best of our knowledge, the only work other than our preliminary communication [79] concerning the dendronization of cellulose was a study describing the surface modification of a regenerated cellulose film through H-bonding of a hybrid linear-dendritic block copolymer to the cellulose hydroxyl groups [80].

We herein report the regioselective preparation and characterization of dendronized cellulose derivatives (**4–10**) having different surface functional groups through homo- and heterogeneous reaction of different focally-substituted isocyanate dendrons (**1–3**). The use of different dendrons in logical combinations, i.e. in a combinatorial-type manner, for the construction of branched architectures leads to the formation of unique asymmetric dendritic materials possessing multiple functionalities, thus giving entrée to versatile new superstructures and utilitarian characteristics [81].

2. Experimental

2.1. General comments

Melting point data were obtained in capillary tubes with an electrothermal 9100 melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 52 MHz, respectively, on a Gemini 300 NMR spectrometer at 25 °C in CDCl$_3$; ^{13}C NMR spectra of the cellulose carbamates were recorded on a Varian INDVA 400 spectrometer at 60 °C in DMSO-d_6. FTIR spectra were recorded on an ATI Mattson Benseis Series FTIR spectrophotometer using KBr technique. Thermogravimetric analyses were performed with a Mettler–Toledo TG50 thermogravimeteric analyzer under nitrogen over 25–700 °C at a heating rate of 10 °C/min; the rate of nitrogen flow was 40 ml/min. Elemental nitrogen analysis was commercially conducted and the degree-of-substitution (DS) of cellulose product was calculated from the nitrogen content as follows:

$$\mathrm{DS} = \frac{162\times 10\times \%\mathrm{N}}{[(100-14)-(M\times \%\mathrm{N})]},\quad \text{where,}$$

M = Molar mass of the substituent

Dynamic mechanical thermal analysis (DMTA) was conducted using Rheometric Scientific DMTA V instrument at frequency of 1 Hz over 0–200 °C at a heating rate of 2 °C/min. The cellulose derivatives were pressed in a mold at 150 °C at 50 MPa to form a $3\times 20\times 0.1$ mm^3 transparent film.

Avicell cellulose [microcrystalline cellulose, degree-of-polymerization (DP) 280], anhydrous dimethylacetamide (DMAc), LiCl, and dibutyltin dilaurylate (DBDL) were purchased from Aldrich and used without further purification. The 1st generation [di-*tert*-butyl 4-isocyanato-4-(*tert*-butylcarbonyl)ethyl-1,7-heptanedicarboxylate (**1**; crystalline, mp 62–63 °C)] [82–86] was prepared from Behera's amine by treatment with triphosgene; the related cyano-(**2**) and silyloxy-(**3**) terminated dendrons were prepared [65,83] in an analogous manner from their respective amine precursor.

The spectroscopic data for dendron **1**: ^{13}C NMR: δ 27.8 (*C*H$_3$), 29.9 (*C*H$_2$CH$_2$CO), 33.9 (*C*H$_2$CO), 61.8 (*C*NCO), 80.6 (*C*Me$_3$), 122.2 (N*C*O), 171.7 (*C*O$_2$); ^{1}H NMR: δ 1.34 (s, C*H*$_3$, 27H), 1.74 (t, $J=4.2$ Hz, C*H*$_2$CO, 6H), 2.18 (t, $J=4.2$ Hz, C*H*$_2$CH$_2$CO, 6H); IR: 2262 (NCO), 1734 (CO$_2$), 1159 (C–O), 835, 750 (CMe$_3$) cm^{-1}. Spectroscopic data for dendron **2**: ^{13}C NMR: δ 18.4 (*C*H$_2$CN), 63.2 (*C*NCO), 65.7, 70.6 (*C*H$_2$O), 117.6 (*C*N), 126.9 (N*C*O); ^{1}H NMR: δ 2.64 (t, $J=6$ Hz, C*H*$_2$CN, 6H), 3.60 (s, C*H*$_2$O, 6H), 3.74 (t, $J=6$ Hz, OC*H*$_2$, 6H); IR: 2268 (NCO) cm^{-1}. Spectroscopic data for **3**: ^{13}C NMR: δ −5.4 [Si(*C*H$_3$)$_2$], 18.2 (*C*Me$_3$), 25.9 [C(*C*H$_3$)$_3$], 27.2 (*C*H$_2$CH$_2$O), 35.8 (*C*H$_2$CH$_2$CH$_2$O), 62.8 (*C*H$_2$O), 63.4 (*C*NCO), 122.1 (N*C*O); ^{1}H NMR: δ 0.03 [s, Si(C*H*$_3$)$_2$, 27H], 1.56 (m, C*H*$_2$, C*H*$_2$C*H*$_2$, 12H), 4.00 (t, $J=6$ Hz, C*H*$_2$O, 6H); IR: 2268 (NCO), 1120 (Si–O), 835, 778 (SiMe$_2$) cm^{-1}.

