

SILYLATION OF CELLULOSE WITH TRICHLOROSILANE AND TRIETHOXY-SILANE IN HOMOGENEOUS LiCl/ N,N-DIMETHYLACETAMIDE SOLUTION*

Hai-qing Liu and Li-na Zhang**

Department of Chemistry, Wuhan University, Wuhan 430072, China

Abstract Silyl celluloses (SiC) were prepared by reacting cellulose with chloropropyltrichlorosilane (CPTCSi) and chloropropyltriethoxysilane (CPTESi) in LiCl/*N,N*-dimethylacetamide (DMAc). The Si content in the silyl cellulose could be controlled by adjustment of the molar ratio of silane and cellulose. FT-IR spectra showed that cellulose was readily reacted with the above two silane reagents, and the reactivity of CPTCSi is higher than that of CPTESi. It was presumed that the reaction process belongs to graft-polymerization. The results of differential thermal analysis (DTA) indicated that the thermostability of the materials produced increased with the increase of Si content in the sample. The acid resistance of the samples SiC in 1 mol/L HCl aqueous solution was improved significantly. When Si content was ca. 20%, the silyl cellulose has excellent thermostability, hydrophobicity, low density and stability in 1 mol/L HCl aqueous solution, owing to crosslinking of cellulose chain with silane.

Keywords Sily cellulose, Chloropropyltrichlorosilane, Chloropropyltriethoxysilane, LiCl/DMAc, Thermostability, Crosslinking

INTRODUCTION

Cellulose has extensive commercial applications in separation processes, medicine and food packaging, because of their relatively low cost, safety, and good compatibility with biological compounds. Polysiloxane is also well known as a useful material for medical packaging. Since the two polymers have different structure, the composite material from them may be developed into a high-performance and highly functional material. It was reported that chiral stationary phases (CSPs) for high-performance liquid chromatography (HPLC) have been prepared by reticulation of cellulose derivatives on silica gels^[1]. In our previous work^[2], preparative size exclusion chromatography with regenerated cellulose gel particles was used to fractionate dextran in water. However, an interaction between the stationary phase and dextran caused by their hydroxyl groups meant that a high-molecular-weight fraction was adsorbed on the gel particles and retarded. Silylation of cellulose may solve this problem.

It is well known that aryl- and alkylsilanes react easily and rapidly with organic or inorganic hydroxyl groups and silanes with various functional group can serve different purposes. Mormann^[3, 4] *et al.* reported the silylation of poly(vinyl alcohol) using monofunctional silane, and Tsukruk and Bliznyuk^[5], Chang and Frank^[6]

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** Corresponding author: Zhang Li-na (张俐娜), E-mail: lnzhang@public.wh.hb.cn

modified the surface of silicon wafers with tri-functional silane. Hybrid materials have been prepared by incorporating tetraethoxysilane into polymers by sol-gel processes. Their tensile modulus and strength showed a significant improvement^[7-9]. The three hydroxyl group per glucose unit on the cellulose backbone can be modified by some silane reagent, thus a cellulose with water repellency was obtained by treatment of cellulose with organosilicon halides^[10]. Among silyl cellulose derivatives, trimethylsilyl cellulose (TMSC) was most studied, and has been used as precursor to regenerated cellulose fiber^[11], Langmuir-Blodgett film^[12], or intermediate for regioselective synthesis^[13].

However, attention has hardly been paid to relating cellulose with multifunctional silane reagents, although many organic-inorganic hybrid materials^[7-9], cellulose/synthetic polymer blends such as cellulose/ poly(*N*-vinyl pyridine), cellulose/polyacrylonitrile and cellulose/poly (ethylene glycol)^[14-16], and composite film of cellulose/polyurethane^[17-19], have been carefully studied, exhibiting new and desirable physicochemical properties without parallel in conventional homopolymers. In this work, a new silyl cellulose derivative was synthesized by homogeneous reaction of cellulose in LiCl/*N,N*-dimethylacetamide (DMAc) solution. In this case, the trifunctional silane plays three roles in the reaction: 1) monomer for self-condensing polymerization, 2) modification reagent reacting with cellulose, 3) crosslinking reagent of cellulose. The structure and properties of the silyl cellulose were characterized and discussed.

