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Preparation of 6-*O*-(4-alkoxytrityl)celluloses and their properties

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Cellulose was reacted with a series of 4-alkoxytrityl chlorides (C_nTCl, *n*: number of carbon atoms in a saturated alkyl chain) under homogeneous reaction conditions in LiCl–*N*,*N*-dimethyl acetoamide to give a series of 6-*O*-(4-alkoxytrityl)-celluloses (C_nTC) with a high degree of substitution (DS), from 0.94 to 0.99, and with high regioselectivity at the 6-*O* position. Solubility of the C_nTC in nonpolar solvents depended on the alkyl chain length: as the alkyl chain lengthens, cellulose derivatives become more hydrophobic and are readily soluble in nonpolar solvents, but not in polar solvents. Acetates of the C_4–C_{18}TC (C_4–C_{18}TCAc) showed anisotropic structures over melting temperatures (T_m) examined under a polarized optical microscope (POM). Over isotropization temperatures (T_i), flow birefringence were detected for C_{12}–C_{18}TCAc.The T_m and T_i decreased linearly with an increasing number of carbon atoms in the alkyl substituent. Wide-angle X-ray scattering (WAXS) studies of C_nTC indicated that the fully extended side chains were perpendicular to the polymer backbone and interdigitated. These C_nTC with the improved solubility may be used as starting materials for further derivatization focused on the secondary hydroxyl groups at the C-2 and C-3 positions.

Introduction

Cellulose is the most abundant biomacromolecule existing mainly in plant cell walls and has excellent material properties with microfibrillar morphology, desirable crystal–amorphous combinations, biodegradability and renewability.[1] This biomacromolecule has been studied and used as fibers[2] and films[3] produced from regenerated cellulose, and versatile cellulose derivatives such as cellulose acetate,[4] carboxymethyl cellulose[5] and alkyl cellulose[6] modified mainly by esterification and etherification. However, because of its specific structure, a strictly linear (1⟶4)-*β*-glucan structure with three reactive hydroxyl groups per anhydroglucose unit, cellulose has broad potential in the design of more advanced polymeric materials such as liquid crystalline polymers, Langmuir–Blodgett film, selective membranes, sensor matrixes, recognition devices, organic–inorganic complex materials and bioactive and biocompatible materials.

For the preparation of these types of advanced materials, the synthesis of highly regioselective substituted cellulose derivatives, with a controlled pattern of functionalization and a well-defined supramolecular nanoscale architecture has been an important goal in recent cellulose research. That is, it is indispensable to establish the method for the preparation of cellulose derivatives with controlled distribution of substituents along the polymer chains as well as within the anhydroglucose units. In particular, derivatization on the C6-primary hydroxyl group in cellulose is fairly easy and of great utility from the above point of view.

Although recently we have succeeded for the first time in the preparation of the seven possible highly regioselectively methylated cellulose molecules by a ring-opening polymerization of glucoseorthopivalates,[7] traditionaly the preparation of regioselectively substituted cellulose derivatives has been carried out by the selective protection at the 6-*O* position with bulky protective groups, such as trityl,[8] trimethylsilyl[9] and thexyldimethylsilyl[10] groups. But the synthetic route needs two additional reactions, introducing and removing a protecting group, which are implicated in various detrimental effects such as a decrease in the regioselectivity, limited reproducibility, insufficient yields and so on.

Therefore, a method for regioselective derivatization without the use of such protecting groups is really important with respect to cellulose. Here, if we used trityl chloride derivatives bearing special functional groups designed in expectation of the desired functions of the cellulose derivatization, the products having these special functional groups at only the 6-*O* position may be obtained by a one step reaction without the introduction and removal of a protective group: such trityl chloride derivatives are actually derivatization reagents, which are regarded as "functional group-carriers" and not as protective reagents.

