

Cellulose Derivatives with Adamantoyl Groups

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ABSTRACT: A new synthesis pattern of adamantoyl esters of cellulose (AdTMSC) is described. The process was approached by two steps. The first one consists in the obtaining of trimethylsilylcellulose (TMSC), by reacting cellulose in *N,N*-dimethylacetamide/lithium chloride (DMA/LiCl) solution with chlorotrimethylsilane and hexamethyldisilazane. The AdTMSC was synthesized by reacting trimethylsilylcellulose with 1-adamantanecarbonyl chloride, at 130°C. The obtained compounds were characterized by elemental analysis, ¹H and ¹³C NMR, FTIR spectroscopy, thermogravimetry method, and X-ray diffraction. From ¹H

NMR spectroscopy and elemental analyses, the degree of substitution (DS) of the cellulose derivatives was established. The AdTMSC is soluble in common organic solvent like chloroform, THF, and DMSO. As revealed by ¹³C NMR spectroscopy, a faster reaction takes place at the O (6)H group from AGU compared with O (2)H or O(3)H groups. Furthermore, other important properties were established by X-ray diffraction and thermogravimetry method. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 105–112, 2006

Key words: cellulose ester; ¹H-NMR; ¹³C-NMR; FTIR

INTRODUCTION

The unique structure and reactivity of cellulose opens up various possibilities for the design of advanced materials based on this biomacromolecule.¹ Its attributes are renewable, biodegradable, and biocompatible so that it will be one of the main chemical resources of the future.

Concerning the chemical modification, the regioselective introduction of two or three different substituents, as well as the search for new protecting or activating substituents, are considered in the center of interest for the near future. A controlled functionalization of the different positions within the AGU can be performed by homogeneous reactions and via special cellulose derivatives. In derivatization process of cellulose under homogeneous conditions, the degree of substitution of the cellulose derivatives, DS, can be controlled by adjusting the molar ratio of derivatizing agent to cellulose. The substituent groups can be introduced regularly, along the natural polymer backbone, features of prime importance for applications of cellulose derivatives.² The physicochemical properties of these products are much better controlled than those prepared under heterogeneous conditions. For derivatization under homogeneous reaction conditions, the binary system *N,N*-dimethylacetamide/lith-

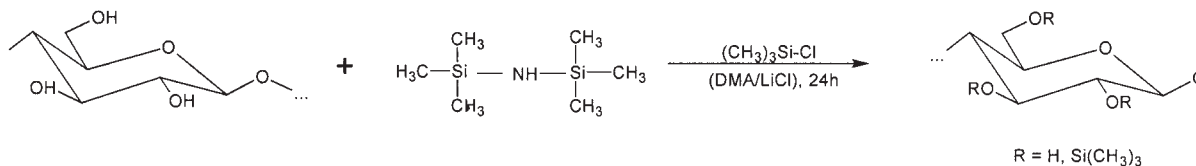
ium chloride (DMA/LiCl) has proven to be the most suitable for preparation of a wide variety of cellulose derivatives.³

To obtain cellulose derivatives with special properties, bulky adamantoyl groups have been incorporated into the cellulose chain. The unusual structure of adamantane imposes many chemical and physical properties, such as high thermal and oxidative stability, extreme lipophilicity, low surface energy, high density, and hydrophobicity.⁴ Numerous adamantane derivatives have been received considerable attention because of their diverse biological activity.⁵ Thus, a number of adamantane compounds were found to possess antibacterial activity,^{6–8} while a few papers reported on their antiviral activity.⁹ Another employed directions are the neurological disorder, e.g., Parkinson's disease^{10,11} and Alzheimer's disease,¹² cancer therapy,^{13,14} and anti HIV inhibitors.^{15,16}

We expect that a combination between cellulose and 1-adamantanecarbonyl chloride will provide active compounds suitable for biological and pharmacological investigations.

In the present article, the synthesis and characterization of the adamantoyl ester of cellulose is presented. The reaction was proceeding via trimethylsilylcellulose (TMSC), which was obtained by a homogeneous phase reaction, in the presence of DMA/LiCl at 130°C.¹⁷ This intermediary step was preferred because of the well-known regio- and stereoselective character and simple and selective removal of the silicon-containing structural units from the original organic compounds. Consequently, the distribution of

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Scheme 1 Synthesis of TMSC.

the functional groups may be controlled by the previous distribution of trimethylsilyl ether groups. This fact leads to a higher DS of cellulose ester obtained through the two-step method than that obtained by the method mentioned in literature.^{18,19} The structural modification determined by the introduction of the bulky adamantoyl groups was investigated by elemental analysis, ¹H and ¹³C NMR spectroscopy, FTIR spectroscopy, thermogravimetry method, and X-ray diffraction.

EXPERIMENTAL

Materials and methods

Avicel HP-101 (Fluka) was used in the air-dry state and was coded as C sample. The solvent *N,N*-dimethylacetamide (DMA) was dried and distilled prior to be used according to conventional methods. Anhydrous LiCl was dried at 130°C for 2 h under vacuum. All other chemicals (Fluka) were used without further purification.