2.2. General procedure

2.2.1. Dissolution of cellulose in DMAc/LiCl and its reaction with the different 1→3 C-branched isocyanate dendrons

Reaction of cellulose with the different isocyanates (**1**–**3**) was conducted using an improved method [87] mediated by DBDL, as the catalyst. Typically, to cellulose (100 mg) in

DMAc/LiCl solution (2.5% cellulose [88] content) at 65 °C, the isocyanate and catalyst were added; the ratio of the isocyanate to cellulose anhydroglucose unit (AGU) was 1:3 and the catalyst concentration was 2%, based on the weight of cellulose. The reaction time was generally 12 h for these 1st-generation dendrons.

In the case of the combinatorial-type reactions with the different 1st-generation isocyanate dendrons, equimolar ratios of the different 1→3 isocyanates (**1**, **2** and/or **3**) were added, the final ratio of cellulose AGU to isocyanate was kept 1:3. At the end of the reaction, the products were precipitated in MeOH/water (70:30), centrifuged, washed with the MeOH/water mixture. The products were then dialyzed for 48 h in MeOH, using a Spectra/Pro membrane to remove residual solvent or non-reacted materials, oven dried at 65 °C overnight, and then lastly dried in vacuo at 25 °C.

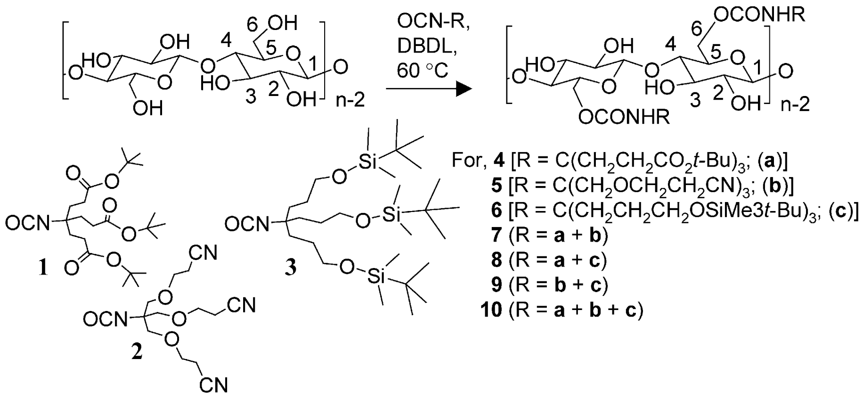
3. Results and discussion

In our preliminary report [79], it was shown that cellulose regioselectively reacted with the different generations of the isocyanates at the C-6, primary hydroxyl groups to give 1st-(**4**), 2nd- and 3rd-generation dendronized cellulose polycarbamates (Scheme 1). The ^{13}C NMR spectrum of the 1st-generation dendronized cellulose carbamate **4** shows a characteristic signal at 154 ppm due to formation of the carbamate bond, an upfield shift from 62 to 57 ppm of the signal for the tertiary carbon, attached to the carbamate group, (CONH*C*CH$_2$) resulting from the replacement of the isocyanate group of dendron **1** with the carbamate moiety. The other carbon signals of the dendritic moiety appeared in the spectrum in addition to the signal of carbons of AGUs of cellulose at 102.6 (C-1), 75.4 (C-2 and C-3), 73 (C-5), and 61 (C-6) ppm supporting the exclusive C-6 substitution pattern. The nitrogen content of these cellulose carbamates showed that only one hydroxyl group was esterified (DS ≈ 1) in spite of an excess of added isocyanate dendrons (molar ratios of 1:3 of AGU:isocyanate dendrons), further corroborating the substitution at the more accessible C-6 position.