Generally, when nonpolar and hydrophobic long chain alkyl groups are introduced into the polar hydrophilic cellulose molecules, such alkylated celluloses are expected to have improved solubilities and meltabilities, which may enable further chemical modification using the usual organic solvents or fusion molding.[11]

In a previous paper, we reported a preparative method for a series of novel 4-alkoxytrityl chlorides (C_nTCl) with different chain lengths and reactions with methyl *α*-D-glucopyranoside as a model compound to give the expected trityl derivatives in high yields with high regioselectivity exclusively at the 6-*O*-position.[12] The obtained trityl derivatives were found to have improved solubility in the usual organic solvents and thermal properties by changing the length of the alkyl side chain.

Herein, we report the preparation of 6-*O*-(4-alkoxytrityl)-celluloses (C_nTC) by homogeneous reaction with a series of C_nTCl as well as several properties of the products.

Results and discussion

Preparation of C_nTC and their structure identifications

The preparation of a series of C_nTC with different chain lengths (*n* = 0, 1, 4, 12, 14, 18: here, *n* = 0 means an unsubstituted trityl group) are shown in Scheme 1. Cellulose dissolved in a LiCl–*N*,*N*-dimethyl acetamide (DMA) system[13] was treated

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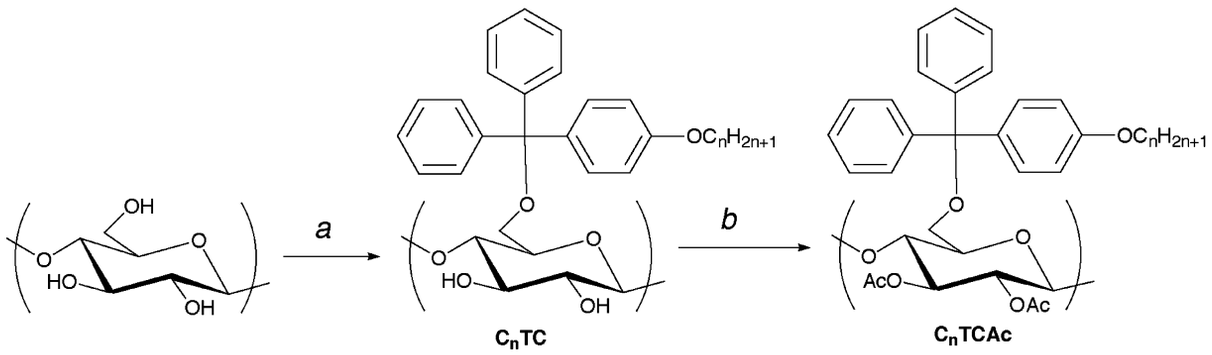

Scheme 1 Synthetic route for C_nTC and C_nTCAc.

Table 1 DP and DS values of C_nTC and C_nTCAc

n	DS[a]	$[\alpha]_D^{25}$[b]	DPn	10^{-3} M[c]	M_W/M_N
0	1.05	—	—	—	—
1	0.98	—	—	—	—
4	0.97	−5.84	79	54.0	3.2
12	0.94	−6.24	69	54.5	4.4
14	0.99	−3.78	76	62.2	3.3
18	0.99	−3.32	68	59.4	3.8

[a] DS was determined from elemental analysis data. [b] Optical rotation of acetylated derivative (*c* 1.0 in $CHCl_3$). [c] Molecular weight of acetylated derivatives determined by GPC using polystylene standards.

with C_nTCl (3.0 equivalents per anhydrous glucose unit (AGU)) in the presence of pyridine (4.5 equivalent per AGU) at 70 °C.

Tritylation of cellulose took 48 h to reach a degree of substitution (DS) about 1.0, while 4-alkoxytritylations took only 4 h to obtain a DS about 1.0. These results indicate that the 4-alkoxyl group enhances the reactivity of tritylation reagents as reported by Klemm *et al*.[8] and that the reactivity of reagents with different chain lengths is almost the same, *i.e*. it is not affected by the chain length, similar to that reported for methyl α-D-glucopyranoside.[12] All trityl celluloses were obtained as colorless powders in 84–97% yields.