Synthesis of trimethylsilylcellulose (TMSC)

Dried cellulose (2 g, 12.3 mmol) was dissolved in 60 mL DMA, kept at 120°C for 2 h under continuous stirring. To replace water bound to cellulose, about 4.25 mL DMA were removed by distillation in nitrogen atmosphere.²⁰ Then, the slurry was allowed to cool to 100°C and 5 g LiCl was added. By cooling to room temperature and stirring, the cellulose was completely dissolved within some hours.

After addition of 0.04 mL (0.4 mmol) chlorotrimethylsilane, 11.6 mL (71.87 mmol) hexamethyldisilazane was added drop wise within 25 min. The mixture was stirred for 24 h at 100°C. Within this time, the trimethylsilylcellulose precipitated. After cooling down to room temperature, the mixture was poured into methanol and dispersed. The modified cellulose was separated and washed with water and methanol. It was dried under vacuum at room temperature and up to 100°C over KOH.

DS = 2.8 (calculated on the basis of carbon content) and 2.68 from ¹H NMR.

FTIR: 1258 cm⁻¹ (Si—CH₃), 1124 cm⁻¹ (Si—OC), 841 cm⁻¹ (Si—OC), and 840 cm⁻¹ (O—SiCH₃).

¹H NMR (CDCl₃): δ = 3.19 (H-2), 3.31 (H-3), 3.61 (H-5), 3.77 (H-4), 4.13 (H-1), and 4.29 (H-6).

Synthesis of adamantoyl esters of cellulose (AdTMSC)

Trimethylsilylcellulose (2 g, 5.3 mmol) was added under nitrogen atmosphere to 4.2 g (21.2 mmol) 1-adamantanecarbonyl chloride (AdCl) molten at 80°C. The mixture was heated for 120 min, at 130°C, and the resulting chlorotrimethylsilane was completely distilled off. After washing the residue with aqueous methanol, the resulting cellulose ester was dried at 50°C under vacuum.

DS = 2.5 (calculated on the basis of carbon content) and 2.41 from ¹H NMR.

FTIR: 1736 cm⁻¹ ν(C=O), 2908, 2852 cm⁻¹ ν(CH).

¹³C NMR (CDCl₃): δ = 26.82 (C-10, 12,14), 35.39 (C-11,13,15), 37.93 (C-9,16,17), 39.83 (C-8), 72.40 (C-6), 82.3 (C-2,3), and 102.12 ppm (C-1).

Measurements

All NMR experiments were performed on a Bruker DRX500 NMR spectrometer or Bruker AC200 FT-NMR, with tetramethylsilane as internal standard in CDCl₃ as solvent. The FTIR spectra were recorded on a Nicolet 5SXB FTIR spectrophotometer.

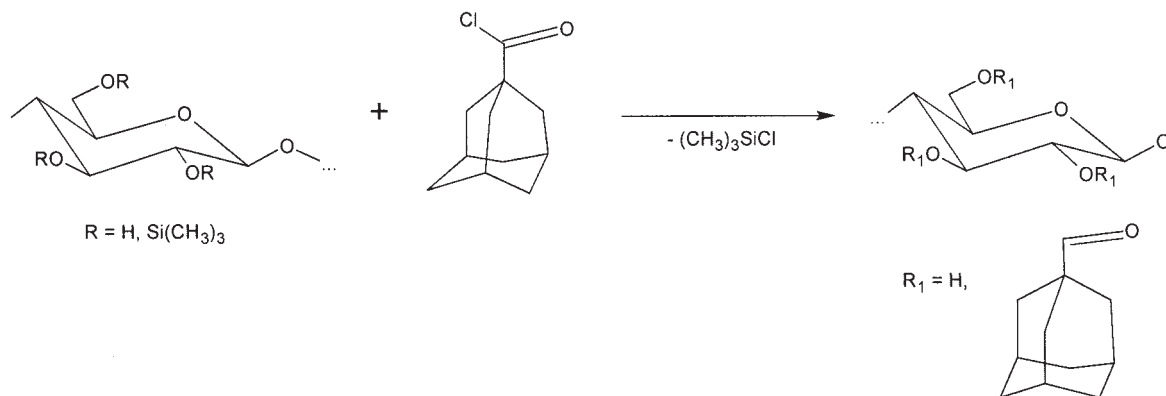
Thermogravimetric analyses were performed with a Erdey, Paulik and Paulik M.O.M. Budapesta Derivatograph at a heating rate of 12°C/min.

