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D. Bontea[a]; G. Caruntu[b]; N. Aelenei[c]
[a] "P. Poni" Institute of Macromolecular Chemistry, Iasi, Romania [b] "Al. I. Cuza" University, Iasi, Romania [c] "Gh. Asachi" Technical University, Iasi, Romania

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THE CHARACTERIZATION OF SOME SILYLCELLULOSE DERIVATIVES BY XRD MEASUREMENTS

D. Bontea*

“P. Poni” Institute of Macromolecular Chemistry
RO-6600, Iasi, Romania

G. Caruntu

“Al. I. Cuza” University
RO-6600, Iasi, Romania

N. Aelenei

“Gh. Asachi” Technical University
RO-6600, Iasi, Romania

Key Words: Trimethylsilylcellulose, Triethylsilylcellulose, Triphenylsilylcellulose, X-ray Diffraction, Crystallinity

ABSTRACT

In order to obtain some silylcellulose derivatives, five types of celluloses with different polymerization degrees (DP =327-1100) were used. The obtained silylcellulose derivatives were characterized from the crystallinity point of view as a function of both the substitution degree and characteristics of the used celluloses in their synthesis. The change of the crystalline structure as the result of silylation reaction was evidenced, the crystallinity of silyl derivatives depending on the substitution degree (DS) and on the nature of substituent used.

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*Author to whom correspondence should be addressed.

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INTRODUCTION

Cellulose and its derivatives contain crystalline and amorphous zones in different proportions, due to the hydrogen inter- and intra-molecular bonds, that influence the physical and chemical properties, function of their contribution. Because of the fact that cellulose contain an abundance of hydroxyl groups this compound is insoluble in water or in organic solvents. Replacement of some or all hydroxyl groups alter radically the properties of this polymer and make it soluble in many usual organic solvents. The crystallinity of cellulose, evidenced by X-ray spectra, depends on the method of treatment. The crystallinity of cellulose derivatives depends, besides the cellulose support properties, on both the substitution degree and the nature of the substituent. To put in evidence for these changes, the cellulose support used for synthesis and the cellulose derivatives obtained, were studied by X-ray diffractometry.

EXPERIMENTAL

For the proposed study, three types of silylcellulose derivatives were synthesized: trimethylsilylcellulose (TMSC), triethylsilylcellulose (TESC) and triphenylsilylcellulose (TFSC). Five samples of cellulose support having different polymerization and crystallinity degrees were used. These samples were obtained from resinous cellulose by depolymerization in NaOH solution (17.5% concentration); defibrillated for 60 minutes at 20°C, and treated then at 40°C for different time intervals.

The polymerization degrees (DP) and viscosimetric molecular weights (M_v) for the cellulose supports were evaluated by viscosimetric method in cupriethylenediamine solution, at 25°C [1], (Table 1).

In order to synthesize the silylcellulose derivatives, the cellulose samples were first activated. This was realized in acetic acid at 25°C for 60 min-

TABLE 1. Main Characteristics of the Cellulose Support Samples

SAMPLE	C_1	C_2	C_3	C_4	C_5
Treatment time, min	300	240	180	60	0
DP	327	588	708	880	1100
M_v, $Kg \cdot mol^{-1}$	53.3	96.4	116.1	144.3	180.0

utes, followed by heating at 120°C till the complete elimination of water and acetic acid.

The sylilation process was realized in heterogeneous medium, treating a suspension of activated cellulose in o-xylene with trimethylchlorosilane, triethychlorosilane and triphenylchlorosilane used as silylation agents. An adequate amount of pyridine was added in the reaction medium in order to remove the hydrochloric acid and to prevent the reverse reaction [2]. The silylation was performed at 115-120°C under nitrogen atmosphere in a glass reaction vessel provided with a back-flow condenser. The cellulose derivatives were separated from the reaction medium by precipitation with isopropanol, followed by a few washings, also with propanol and a final wash-up with acetone. These samples showed a pronounced tendency of hydrolysis, becoming partially insoluble. At the same time, preliminarily DSC studies indicated a lower thermal stability. In order to raise the stability degrees of these samples, a supplementary purification was requested and it has performed by successive reprecipitation with isopropanol from benzene and chloroform. After a final washing with acetone, the samples were centrifuged and dried under vacuum at 60°C, then packed and kept in nitrogen atmosphere.

After this, by supplementary purification the hydrocloric acid and pyridine hydrochloride were completely removed from the TMSC samples. The number average molecular weights (M_n) of these derivatives were determined with a Hewlett-Packard type membrane osmometer - model 502, in o-xylene, using cellulose membranes. For the same samples, the substitution degree (DS) was determined by acid decomposition method [3-4]. The characteristics of silyl derivatives synthesized are presented in Table 2.

TABLE 2. Main Characteristics of the Silylcellulose Derivatives

SAMPLE	$TMSC_1$	$TMSC_2$	$TMSC_3$	$TMSC_4$	$TMSC_5$
M_n, kg ·mol^{-1}	92.5	172.9	200.0	226.2	357.0
DS	2.85	2.84	2.82	2.75	2.85
SAMPLE	$TESC_1$	$TESC_2$	$TESC_3$	$TESC_4$	$TESC_5$
M_n, kg ·mol^{-1}	102.0	135.0	148.3	167.5	182.2
DS	2.82	2.83	2.85	2.82	2.72
SAMPLE	$TFSC_1$	$TFSC_2$	$TFSC_3$	$TFSC_4$	$TFSC_5$
M_n kg ·mol^{-1}	128.2	152.4	167.9	188.0	207.4
DS	2.89	2.81	2.75	2.75	2.70

TABLE 3. Samples with Different Substitution Degrees

SAMPLE	$TMSC_2$	$TMSC_2'$	$TMSC_2''$
DS	2.82	2.20	1.60

Also, varying the silylation time, three TMSC samples with different substitution degrees were prepared and analyzed in respect to their substitution degree. The results are presented in Table 3.