Excess C_nTCl was recovered as ethyl trityl ether by the addition of ethanol to the reaction mixture. The obtained ethyl trityl ether was hydrolyzed easily with hydrochloric acid to give a 4-alkoxytrityl alcohol (C_nTOH), which is used again as a tritylation reagent after chlorination.[12]

Table 1 shows the DS, $[\alpha]_D$ and degree of polymerization (DP) of the products. The DS of the products has been calculated from the elemental analysis data and was found to be almost 1.0. The $[\alpha]_D$ and DPs are those of the acetylated derivatives (C_nTCAc), obtained by treatment with acetic anhydride and pyridine at 70 °C overnight as shown in Scheme 1. All products have small negative $[\alpha]_D$ values. The DPs of the products range from about 70 to 80, indicating that depolymerization occurs to some extent under tritylation or acetylation reaction conditions.

Fig. 1 shows the H–H COSY spectrum of 4-methoxytrityl cellulose acetate from a low DP (*ca*. 10) cellulose prepared from cotton cellulose by a phosphoric acid hydrolysis reported by Atalla.[14] All peaks of AGU protons were assigned as shown in Fig. 1. ^{1}H NMR spectra of C_nTCAc are shown in Fig. 2. All trityl derivatives (n = 1–18) gave almost the same pattern of ^{1}H NMR spectra especially, the protons, H1-H6 of these derivatives which have almost the same chemical shifts, indicating that they are not affected by the chain length of the trityl group. Thus, the structures of the obtained trityl celluloses were supported by these NMR data.

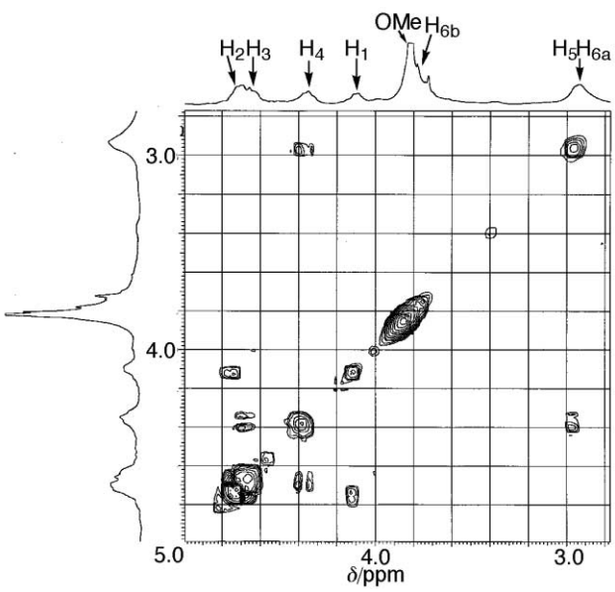

Fig. 1 H–H COSY spectrum of low DP C_1TCAc.

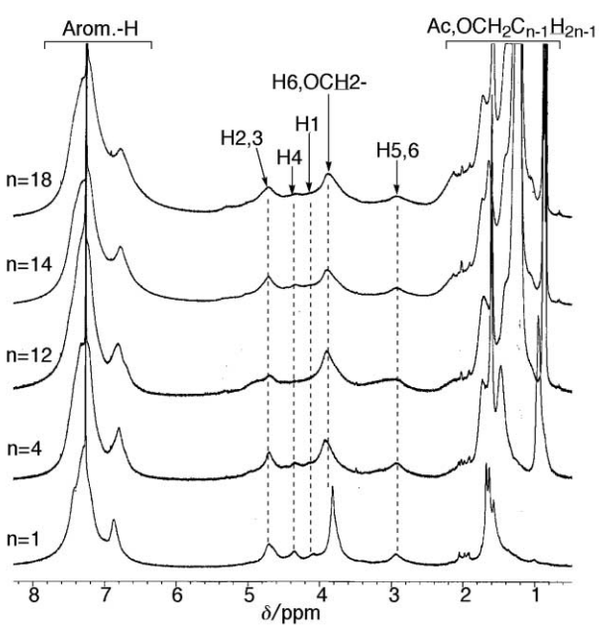

Fig. 2 ^{1}H NMR spectra of C_nTCAc.