3.1. Homogeneous reaction of cellulose with the 1st-generation 1→3 C-branched isocyanates

The AB$_3$ isocyanate dendrons possess a triad of protected ester, cyano (protected acid or amine), and silyloxy (protected alcohol) functionality, respectively, a 1→3 C-branching motif, and a reactive but structurally and sterically similar focal isocyanate moiety. An important characteristic of these dendrons is their mutually compatible functionality, as well as the ability of each member of this series to react at a comparable reaction rate; mutual compatibility is required for their ability to react in a heterogeneous mixture of these dendrons with a polyfunctional substrate (i.e. they should be inert toward reaction with each other) [81]. It has been previously shown that these 1st generation dendron with the isocyanate focal group react specifically with primary alcohols and that reaction with secondary and tertiary hydroxy groups is exceedingly slow or nonexistent, respectively. When triester **1** was treated with cellulose, the resultant cellulose carbamate products were regioselectively derived from exclusive reaction at the C-6 hydroxyl position.

The nitrogen content of the carbamates (**4–6**), prepared by reaction of cellulose in DMAc/LiCl with the dendrons **1–3** on a homogeneous basis, is shown in Table 1. Under the reaction conditions used, a DS ≈ 1 was obtained for the ester- and cyano-modified carbamate derivatives **4** and **5**; while a DS ≈ 0.5 was obtained for the siloxy-coated carbamate **6**. This may be due to the relative instability of the isocyanate dendron **3** in the reaction medium (DMAc/LiCl); it was recently reported that heating of DMAc and LiCl at > 85 °C in the presence of cellulose or MeOH results in formation of other products, namely ketene aminal and *N*,*N*-dimethyl keteniminum ions, which are known for the cleavage of ethers and acetals [89]. The slow degradation of the siloxy dendron was confirmed by heating the isocyanate dendron **3**. Fig. 1 shows the ^{13}C NMR of the isocyanate dendron **3** before and after heating **3** in DMAc/



Scheme 1. Reaction of cellulose with isocyanate dendrons (i.e. **1**, **2** or **3**) to afford homogeneous- and heterogeneous-modified polymers.

Table 1
Nitrogen content determined for the homogeneous polycarbamates **4–6**

Dendronized cellulose carbamate	Nitrogen content found (%)	Nitrogen content calcd (%) for DS = 1
4	2.32	2.42
5	10.41	11.95
6	1.00	2.04

LiCl for 12 h at 60 °C. In addition to the carbon signals for DMAc at 19, 32, 35, and 175 ppm, new signals appeared when compared to the non-heated silyloxy dendron; however, the degradation was also shown to be relatively slow and that ca. 50% decomposition of **3** had occurred under these reaction conditions.

The ^{13}C NMR spectra for the homogeneous series of carbamates derived from cellulose possessing different isocyanates (**1–3**) are shown in Fig. 2. The ^{13}C NMR spectra of the resultant carbamates **4–6** showed a typical signal at 154 ppm due to the formation of the new carbamate bond at C-6 as well as an up-field shift from 62 to 57 ppm of the signal assigned to the new CONH$^{4\circ}$ C connectivity, as well as the expected resonances attributed to the different branched frameworks and the AGU backbone.

The FTIR spectra of dendronized cellulose constructs **4–6** (Fig. 3) reveal the appearance of the carbamate bands at 1730 and 1540 cm^{-1} in addition to the other characteristic peaks of the different functional groups terminating the dendritic moieties, i.e. the *tert*-butyl methyl groups at 850 and 754 cm^{-1} for **4**, the cyano group at 2216 cm^{-1} for **5**, and Si(CH$_3$)$_2$ at 840 and 777 cm^{-1} for **6**.

3.2. Heterogeneous (combinatorial-type) treatment of cellulose with mixtures of different dendron isocyanates

Combinatorial-type reaction of dendrons **1–3** with cellulose using molar ratios of 1:1.5:1.5 of AGU:**1**:**2**, AGU:**1**:**3**, or AGU:**2**:**3** resulted in the formation of the heterogeneous-surfaced derivatives **7**, **8**, and **9**, respectively. Similarly, a combinatorial-type reaction of cellulose with AGU:**1**:**2**:**3** at an equimolar ratio afforded the trifunctionalized cellulose derivative **10**. The nitrogen content of these derivatives (Table 2) was generally in accord with that observed for the reaction of each dendron with cellulose on an individual basis, except for the combinatorial-based carbamates containing silyloxy terminal groups (**8** to **10**) which had a lower (ca. 50%) nitrogen content than the theoretical value due to dendron instability and possible side reactions, as noted above. Thus, the nitrogen content of the tricoated carbamate **10** indicates a greater percentage of cyano and *tert*-butyl ester dendron attachment predicated on siloxane dendron degradation.