X-ray diffraction patterns of the samples were collected on a RIGAKU RINT 2500 apparatus and equipped with a transmission type goniometer using nickel-filtered, CuK_α radiation at 40 kV. The goniometer was scanned stepwise every 0.10° from 10 to 40° in the 2θ range. The resulting diffraction patterns ex-

TABLE I
Silylation of the Cellulose in DMA/LiCl Solution

Sample	Reaction conditions			DS	
	Temperature (°C)	Time (h)	Yield (%)	Elemental analysis ^a	¹ H NMR
TMSC	100	24	90	2.8	2.68

^a Based on the C content.



Scheme 2 Synthesis of AdTMSC.

hibited peaks, which were deconvoluted from a background scattering by using Lorentzian functions, while the diffraction pattern of an artificially amorphized sample was approximated by a Gaussian functions curve fitting analysis.²¹ The estimation of the degree of crystallinity of cellulose samples was obtained from the ratio of crystallinity area (S_C) and total area (S_T):²² Cr.I. (%) = S_C/S_T .

RESULTS AND DISCUSSION

Cellulose was dissolved in DMA/LiCl and silylated in the presence of chlorotrimethylsilane and hexamethyldisilazane, at 100°C (Scheme 1).

The obtained TMSC is soluble in common organic solvents, like chloroform and hexane. The degree of substitution (DS) was determined by elemental analysis and by ¹H NMR spectroscopy, and the values presented in Table I shows the correlation between these two methods. In the second case, the DS values were calculated as a ratio of integral values of H atoms characteristic for cellulose and for TMSC, respectively.

The reaction of TMSC with 1-adamantanecarbonyl chloride leads to cellulose ester with adamantoyl groups (AdTMSC), as is shown in Scheme 2. At a TMSC/AdCl molar ratio of 1/4 and a reaction temperature of 130°C, a sample with a DS of 2.41 (Table II) was obtained, which is soluble in chloroform, THF, and DMSO.

TABLE II
Reaction of Cellulose with 1-Adamantanecarbonyl Chloride—Conditions and Results

Sample	Reaction conditions			DS	
	Temperature (°C)	Time (h)	Yield (%)	Elemental analysis ^a	¹ H NMR
AdTMSC	130	120	89	2.5	2.41

^a Based on the C content.

For the characterization of regioselectivity, the knowledge of the distribution of functional groups within the AGU and along the polymer chains of modified cellulose is essential. To obtain these informations, ¹H and ¹³C NMR spectroscopy were used.

In the case of TMSC, a complete 6-O silylation and an additional O-2 and O-3 silylation have been observed by ¹H NMR (Fig. 1). The resonances assigned to the hydrogen atoms of AGU are visible in the region $\delta = 4.29$ – 3.19 ppm, while the resonances characteristic for silyl groups appears at $\delta = -0.03$ to 0.05 ppm.

Figure 2 shows the resonances assigned to the carbon atoms of the 1-adamantanecarbonyl chloride recorded in CDCl₃ spectrum analyzed in comparison with Figure 3, which present the spectrum of adamantoyl cellulose ester. The signal of 1-adamantanecarbonyl chloride appears at $\delta = 28.27$ (C-4,6,8), 36.45 (C-5,7,9), 39 (C-2), 39.4 (C-3,10,11), and 180.34 ppm (C-1). In the ¹³C NMR spectrum of adamantoyl cellulose beside characteristic signals of adamantoyl groups appear the resonances corresponding to the carbon atoms of the modified AGU, detectable in the region of $\delta = 65$ – 105 ppm.

To explain the structural changes underwent by unmodified cellulose, the FTIR spectra of C, TMSC, and AdTMSC samples were compared (Fig. 4).

It is known that there are only four distinct bands in the cellulose FTIR spectra, which could be assigned to the vibrations of OH groups. Brazhnik and coworkers²³ established the existence of individual types of hydrogen bond on the basis of the dependence of the position of the band (OH) and the energy and length of the possible hydrogen bond.

In the present study, it was observed that the bands, which could be assigned to the vibration of OH groups, are shifted to higher wave numbers from unmodified sample –C, to TMSC and to AdTMSC, finally. These changes might be attributed to a diminution of the hydrogen bond energy determined by a