It is interesting to compare these chemical shifts with those of 2,3-di-*O*-acetyl-6-*O*-methyl cellulose (2,3Ac6M)[7] to see the π-electron effects of the trityl groups on the chemical shifts, as shown in Table 2. The trityl group affected the chemical shifts:

Table 2 ^{1}H NMR chemical shifts (δ) of 2,3Ac6M and C_nTCAc

	δ/ppm						
	1H	2H	3H	4H	5H	6Ha	6Hb
2,3Ac6M	4.40	4.81	5.03	3.85	3.38	3.56	3.56
C_nTCAc	4.09	4.69	4.66	4.35	2.93	2.93	3.78
$\Delta\delta^a$	−0.31	−0.12	−0.37	+0.50	−0.45	−0.63	+0.22

[a] $\Delta\delta = \delta$ CnTCAc − δ 2,3Ac6M

Table 3 Solubility[a] of C_nTCs

		n [c]					
Solvent	δ[b]	0	1	4	12	14	18
DMSO	12.8	+	+	+	−	−	−
DMF	11.5	+	+	+	+	+	−
DMA	10.8	+	+	+	+	+	+
Pyridine	10.4	+	+	+	+	+	+
1,4-Dioxane	9.8	+	+	+	+	+	+
CH_2Cl_2	9.6	(+)	(+)	+	+	+	+
Benzene	9.2	−	−	(+)	(+)	(+)	(+)
THF	9.1	+	+	+	+	+	+
$CHCl_3$	9.1	(+)	(+)	+	+	+	+
EtOAc	9.1	−	−	(+)	(+)	(+)	(+)
Toluene	8.9	−	−	(+)	(+)	(+)	(+)

+: Soluble, (+): Swollen, −: Insoluble. [a] Evaluated at a concentration of 10 mg mL^{-1}. [b] Solubility parameter. [c] 6-*O*-Trityl cellulose.

the protons (1H, 2H, 3H, 5H, 6H$_a$) in AGU are shielded by the trityl group and appear at higher magnetic fields, but two protons (4H and 6H$_b$) are deshielded and appear at lower magnetic fields. These results suggest that 4H and 6H$_b$ may be arranged on the same plane as the benzene ring of the trityl group resulting in these two protons being influenced by the deshielding effect of the benzene ring. These results may serve as the conformational analysis of the 6-*O*-(4-alkoxytrityl) group around the *exo*-ring C5—C6 bond with respect to C5—O5 and C5—C4 bond directions.[15]

Solubility of 6-*O*-trityl and (4-alkoxytrityl)celluloses

Table 3 shows the solubility of 6-*O*-trityl and (4-alkoxytrityl)-celluloses. The solubility was evaluated by dissolving 10 mg of each sample in 1 mL of solvent. All these trityl cellulose derivatives dissolved in DMA, pyridine, 1,4-dioxane and tetrahydrofuran (THF). The solubility, of course, depends on the alkyl chain length: increasing the chain length increases the solubility in less polar solvents such as CH_2Cl_2 and $CHCl_3$, but decreases the solubility in polar solvents such as DMSO and DMF. In fact, trityl compounds with n = 12–18 did not dissolve in dimethyl sulfoxide (DMSO) and those with n = 18 also did not dissolve in *N*,*N*-dimethylfolmamide (DMF). On the other hand, those compounds with n = 12–18 dissolved in CH_2Cl_2 and $CHCl_3$, but those with n = 0 and 1 swelled in these solvents. All compounds only swelled in benzene, ethyl acetate and toluene.

Thermal transition of 6-*O*-(4-alkoxytrityl)celluloses and their acetates

Thermal properties of a series of C_nTC and their acetates (C_nTCAc) were studied by differential scanning calorimetry (DSC) heated from room temperature to the thermal decomposition temperature at a rate of 10 °C min^{-1} and by visual observation using polarized optical microscopy (POM). In general, the melting point declines sharply with increasing substituent length in a cellulose with a series of *n*-alkyl chains.[16] However, all C_nTC did not display transitions up to thermal decomposition, probably resulting from the stiff intra- and intermolecular hydrogen bondings of free hydroxyl groups at C-2 and C-3 positions, although insolubility of cellulose is explained only by the intermolecular hydrogen bondings at 6-OH.