EXPERIMENTAL

Materials

Cellulose was regenerated from cellulose acetate by a conventional method^[20]. Lithium chloride and cellulose were dried at 100 °C under vacuum before use. *N,N*-Dimethylacetamide and pyridine were distilled. Chloropropyltrichlorosilane (CPTCSi) was used as received. Chloropropyltriethoxysilane (CPTESi) was obtained by reacting CPTCSi with excess dehydrated ethanol; the fraction distilling at b.p. 160~163 °C was collected. All other reagents were analytical grade and were used without further purification.

Cellulose/LiCl-DMAc Solution

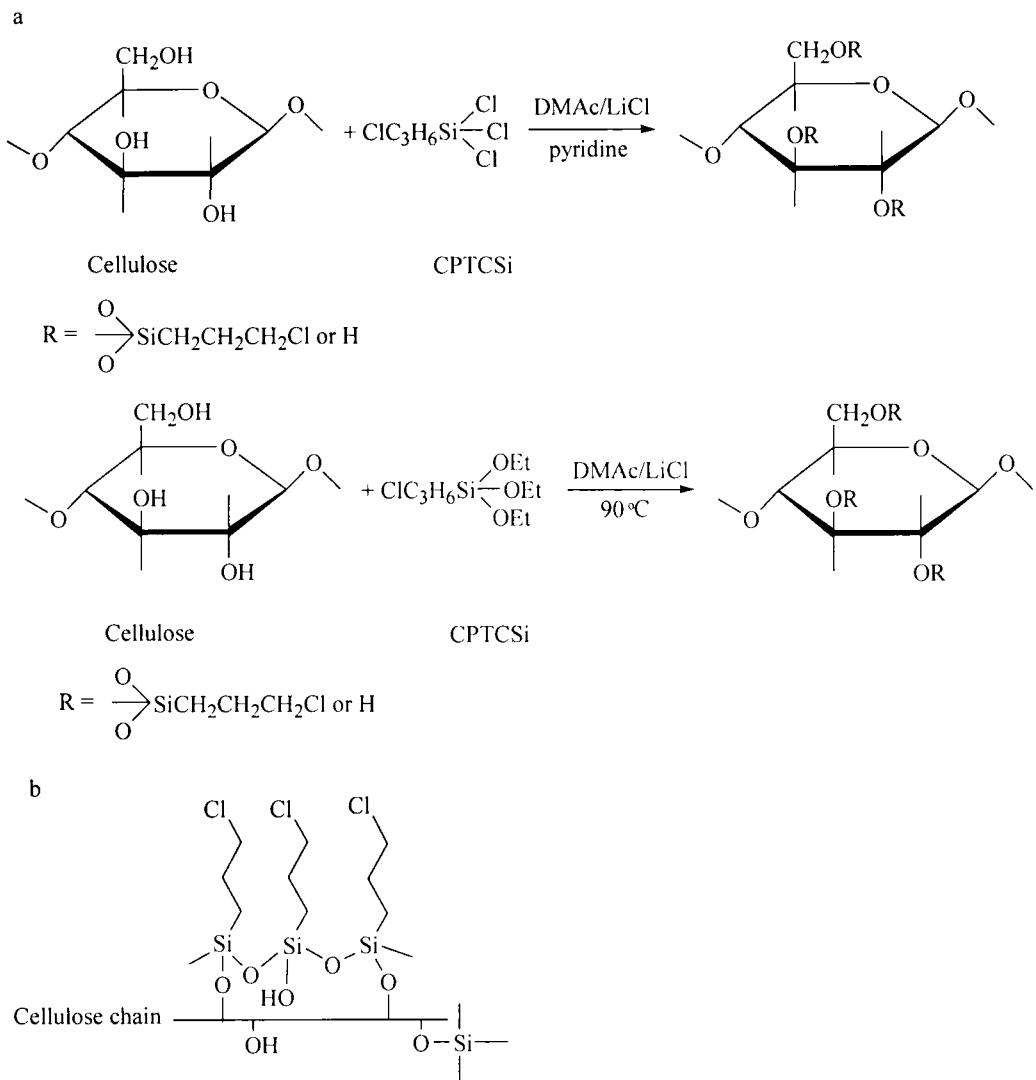
2% cellulose in LiCl/DMAc solution was prepared according to the method reported by McCormick^[21]. Namely, 4 g of cellulose was added to three-necked round bottom flask containing 176 g of DMAc. The mixture was heated from room temperature to 120 °C during a 1 h period, and kept another 1 h at 120 °C. The temperature was then decreased to 100 °C, and then 20 g of LiCl was added while stirring. After 1 h, it was cooled to room temperature, and still stirred till a transparent viscous solution was obtained.