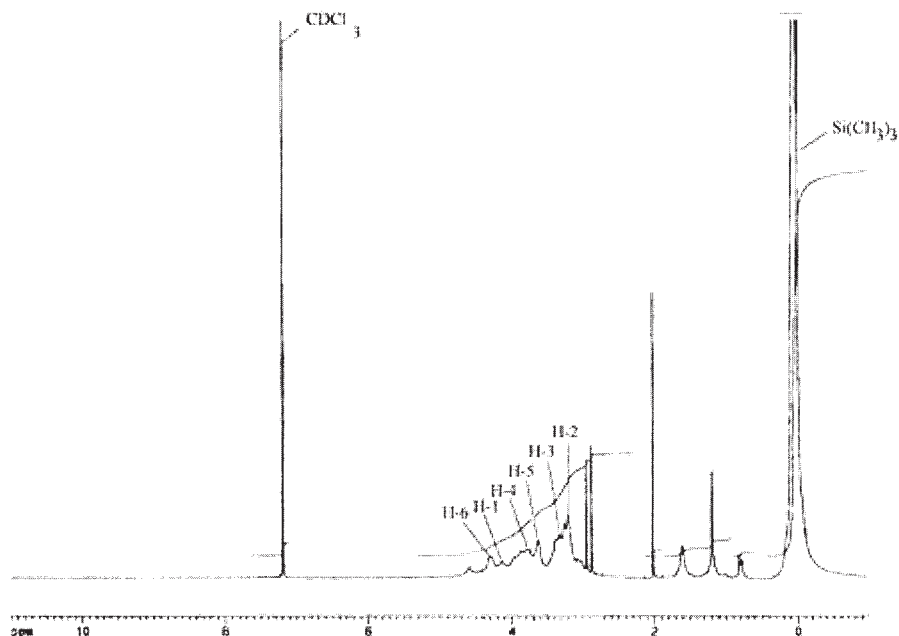


Figure 1 ^1H NMR spectrum of trimethylsilylcellulose (TMSC) recorded in CDCl_3 .

reduction of the number of hydrogen bonds; therefore, to an increase of the less-ordered domains. This fact is also emphasized by the decrease in the intensity of the absorbance bands of the OH groups. For TMSC sample, the broad band in the OH region appears contracted compared with the unmodified sample as a

consequence of the transformation of the hydroxyl groups into silyl ether function.

This observation is emphasized by the characteristics of the absorption of "amorphous band" -898 cm^{-1} .²⁴ The profile of this vibration band is changed in the case of TMSC sample by an important increase

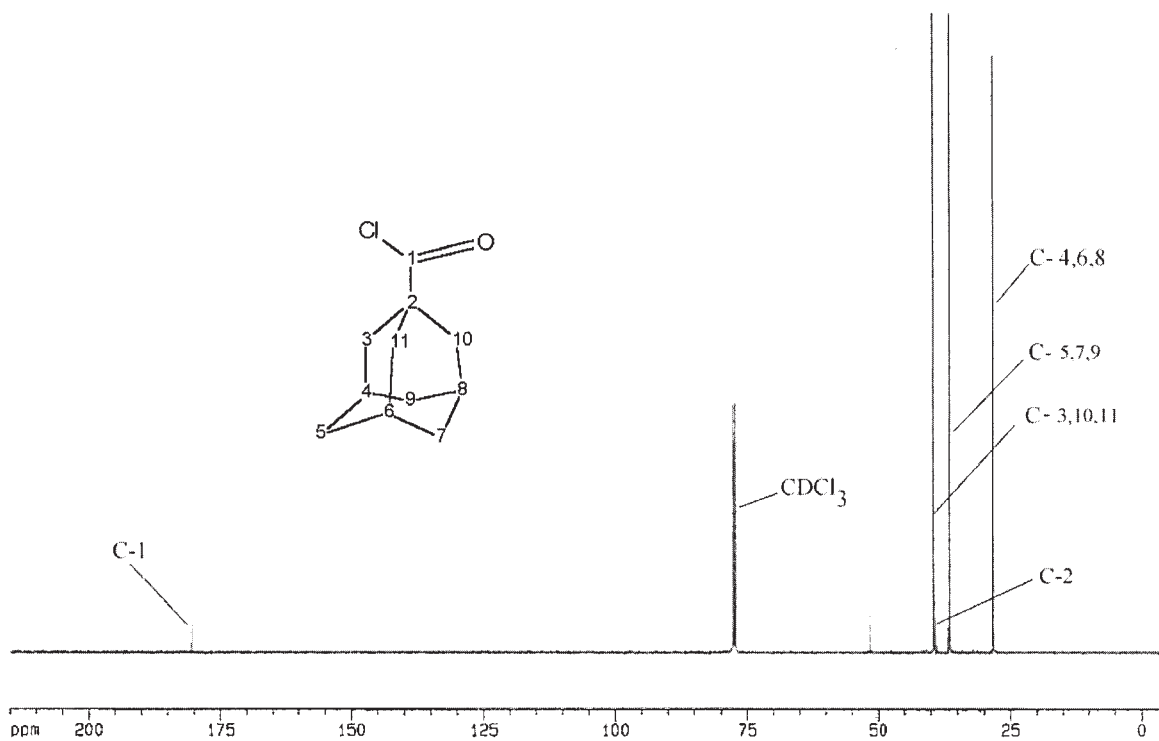


Figure 2 ^{13}C NMR spectrum of 1-adamantanecarbonyl chloride in CDCl_3 .