The 2,3-di-*O*-acetates (C_nTCAc) were also studied. Thermal analysis by DSC revealed separate and distinct transitions for these acetates as shown in Fig. 3. Both C_0TCAc and C_1TCAc decomposed on heating before melting. The other acetates displayed weak melt endotherms (peak temperature designated as T_m). The T_m decreased linearly with increasing substituent length from 206 °C for C_4TCAc to 131 °C for C_{18}TCAc. When these samples were melted, unisotropic spherulite-like structures developed. Then, subtle endotherm peaks designated as T_i appeared resulting in isotropic states. The flow birefingence was detected for these isotropic samples under POM.

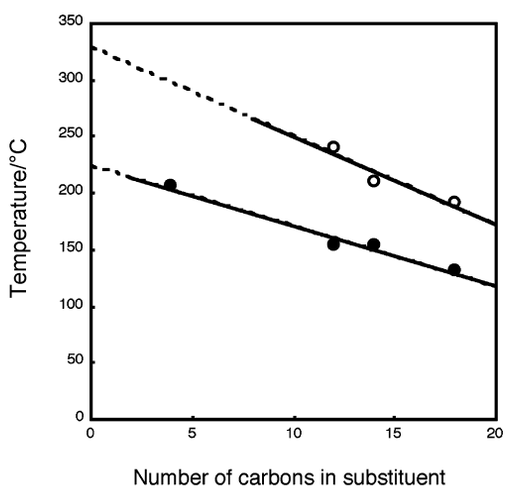

Fig. 3 Thermal transisions of C_nTCAc; T_m (solid circles) and T_i (open circles).

C_4TCAc showed only the degradation temperature without T_i. The T_i also decreased as the alkyl substituent increased in length from 210 °C for C_{12}TCAc to 190 °C for C_{18}TAc.

X-Ray diffraction patterns and possible molecular assembly of 6-*O*-(4-alkoxytrityl)celluloses

X-Ray diffraction patterns of the colorless powder state of C_nTC are shown in Fig. 4. A broad reflection at the low-angles region (2θ = 2.45–6.70°) was observed. The results of d spacing for these derivatives carrying a series of alkyl groups are shown in Fig. 5. Each relationship between d and n is essentially a straight line. The experimental function for d *vs.* n of these cellulose derivatives is expressed by the following equation: $d = 1.2593n + 12.74$, $R^2 = 0.995$. The extrapolated intercept of the d *vs.* n plot at the ordinate axis was 12.74 Å. The average increment in d spacing per CH_2 unit was 1.2593 Å. Based on the assumption of linear, elongated side chains oriented perpendicularly on the cellulose backbone, the increment was calculated to 1.257 Å (C–C distance = 1.541 Å, C–C–C angle = 109.28°). Calculation of the average d spacing increment

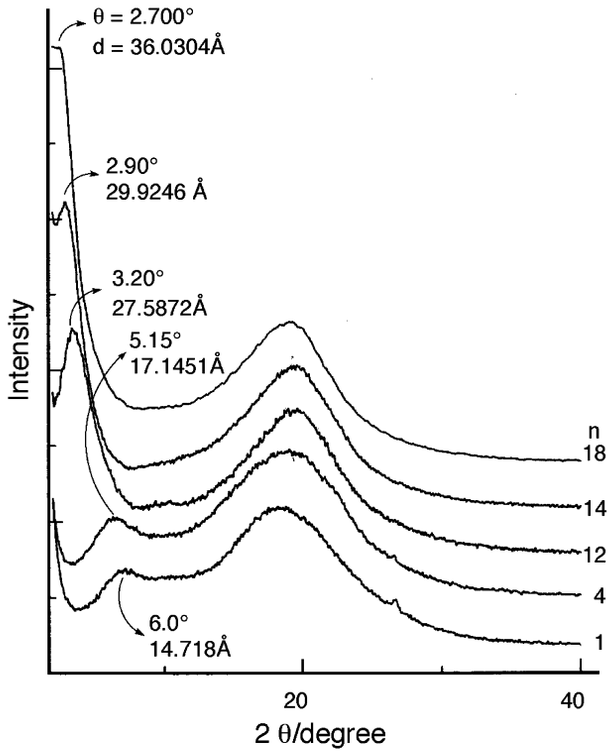

Fig. 4 X-Ray diagram of the C_nTC.