Synthesis of Silyl Cellulose (SiC)

To a three-necked-round bottom flask equipped with stirrer, drying tube and N₂ inlet, containing 30 g of the cellulose solution mentioned above, 10 mL of pyridine was added. After 1 h stirring at room temperature, CPTCSi in DMAc was introduced dropwise by a syringe. 5 h later, the reaction was stopped by pouring the solution into methanol. The precipitate was collected by filtration and washed thoroughly by toluene and methanol, then dried at 60 °C under vacuum for 10 h. The samples thus obtained were coded as SiC-1, SiC-2, SiC-3 and SiC-4 according to the reaction condition shown in Table 1. For sample SiC-5, the procedure was same, except the substitution of CPTESi for CPTCSi and the absence of pyridine. The reaction temperature was 90 °C. Scheme 1 shows the reaction of CPTESi and CPTCSi with cellulose.

Self-condensing polymerization of CPTCSi was performed by hydrolysis in distilled water. The white powder polymer obtained was washed thoroughly with water and acetone, then dried and coded as P(CPTCSi).

The FT-IR showed the absorbance at 3100~3430 cm^{-1} ($\nu_{\text{Si-OH}}$) and 1000~1130 cm^{-1} ($\nu_{\text{Si-O-Si}}$).



Scheme 1 The reaction of CPTCSi and CPTESi with cellulose a); hypothetical structure of the product b)

Characterization

Infrared spectra (IR) were recorded with a Nicolet 170SX FT-IR spectrometer. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed using a TG-DTA/PRT-2 Thermal Balance (Peking Optical Instrument, China). The samples were measured under a nitrogen atmosphere from room temperature to 600 °C at a heating rate of 10 K/min. Silicon (SiO_2) elemental analysis (gravimetrically) was carried out after fusion of the samples in a muffle furnace at 700 °C.

Density measurements were made at 30 °C with a value-calibrated pycnometer. The volume of the pycnometer was determined with distilled water, and a mixture of glycerin and ethanol was used as the solvent. The density of the mixed solvent was considered as the density of the sample, when sample was suspended in the mixed solvent rather than at the surface or bottom of the solvent. The densities are the average of three measurements.

RESULTS AND DISCUSSION

Mechanism of Reaction

According to Scheme 1a), silyl cellulose can be prepared by using silylation with CPTCSi or CPTESi in homogeneous cellulose solution in DMAc/LiCl. Due to their high reactivity alkylhalosilanes can react with the hydroxyl group of cellulose, and the remaining unreacted Si—Cl group can perform self-condensing polymerization in the presence of water (Scheme 1b). In addition, the silane can react not only with the —OH group of one cellulose chain but also with the —OH group of another cellulose chain. Therefore it may act as monomer for self-condensing polymerization, modification and crosslinking reagent. Interestingly, the product precipitated from the solution with the reaction proceeding, indicated heterogeneous reaction in the late period of the reaction.