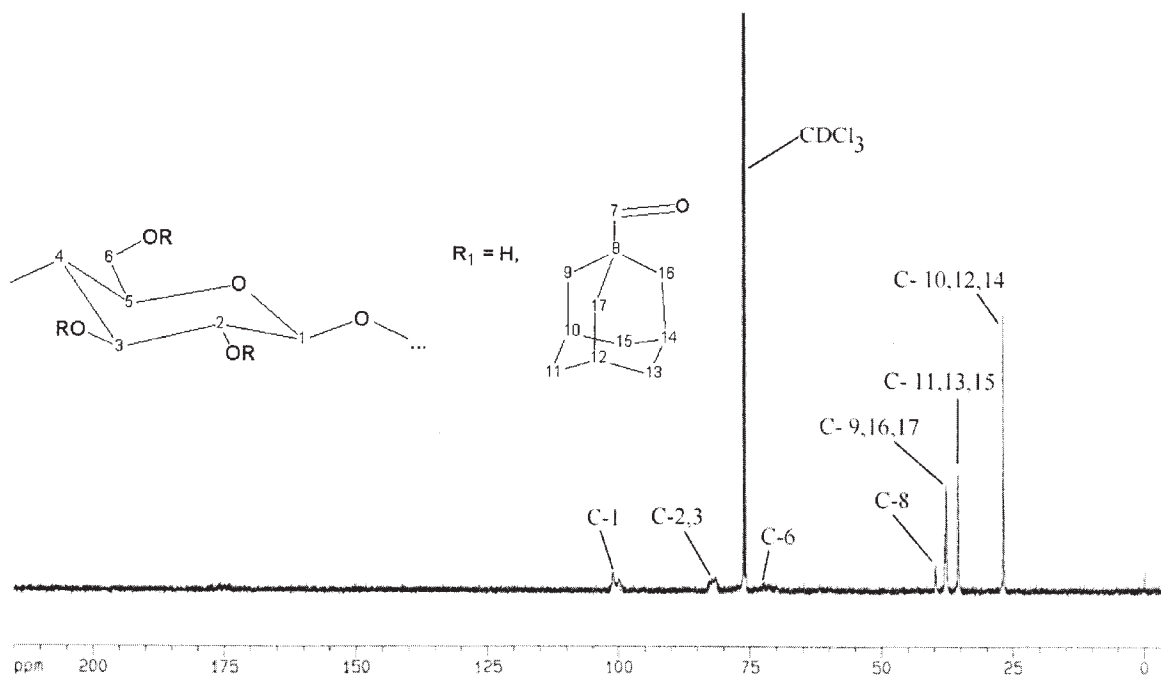


Figure 3 ^{13}C NMR spectrum of adamantyl ester of cellulose in CDCl_3 .