FTIR and ^{13}C NMR spectra of the heterogeneous-dendronized derivatives (**7–10**; Figs. 3 and 4, respectively) support successful attachment of the isocyanate dendrons.

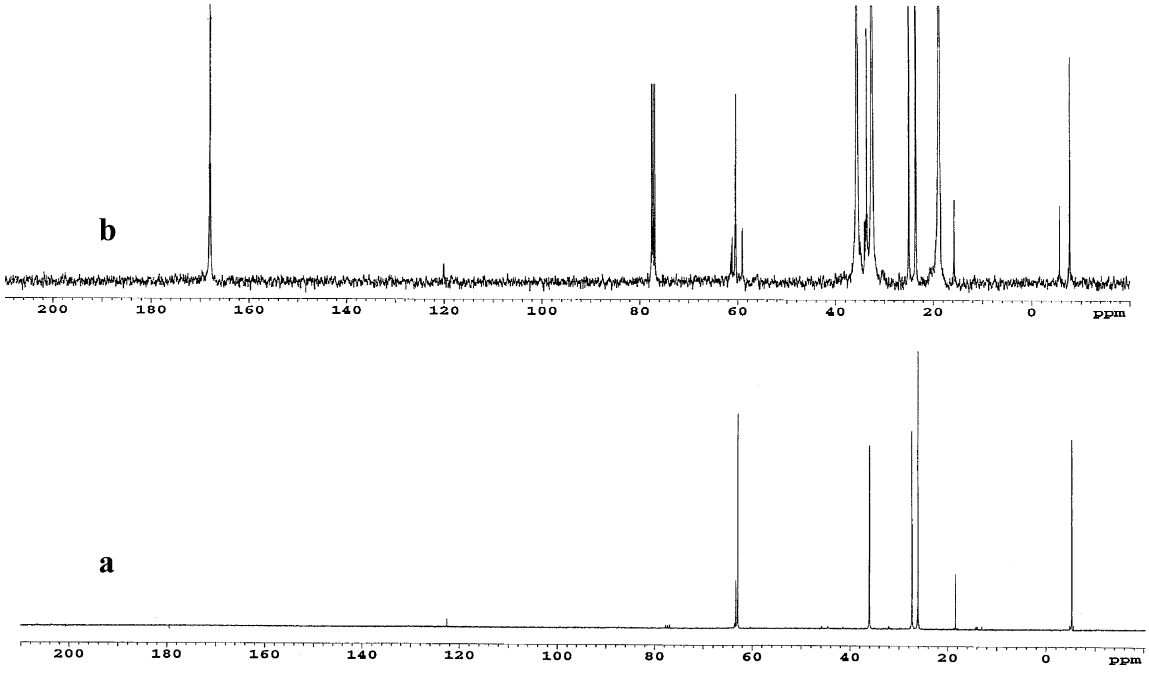


Fig. 1. ^{13}C NMR spectra of the trisiloxane isocyanate dendron **3** (a) in CDCl$_3$ and (b) in CDCl$_3$ after heating at 65 °C for 12 h.