The above description of the reaction was verified by FT-IR results. Figure 1 shows the FT-IR spectra of the samples SiC-3, SiC-4 and SiC-5. It indicated that the broad absorbency at $3000\sim3600\text{ cm}^{-1}$ for the —OH group of cellulose was weakened and shifted to a higher wave number with the increase of the Si content in the sample, suggesting reduction of —OH groups and intermolecular hydrogen bonds in cellulose after reaction. Interestingly, even though the Si content of sample SiC-4 is as high as 19.8% (the corresponding value for SiO_2 is 42.4%), the hydroxyl group absorption is still present, suggesting the existence of unreacted —OH group on cellulose chain and small amount of silanol group (Si—OH) derived from Si—Cl by hydrolysis, although most of the Si—OH group undergoes reaction with —OH group of cellulose and self-condensing polymerization. It is worth noting that trifunctional silane can readily self-condense to form a Si—O—Si network via hydrolysis with acid as catalyst^[5, 6]. In addition, the absorption peak at 1640 cm^{-1} ($\nu_{\text{C}=\text{O}-\text{C}}$ in anhydroglucose unit of cellulose^[22]) of the samples SiC-3 and SiC-4 also decreased with increase of Si content, implying the crosslinking of cellulose chain by the silane reagent, which can hinder the stretching vibration of C—O—C group. The band at $1000\sim1130\text{ cm}^{-1}$ is assigned to the stretching vibration of Si—O—Si and C—O group. The new peaks around 790 cm^{-1} and 700 cm^{-1} for samples SiC-3 and -4 are caused by $\nu_{\text{C}-\text{Cl}}$ and $\delta_{\text{C}-\text{H}}$ of the alkyl group in the silane, respectively. No trace of $\nu_{\text{Si}-\text{Cl}}$ at 475 cm^{-1} was found, indicating that Si—Cl group was completely changed into Si—O group. These facts showed that the reaction of silane with cellulose and itself occurred.

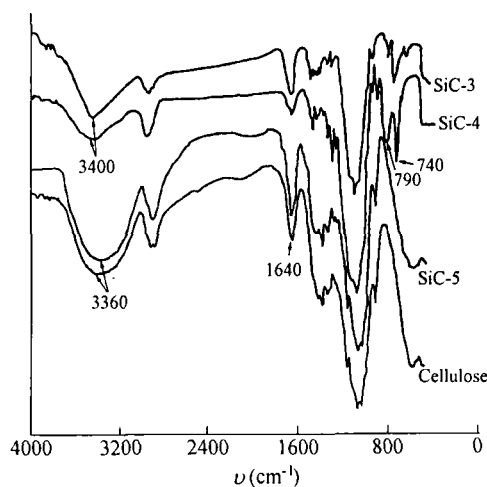


Fig. 1 FT-IR spectra of sample cellulose, SiC-5, SiC-4, SiC-3 from bottom to top

Table 1 shows the reaction conditions and some analysis results of the samples. In the experimental range, the Si content increased with the increase of introduced silane reagent. In this work, the reaction can be controlled quantitatively, since the Si content of sample SiC-4 and SiC-3 are almost 3 and 2 times that of sample SiC-1. However, the etherification of cellulose could not usually be controlled so well^[23, 24]. From the table, it can also be seen that the reactivity of CPTESi is much lower than that of CPTCSi. Interestingly, sample SiC-4 is a kind of hydrophobic material. Because of the hydrophobic property of chloropropyl group of CPTCSi/CPTESi, the silylcellulose derivatives can alter from hydrophilic to hydrophobic. The cellulose derivative with hydrophobic alkylsilane group may have promising application as a packing material for size exclusion chromatography to avoid adsorption caused by its hydroxyl groups. The Cl content of the sample is also listed in Table 1. The molar ratio of Si/Cl almost equal to 1.0 for all the silyl cellulose, indicating that Cl in the chloropropyl group did not react with the —OH group in cellulose, as shown in Scheme 1.