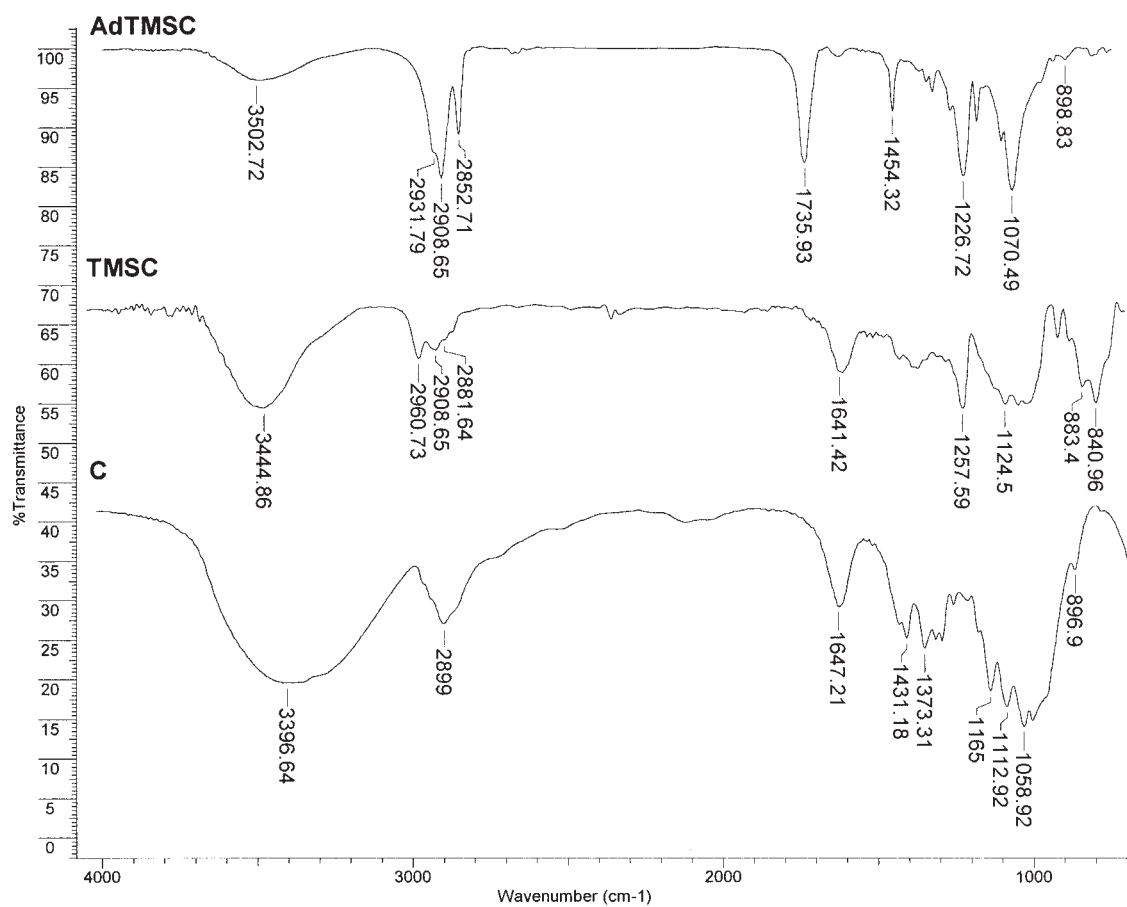


Figure 4 FTIR spectra of C, TMS, and AdTMS samples.

in the intensity, accompanied by the splitting of the band, fact which indicated a strong decrease in crystallinity of the sample.

The typical absorptions bands that confirm the presence of the silyl groups are: 1258 cm^{-1} (Si—CH₃), 1124 cm^{-1} (Si—OC), 841 cm^{-1} (Si—OC), and 840 cm^{-1} (O—SiCH₃).

In the case of AdTMSC sample, a diminishing of crystalline area, illustrated by a decrease in the intensity of the absorbance band of OH groups (3502 cm^{-1}), was observed. The increase of amorphous area can be explained by the presence of adamantoyl groups, which was determined by a split between the cellulose chains because of its bulky structure. The weak vibration band from 3502 cm^{-1} shows the absence of the free OH groups, which are transformed in ester groups.

In the FTIR spectra of AdTMSC sample, the characteristic band of the ester group appears at 1736 cm^{-1} $\nu(\text{C}=\text{O})$, and the typical absorption bands for the adamantoyl groups are found at 2908 and 2852 cm^{-1} $\nu(\text{CH})$.

The X-ray diffraction patterns of C, TMSC, and AdTMSC samples are shown in Figures 5, 6, and 7. The unmodified cellulose revealed reflection characteristic to cellulose I, i.e., the reflex of the (101) plane appear to 14.7° , (10 $\bar{1}$) to 16.5° and for 002 to a 2θ angle of 22.6° . The profile corresponds for TMSC revealed that this sample is completely amorphous.

The diffraction pattern of AdTMSC indicates peaks, which were deconvoluted from a background scattering by using Lorentzian functions. The peak that appears at 15.5° can be attributed to (111) plane of adamantoyl group and the one from 22.2° corresponding to (002) plane from cellulose.

It is generally accepted that the formation of levoglucosan from crystalline regions and its evaporation produces the endothermic peak observed during differential thermal analysis.²⁵ The different effects of supramolecular structure of synthesized compounds

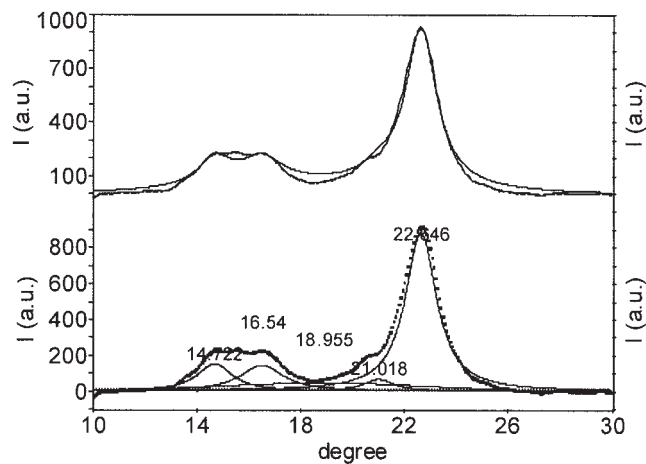


Figure 5 X-ray diffraction curves of C sample.

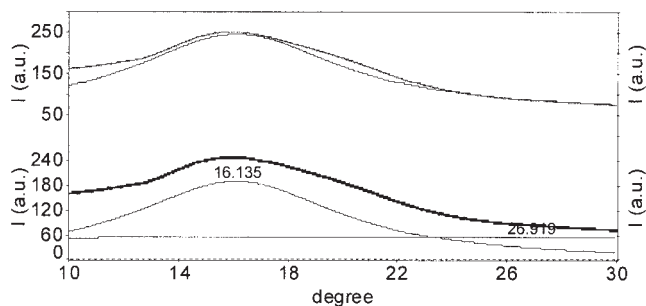


Figure 6 X-ray diffraction curves of TMSC sample.

on the DTA characteristics have been investigated (Fig. 8).

In the case of untreated cellulose, two endothermic peaks, a major one at 340°C and a smaller one at 380°C , were observed. The DTA curve of silylated derivative of cellulose shows a series of new exothermic peaks between 250 and 360°C . This result indicates a change in the type of pyrolysis reactions, corresponding to a major decrease in crystallinity of the sample.