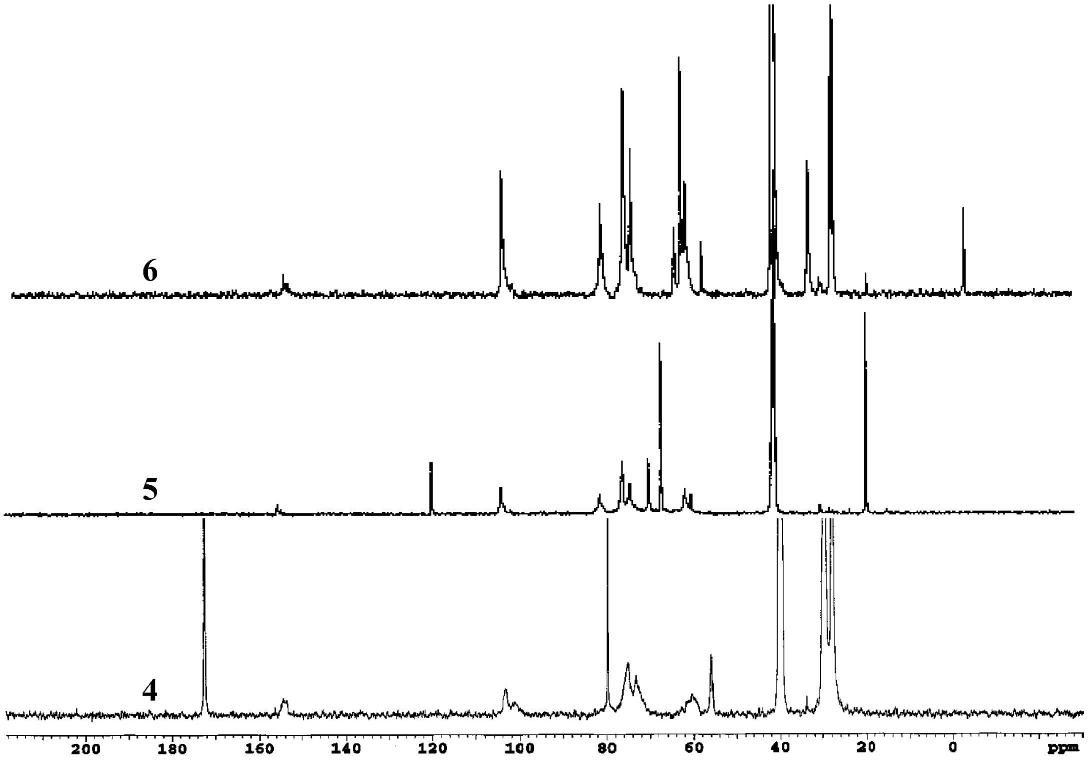


Fig. 2. ^{13}C NMR spectra of the ester-, cyano-, and silyloxy-modified cellulose, i.e. **4**–**6**, respectively.

In the ^{13}C NMR spectra, the carbamate carbonyl signals appeared at 153 ppm in addition to the typical resonances assigned to the different superstructures.

These carbamate derivatives showed good solubility in DMSO and DMAc. The dendronized cellulose derivative **5** with terminal cyano groups showed solubility in MeOH due to the high polarity of the cyano terminal groups. As a result of the combinatorial-type reaction, the heterogeneous carbamates containing terminal cyano groups showed partial solubility in MeOH.

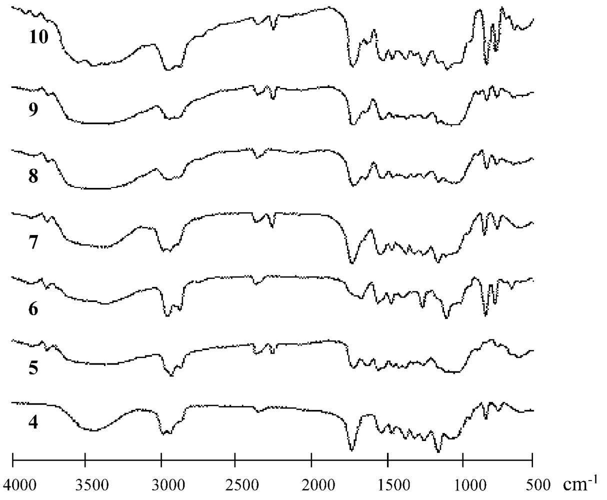


Fig. 3. FTIR spectra of the homogeneous-(**4**–**6**) and heterogeneous-(**7**–**10**) surfaced cellulose.

3.3. Effect of dendrimerization and combinatorial-type modification on glass transition temperature of cellulose

Cellulose is a homopolymer that when esterified exhibits thermoplastic behavior, in many cases. In this work, the effect of dendronization of cellulose on its glass transition temperature (T_g) was investigated in order to demonstrate the advantage of the facile combinatorial-type property modification of cellulose, as well as other materials and substrates.