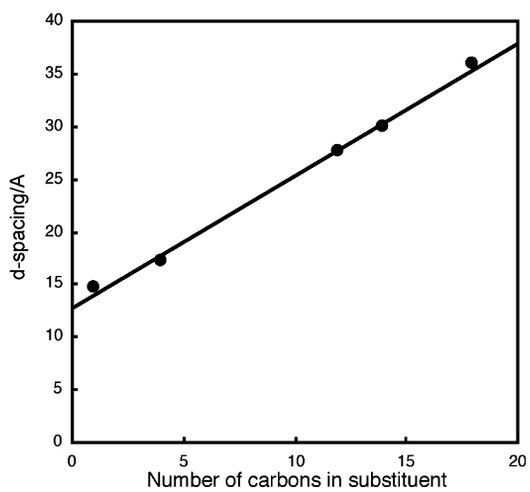

Fig. 5 Variation of the layer distance with the length of the alkyl substituents.

(1.2593 Å) is in reasonable agreement with the theoretical value (1.257 Å).

Although it is impossible to derive an exact structural description of the packing of the chain molecules from the X-ray diagram, a structural model which is not in contradiction to the obtained results so far will be proposed.

The simplest possibility would involve a layered structure as shown in Fig. 6. The relatively stiff backbones due to hydrogen bonding of the C2 and C3–OH, were assumed to be arranged in a parallel fashion. The fully extended side groups are also parallel to each other in this plane and perpendicular to the polymer backbone and interdigitation takes place. Because the alkyl side chains of C_nTCs are most likely interdigitated as the side chains on the C-2 and C-3 positions are free, there will be sufficient space to accommodate another incoming alkyl chain from the opposite direction. In addition, the *d* spacing between main chains supports the above assumption. Intensity of the X-ray diffraction spectrum increased with increasing the number of carbons in the alkyl chain due to the longer alkyl chains being easily interdigitated. The schematic representation shown in Fig. 6 is also supported by the optimized assembled structure of C_{18}TC with DP 10 by the molecular mechanics simulation shown in Fig. 7. Three layers of interdigitated structure were maintained.

A second possibility would be the bilayer model by Wegner[17] in which the side chains were not interdigitated. But without interdigitation, the side group would be tilted in respect to the linear backbone and the tilt angle between the backbone and the side chains would theoretically be in the range below 30° to be found a *d* value, which is actually highly improbable, because of the steric hindrance.

In fact, layered structures as described above were found for several semi-flexible polymers.[18] Kwei *et al.*[19] used a similar model to describe the structure of several derivatives of hydroxypropylcellulose (HPC) with various side chain lengths, according to Wegner's model for substituted aromatic polyesters. Gray *et al.*[20] reported a parallel alignment of the HPC esters. The distance between the backbones is controlled by the length of the side groups.[18]

Conclusion

This work deals with new applications of a series of C_nTCl on regioselective 6-*O*-cellulose derivatization. Thus, C_nTC with DS values of about 1.0 were obtained at 70 °C in DMA–LiCl–pyridine in high yields. Resulting cellulose ethers became soluble in less polar solvents but rather insoluble in polar solvents with an increasing number of carbon atoms in the alkyl substituent. A diagram of phase transition temperatures for a series of C_nTCAc was designed by POM and DSC studies. T_m and T_i were linearly decreased with lengthening the alkyl chain. All the C_nTC showed reflections in the low-angle region of the WAXS profiles, proposing that the extended alkyl side chains were perpendicular to the main-chain and interdigitated. The obtained C_nTCs are expected to be used towards further derivatization on the residual secondary hydroxyl groups at C-2 and C-3 of the AGU.