Table 1. Reaction condition and analysis results of the silylcellulose

Sample	Amount of reagent		Si (%)	Cl (%)	Wettability	Density (g/cm ³)
	Cellulose:Pyridine:Silan					
SiC-1	0.6:10:1		6.7	8.3	+	1.23
SiC-2	0.6:10:1.5		10.0	12.2	+	1.13
SiC-3	0.6:10:2		11.4	14.4	+	1.1
SiC-4	0.6:10:4		19.8	23.8	–	0.93
SiC-5	0.6:0.3		4.2	5.16	+	1.25

- a) The silane reagent is CPTESi, and the other sample are from CPTCSi;
- b) Determined by the naked eye, + and – represent hydrophilic and hydrophobic, respectively;
- c) Titrated by aq. AgNO3 after treatment.

Solvent Resistance of SiC

Table 2 shows the solubility of silyl cellulose in different solvents. No matter how much the Si content is, they cannot be dissolved in most polar or nonpolar solvent, unlike trimethylsilylcellulose (TMSC)^[25], which can be dissolved in chloroform and THF when DS ≥ 1.99. The samples SiC-3 and SiC-5 with low substitution were soluble in cadoxen, which is a good solvent for cellulose^[26], and can swell in aq. NaOH (5 wt%) solution. It suggests that silyl cellulose prepared with little modification of cellulose maintained the character of cellulose. However, the sample SiC-4 with high Si content was not soluble in cadoxen, indicating that it is a completely new polymer from cellulose. The poor solubility of sample SiC-4 maybe related to the crosslinking of the cellulose chain with silane. The density of sample SiC-4 was much lower than that of the other (Table 1), suggesting that the intermolecular hydrogen bonds in cellulose were broken, crosslinking increased and more amorphous region formed. Usually, the density of the blends is in accordance with that calculated from the simple rule of mixtures^[27]. Therefore, the decrease of density also contributed to the grafted polymerization of CPTCSi or CPTESi on cellulose. Since the density of the polymer P(CPTCSi) is 0.87, the density of the grafted cellulose, i.e., silyl cellulose, will decrease with the increase of P(CPTCSi) content in the sample.

Table 2. Solubility of silyl cellulose

Sample	Toluene	Ethylacetate	DMF	NaOH (5 wt%)	Cadoxen
SiC-3	–	–	–	s	+
SiC-4	–	–	–	–	a
SiC-5	–	–	–	s	+

(–) insoluble; (+) soluble; (a) soluble in low concentration; (s) swell; Cadoxen is Cd(H₂NC₂H₄NH₂)₂

No apparent weight loss was observed after 24 h immersion of the samples in 1 mol/L aq. HCl solution at 25°C. However, it was reported that trimethylsilylcellulose was unstable under such conditions^[11, 25]. Thus, the conclusion can be drawn that the structure presented in Scheme 1B is effective for the stability in acid solution.

Thermostability of SiC

The effect of the silyl group on the thermal stability of the silyl cellulose is shown in Fig. 2. Each sample undergoes thermal degradation in a nitrogen atmosphere. The degrees of the thermal decomposition changed with Si content in samples. Table 3 summarizes the TGA data, and T_{10} , T_{30} and T_{50} are temperatures for 10%, 30% and 50% weight loss, respectively. From these results, it can be found that the thermostability of sample SiC-4 is much higher than those of the others, and follows the order of SiC-4>SiC-3>SiC-2>SiC-1, namely, increasing with the increase of Si content. The reduction of density and enhancement in thermostability for sample SiC-4 could be attributed to crosslinking of the cellulose chain with silanes, similar to interpenetrating polymer networks (IPN) from nitrocellulose/polyurethane, in which a crosslinkage was confirmed to be the contributing factor^[28]. The Si content obtained by subtracting residue weight of cellulose from that of sample SiC (Table 3) was a little larger than the content of Si listed in Table 1. It can be explained that the crosslinking of cellulose with silane enhanced the thermostability of cellulose, resulting in larger residual weight.