The T_gs of selected dendronized cellulose carbamates, namely **4**, **5**, and **7**, were determined using dynamic mechanical thermal analysis (DMTA), which allowed access to the mechanical properties, such as the dynamic modulus, damping factor, and thermal transitions. However, the damping factor (tan δ) is often the most sensitive indicator of molecular motion, even in the solid state [90]. Fig. 5 shows the damping factor of these derivatives as a function of temperature. The tan δ peak indicated onset of molecular motion of large segments of the polymeric components, i.e. T_g. Ester-modified cellulose **4** exhibited a T_g at 162 °C and the cyano analog **5** showed a T_g at 137 °C. While, the carbamate containing both cyano and ester terminal groups **7** revealed a T_g at 142 °C. The T_g of the dendronized cellulose derivative **6** is close to its onset degradation temperature as will be seen later from the thermogravimetric analysis. Thus, heterogeneous functionalization of cellulose can be easily used to alter the thermal, as well as chemical properties of cellulose.

Table 2
Nitrogen content determined for the heterogeneous polycarbamates **7–10**

Dendronized cellulose carbamate	Nitrogen content found (%)	Nitrogen content calcd (%) for DS = 1[a]
7	5.40	7.12
8	1.20	2.2
9	3.84	6.99
10	4.06	5.47

[a] Nitrogen content was calculated using a the degree of substitution (DS) equal to 1 based on the assumption of equal dendron reactivity.

3.4. Thermal stability of the dendronized cellulose carbamates

Cellulose is a polymer of moderate thermal stability. It has long been known that the range of temperature for the material's application is limited not by melting, but by a rapid chemical decomposition between 250 and 350 °C [88]. Hence, the thermal stability of the different cellulose materials was studied. Fig. 6 shows the thermogravimetric analysis (TGA) curves of cellulose, as the standard, and the homogeneous dendronized series **4–6** (top) and the data of these curves are summarized in Table 3. Cellulose exhibits two main thermal degradation stages, in addition to the first weight loss due to dehydration. The thermal degradation of cellulose is known to be due to a pyrolytic fragmentation that leads to aromatized entities and finally most probably to a highly cross linked carbon skeleton [88]. The simple ester-modified derivative **4** showed three stages of thermal degradation and had a lower thermal stability than cellulose, as indicated by the onset degradation temperature; however, derivatized cellulose **4** showed a higher char yield at 350 °C than that of cellulose, i.e. a lower rate of thermal decomposition. The onset degradation of this material (**4**) is due to the well-known, thermally-induced, isobutylene elimination [91] from the terminal *tert*-butyl ester moieties [65]. These data also showed that both the polymers with cyano or siloxy terminal groups (**5** and **6**, respectively) had a higher thermal stability than *tert*-butyl construct **4**. The lower char yield at 350 °C of the siloxy-terminated cellulose compared to cellulose derivative **4** and **6** is also due, in part, to the lower DS of this derivative (DS ≈ 0.5).