Experimental

Materials

Cellulose microcristalline (Avicel®, DP = 114) was purchased from Merck. The other reagents were purchased from Nakarai Tesque Inc. (Kyoto, Japan) or Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

Measurements

^{1}H NMR spectra were recorded with a Varian INOVA300 FT-NMR (300 MHz) spectrometer in chloroform-*d* with tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) and coupling constants (*J*) are given in δ values (ppm) and Hz, respectively. Optical rotations were measured at 25 °C (*c* 1.0 in $CHCl_3$) using a JASCO Dip-1000 digital polarimeter. The molecular weights of cellulose and the tritylated derivatives were obtained by measuring the molecular weight of the acetylated cellulose by means of gel permeation chromatography (GPC) in chloroform at 40 °C. Calibration curves were obtained by using polystyrene standards (Shodex). A Shimadzu liquid chromatography injector (LC-10ATvp), a Shimadzu column over (CTO-10Avp), a Shimadzu UV–vis detector (RID-10A), a Shimadzu communication bus module (CBM-10A), a Shimadzu LC workstation (CLASS-LC10), and Shodex columuns (KF802, KF802.5, KF803 and K805) were used. The flow rate was 1.0 mL min^{-1}. Wide angle X-ray scattering was measured by means of a Rigaku X-ray diffractometer (RINT2200V, Rigaku, Co. Ltd., Tokyo). DSC studies were carried out on a Rigaku Thermoflex DSC 8230. About 1.5 mg of each sample was used at 10 °C min^{-1} under nitrogen. An optical microscope (OLYMPUS BHS-751–1) equipped with

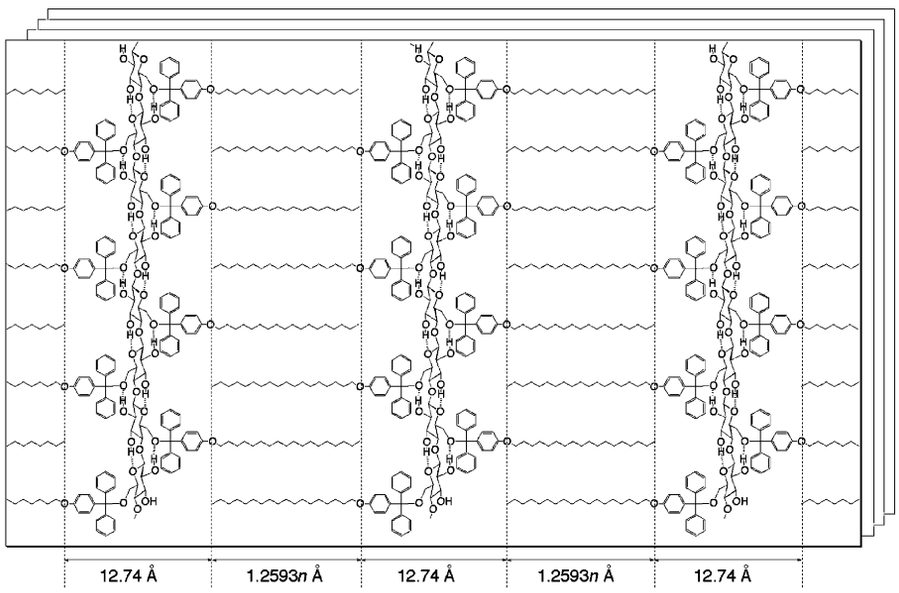

Fig. 6 Schematic representation for the macromolecule packing model of the cellulose chains.