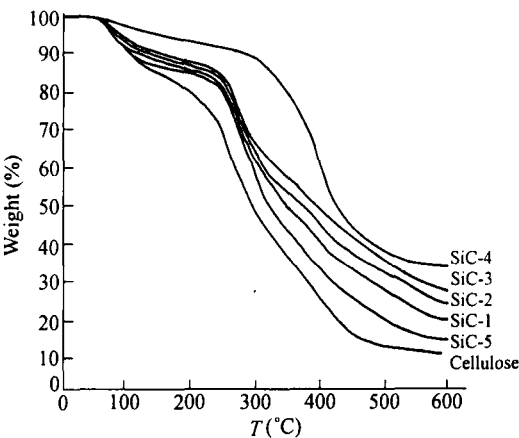


Fig. 2 TGA thermograms of sample cellulose, SiC-1, SiC-2 SiC-3, SiC-4 and SiC-5

Table 3. TGA data of the samples

Sample No.	T_{10}	T_{30}	T_{50}	Residual weight (%)
Cellulose	107	250	293	11
SiC-1	120	283	343	21
SiC-2	133	290	367	25
SiC-3	153	293	390	29
SiC-4	270	387	430	33
SiC-5	107	280	317	16

Figure 3 shows DTA curves of the samples. An endothermic peak in the range of 60~100°C was caused by elimination of the absorbed water in cellulose except sample SiC-4, which is hydrophobic. The endothermic peak for silyl cellulose at 180~210°C was assigned to the chain scission of the grafted polysiloxane by self-condensation. The following endothermic peak at 220~246°C was assigned to chain scission and loss of water molecules coming from the primary —OH groups of cellulose^[29] for samples SiC-1, -2 and -5. However, in the

case of SiC-3, -4, no clear peak exists in this temperature range because of the Si content; the crosslinkage can restrict the above two reactions of the cellulose chain. Usually, an endothermic process at 340°C exhibits that cellulose degrades completely by the loss of —OH groups and by the breakdown of the pyranosic rings^[29]. But for samples SiC-1, -2, -3, -4 and -5, it was overlapped by a large exothermic peak at ca. 380°C, which may be attributed to the crosslinking between silanol group and silanol group with remaining —OH group of cellulose.

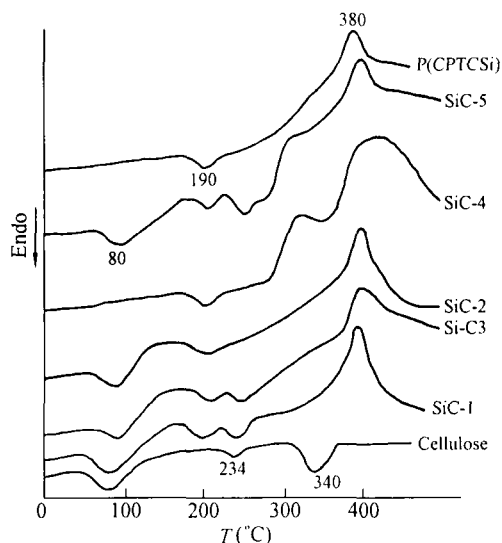


Fig. 3 DSC curves of sample cellulose, SiC-1, SiC-2, SiC-3, SiC-4, SiC-5 and P(CPTCSi)

CONCLUSION

A novel cellulose derivative silyl cellulose was prepared in homogeneous cellulose solution. The high reactivity of chloropropyltrichlorosilane made it possible that the Si content in the silyl cellulose could be controlled quantitatively. With the increase of Si content in the silyl cellulose, it can change to hydrophobic from hydrophilic, and its stability in acid aqueous solution or in most organic solvents and its thermostability were improved. It is promising to use it as packing for size exclusion chromatography, with excellent stability and low adsorption caused by the hydroxyl group in the cellulose.

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