The TG curves of combinatorially-derived materials

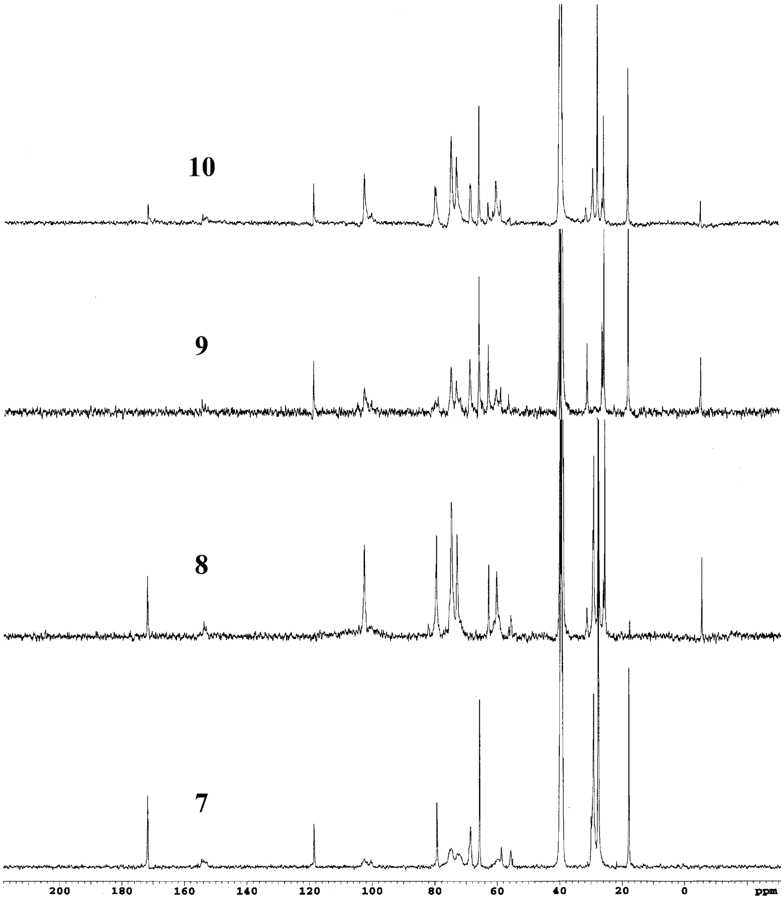


Fig. 4. ^{13}C NMR spectra of the heterogeneous-surfaced cellulose derivatives cyanotriester **7**, siloxytriester **8**, cyanosiloxy **9**, and cyanosiloxytriester **10**.

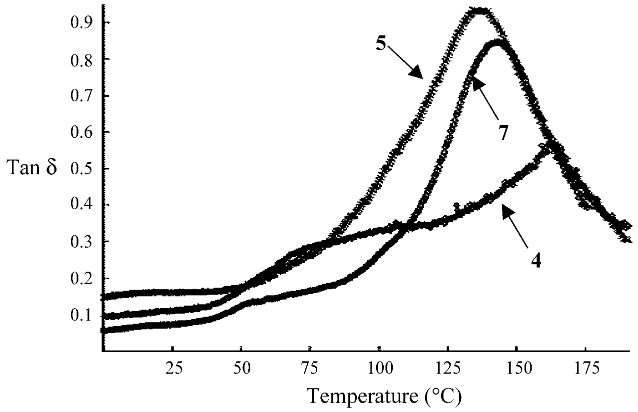


Fig. 5. Dynamic mechanical thermal analysis (DTMA) of the *tert*-butyl ester-, cyano-, and ester- plus cyano-modified cellulose derivatives **4**, **5** and **7**, respectively.

7–10 (Fig. 6 bottom) were, as expected, more complex and the first stage of thermal degradation split into sub-stages due to the different possible degradation reactions. The thermal stability of these combinatorial derivatives was not always in accordance with the thermal behavior of the separate dendronized cellulose derivatives **4–6**. The combinatorial dendronized cellulose derivatives that contain silyloxy and *tert*-butyl ester terminal groups (**8** and **10**) showed onset degradation temperatures higher than that of **4**. Also, the cellulose derivative **8** containing *tert*-butyl ester and silyloxy terminal groups had the highest char residue at 350 and 500 °C.

The preparation of organo-soluble, regioselectively functionalized cellulose derivatives was possible through the reaction of cellulose with a series of isocyanate dendrons. Due to the steric hindrance at the isocyanate