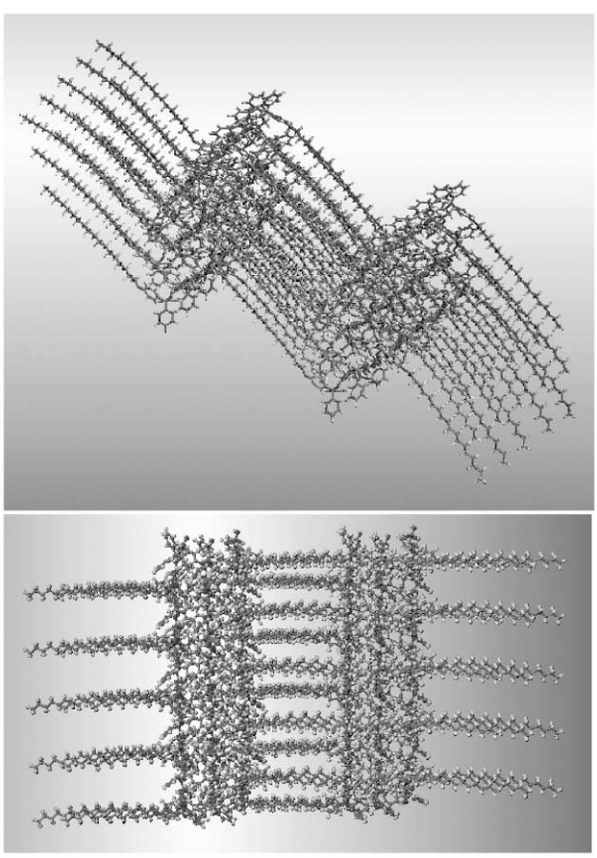

Fig. 7 Structural model for the packing of cellulose chains from a molecular mechanics simulation.

a hot stage was used to observe the morphological features and phase transitions of the polymers. The molecular model structure was built up using the Material Studio Visualizer released from Accelrys, Inc., and then optimized under the CFF91 Force Field using the Molecular Simulation Software, DISCOVER, also released from Accelrys, Inc. The most stable optimized model structures were piled up in the triple layer and then further optimized also under the CFF91 Force Field. All calculations were executed on the SGI-CRAY ORIGIN 3800 at the Super Computer Laboratory, Institute for Chemical Research, Kyoto University.

6-*O*-(4-Alkoxytrityl)celluloses (C_nTC)

A series of C_nTCl were synthesized according to the procedure described in ref. 12 and C_0TC and C_1TC were according to ref. 8. Microcrystalline cellulose (100 mg) was dried at 100 °C for 1 h under vacuum and was suspended in 2 mL of DMA and kept at 130 °C for 2 h under stirring. After the slurry had been allowed to cool to 100 °C, 150 mg of LiCl (dried at 130 °C for 2 h under vacuum) were added. By cooling to room temperature under stirring, the cellulose dissolved completely. After standing overnight, 224 µl of anhydrous pyridine (2.79 mmol, 4.5 equivalent per AGU) freshly distilled over potassium hydroxide were added. Then, C_nTCls (n = 4, 12, 14, 18; 1.86 mmol, 3.0 equivalent per AGU) dissolved in 1 mL of DMA were added under stirring at room temperature. The homogeneous reaction mixtures were stirred for 4 h at 70 °C, then cooled to room temperature, poured into 100 mL of ethanol under stirring, the precipitates were filtered off. The precipitates were dissolved in 5 mL of THF, then poured into 100 mL of ethanol for purification to give colorless precipitates. The precipitate was washed with 30 mL of ethanol, the sample was air-dried and then dried at 40 °C under vacuum to give C_nTCs (n = 4, 12, 14, 18) as a colorless powder (84–97%).

Hydrolysis of ethyl 4-alkoxytrityl ether to recover tritylation reagent as C_nTOH

After filtration of C_nTC in the above experimental procedure, the filtrate was concentrated *in vacuo* and diluted with EtOAc. The EtOAc was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. Then, 3 mL of DMF and 0.5 mL of 1 M H_2SO_4 were added and the mixture stirred at 100 °C for 1 h. The solution was concentrated *in vacuo* to remove ethanol, diluted with EtOAc, washed with aqueous $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was crystallized from *n*-hexane to give C_nTOH as a colorless powder.

2,3-Di-*O*-acetyl-6-*O*-(4-alkoxytrityl)celluloses (C_nTCAc)

The cellulose derivatives C_nTC (0.1 mmol) were treated with 0.47 mL (5 mmol) of acetic anhydride and 1 mL of pyridine at 50 °C overnight. The reaction mixtures were concentrated *in vacuo*, and dissolved in a small amount of chloroform, The chloroform mixture was poured into 50 mL of ethanol to give precipitate. The acetylated cellulose derivatives (C_nTCAc) were filtered off, washed with 15 mL of ethanol, air-dried and collected. The samples were dried under vacuum at 40 °C to give C_nTCAc as a colorless powder.

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