The DTA curve of AdTMSC presents two exothermic peaks. The first one corresponds to a complete degradation of the sample, confirmed by DTG curve (Fig. 9), while the second one to a structural rearrangement of the residuum, because of the absence of a weight loss in that temperature range.

The DTG curves of TMSC present an endothermic peak at highest temperature (347°C) compared with unmodified cellulose and AdTMSC, indicating a high thermal stability. Also, it can be observed that the cellulose ester, AdTMSC, is more stable than C sample (Table III).

Interesting for this new ester of cellulose is the rapid thermal decomposition, in a single step fact, which may be determined by the structural destabilization produced by the introduction of the bulky adamantoyl groups in the macromolecular chains of TMSC sample. Also, the DTG curve of AdTMSC, because of its

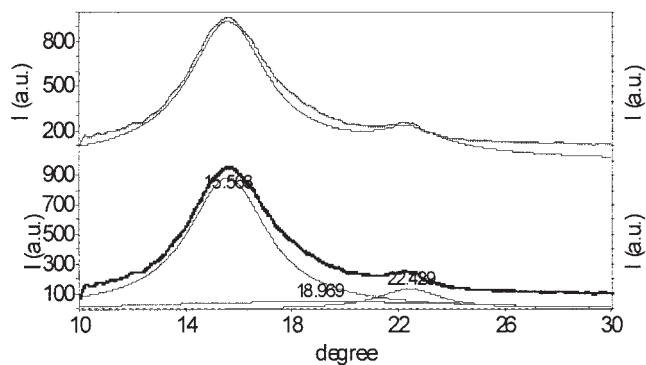


Figure 7 X-ray diffraction curves of Adams sample.

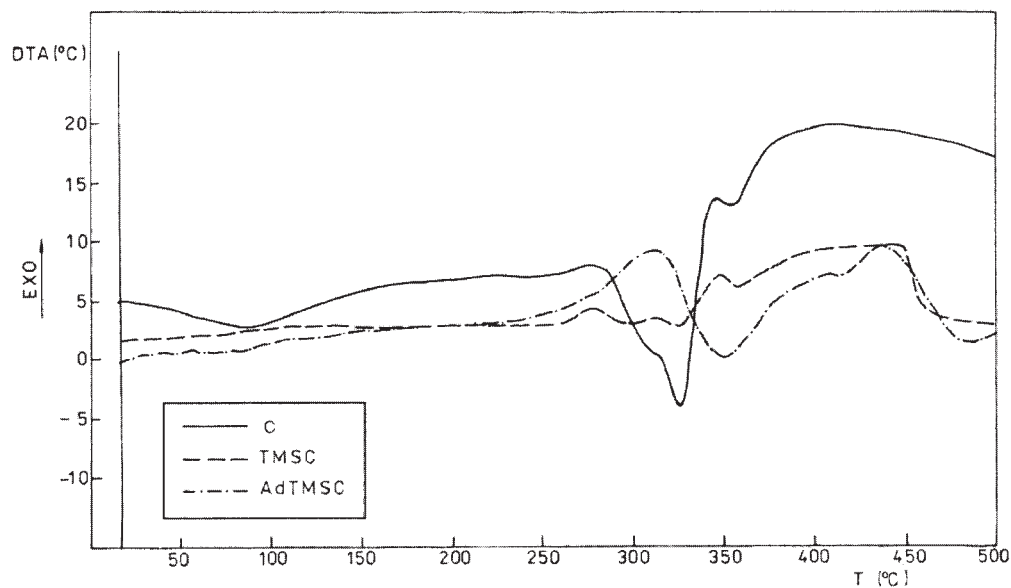


Figure 8 DTA curves for untreated cellulose (C), TMSC, and AdTMSC samples.