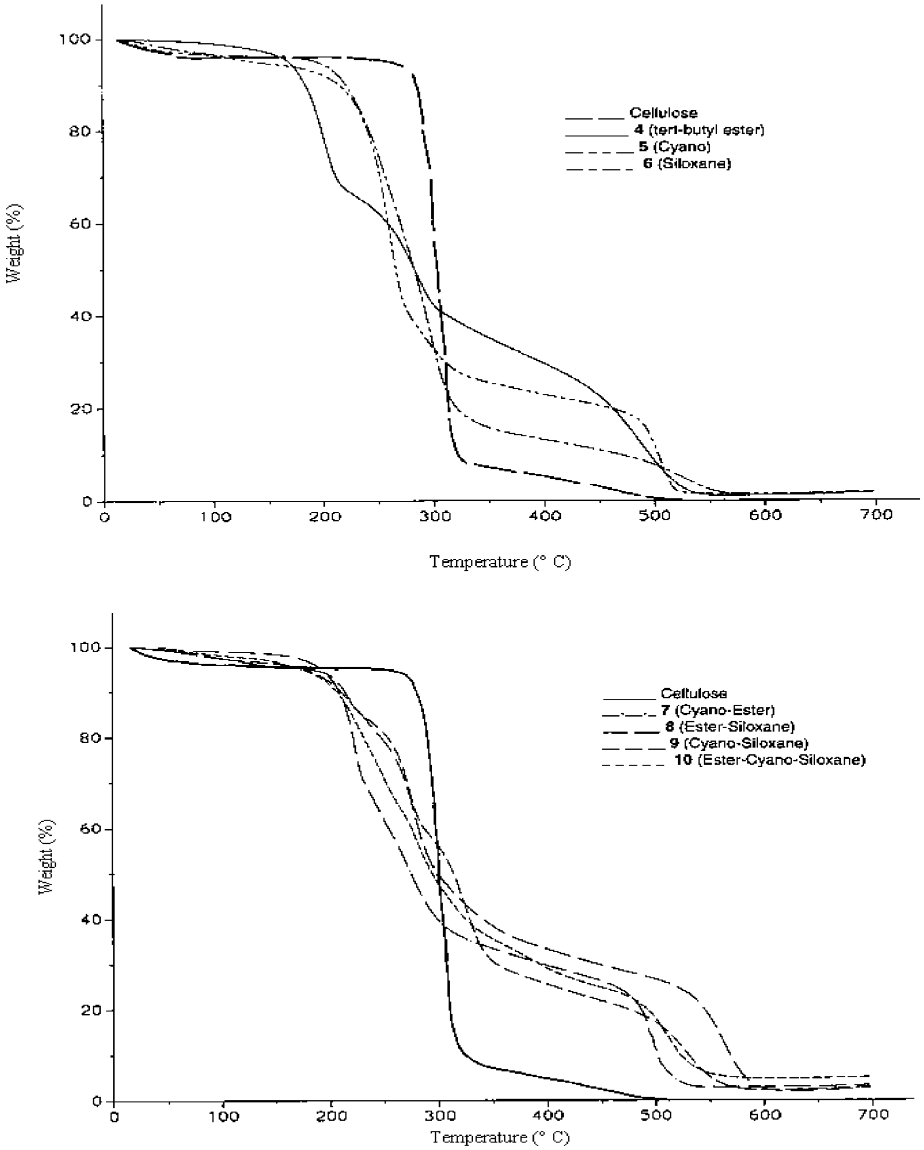


Fig. 6. Thermal gravimetric analysis (TGA) data for the homogeneous-dendronized cellulose derivatives **4–6** (top) and the heterogeneous-analogs **7–10** (bottom).

Table 3
Thermogravimetric analysis (TGA) data for cellulose and the dendron-modified derivatives **4–10**

Polymer	Onset degradation temperature (°C)	Maximum wt. loss temperature[a] for the first stage (°C)	Residual wt. percent at 350 °C	Residual wt. percent at 500 °C
Cellulose	260	303	6	1
4 (Ester-coated)	174	213	28	1.5
5 (Cyano-coated)	185	259	26	13
6 (Siloxane-coated)	187	258	17	10
7 (Ester-cyano-coated)	171	221, 246, 269	33	13
8 (Ester-siloxane-coated)	190	213, 294	38	26
9 (Cyano-siloxane-coated)	188	218, 272, 323	30	17
10 (Ester-cyano-silaxane-coated)	180	228, 247, 277	36	20

[a] Maximum wt. loss temperatures were determined via the first derivatives of the TGA curves.

groups, their attachment was restricted exclusively to the C-6 position of the cellulose AGUs. Combinatorial reaction of cellulose with different isocyanate dendrons leads to dendritic cellulose derivatives with a wide variety of properties. Although all these dendritic cellulose carbamates were thermally less stable than the parent cellulose, they show a lower rate of thermal degradation as evident from the percent of char at 350 °C. The thermal stability was observed to be dependent on the type of dendritic terminal moieties used, although the combinatorial cellulose derivatives revealed thermal behavior that was not always in agreement with that of the homogeneous counterparts.

4. Conclusions

Novel regioselective, homo- and heterogeneous, dendronized cellulose derivatives were synthesized by the treatment of cellulose with diverse $1\rightarrow3$ C-branched dendrons possessing an isocyanate focal group in a DMAc/LiCl solvent mixture. These polyfunctionally coated cellulose-based materials were fully characterized using FTIR, ^{13}C NMR, TGA, and DMTA as well as shown to possess a wide range of solubilities in organic solvents ranging from DMAc to methyl alcohol.

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