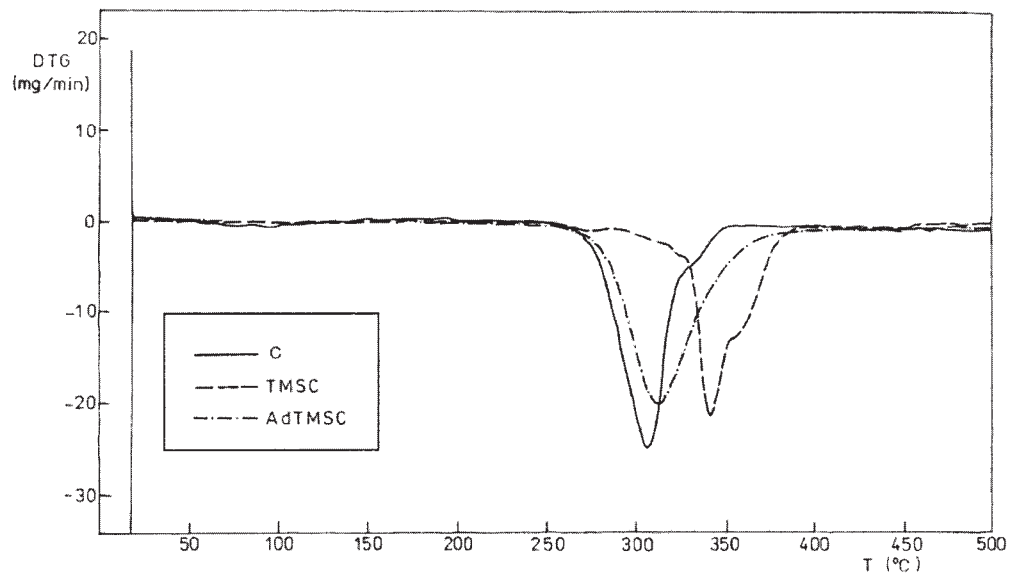


Figure 9 DTG curves for untreated cellulose, TMSC, and AdTMSC samples.

TABLE III
Thermal Decomposition Behaviour of C, TMSC, and AdTMSC samples

Sample	T_i (°C)	T_m (°C)	T_f (°C)	Δw (%)	E_a (kcal/mol)	n	Cr.I. (%)
C	286	320	378	76.7	69.9	0.5	81
TMSC	294	347	397	67.4	33.1	1.3	39
AdTMSC	260	328	403	88.5	88.5	1.6	88

uniformity, indicates a homogeneous structure with a rapid decomposition against the C and TMSC samples, which present slower decompositions, in more steps.

The TG curves of the studied samples indicate that the rate of pyrolysis of cellulose is a function of crystallinity (Fig. 10).

The apparent activation energy measured by dynamic TG pyrolysis can be correlated with the degree of crystallinity obtained from X-ray diffraction patterns of modified celluloses. Thus, the less-ordered sample (TMSC) presents the lowest value of activation energy, while the crystalline sample (AdTMSC), the highest one (Table III).

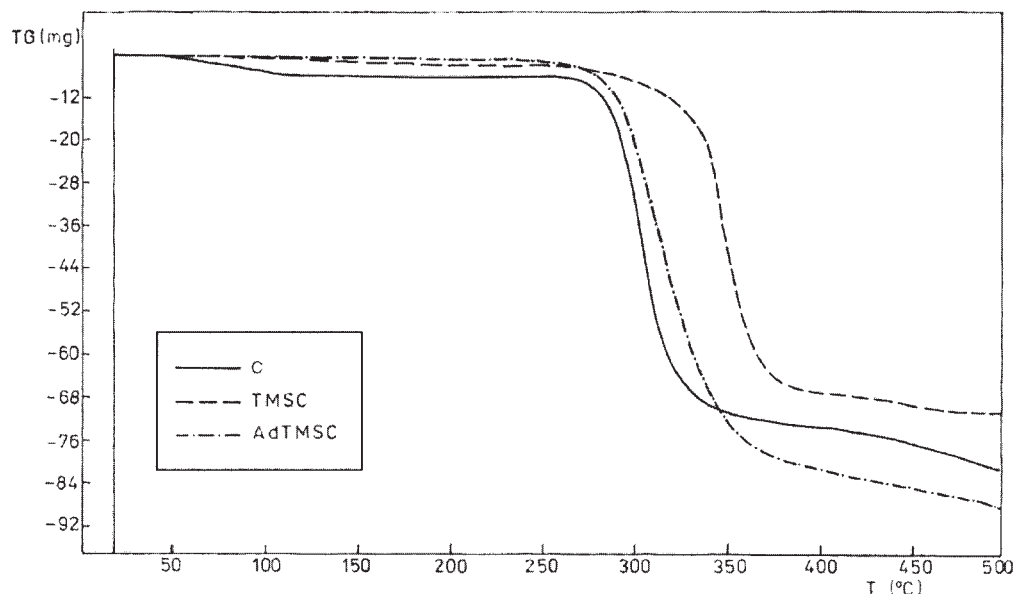


Figure 10 TG curves for untreated cellulose, TMS-C, and AdTMS-C samples.

CONCLUSIONS

The controlled functionalization of cellulose, via silyl-cellulose, represents the suitable methods for the preparation of adamantoyl esters of cellulose with high degrees of substitution. The obtained cellulose ester is soluble in different organic solvents, such as chloroform, DMSO, and THF, which is an important characteristic to study the structure-property relationships of the products. As revealed by ^{13}C NMR spectroscopy, a faster reaction takes place at the O(6) atom from AGU compared with O(2) or O(3) atoms. The effect of the large size of adamantoyl groups consist in an increase of the distances between cellulose macromolecular chains, determining an increase of amorphous domain of the sample, established from X-ray diffraction of adamantoyl ester of cellulose. The cellulose ester is thermally more stable than starting cellulose and its degradation is realized in a rapid single step. Detailed studies about the revealed physicochemical properties of adamantoyl cellulose that confer biological activity, as antimicrobial effects, are now in progress.

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