The substitution degree was also determined by acid decomposition method and checked by IR spectra. The IR spectra were recorded on a SPECORD M90 Carl Zeiss Jena apparatus using KBr pellet technique.The unsubstituted OH groups from the three TMSC samples analyzed are evidenced in Figure 1.

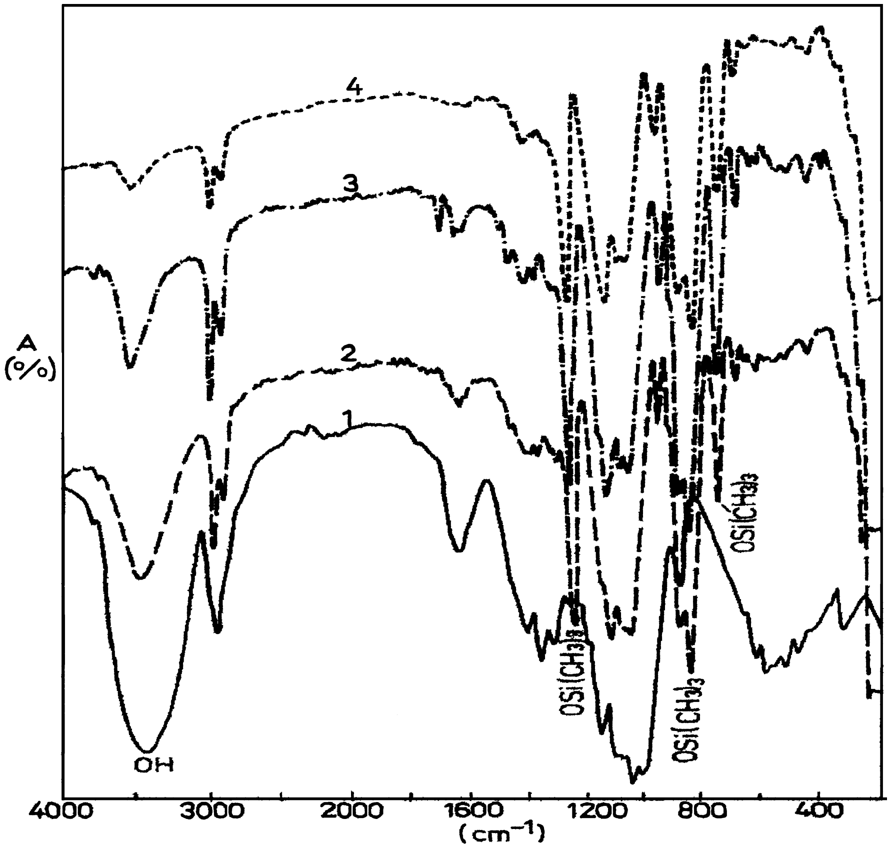


Figure 1. Solid state IR spectra of cellulose support and TMSC with different substitution degrees. 1 - Cellulose support; 2 - $TMSC_2''$; 3 - $TMSC_2'$; 3 - $TMSC_2$.

These spectra confirm the structural changes produced by the etherification process when the -OH groups were substituted by O-Si$(CH_3)_3$ groups. Thus, in the TMSC spectrum, several new pronounced peaks appear, being characteristic to the valence vibrations in the substituted groups, namely: 750-760 cm^{-1} (Si$(CH_3)_3$); 850 cm^{-1} (Si-C). The peaks associated with deformation vibrations, as 970 cm^{-1} (Si-O) and 1470 cm^{-1} (SiCH_3) can also be identified. The characteristic absorption band associated to the OH valence vibration (ν =3450-3500 cm^{-1}) is lower in the silylated compounds, as compared with the corresponding band in cellulose spectrum. This decrease is proportional with the substitution degree and can be used for a rather qualitative determination of the substitution degree. Due to the fact that the pellet composition and thickness, as well as the amplification factor of the apparatus are less controlable parameters, a relative method is recommended. For this purpose, the peak stayed at 1120-1130 cm^{-1}, corresponding to the C-O-C vibration and present in the all spectra, was used as reference band To characterize the crystallinity of cellulose supports and their silylcellulose derivatives, we used a X-ray diffractometer SIEMENS type D500 working with CuK$_\alpha$ radiation.

RESULTS AND DISCUSSION

Although the main methods in X-ray diffraction to calculate the crystallinity are relative methods, they are currently used with relevant results in the crystallinity estimation for celluloses and their derivatives [5-9].

To calculate the crystallinity index of both celluloses samples and synthesized silylcellulose derivatives, we used the amorphous cellulose as standard [10] (curve 0 for all diffractograms illustrated in Figures 2-6). The standards were obtained by the regeneration of cellulose and its derivatives [11-16]. The X-rays diffractograms of celluloses and silylcellulose derivatives are presented in Figures 2-6.

From the diffractograms presented in Figure 2 for the five cellulose samples, it can be observed that the maximum from $2\theta = 23°$ and from $2\theta = 15°$ decrease progressively with the decrease of the polymerization degree, respectively the treatment time of cellulose from C_5 to C_1, that demonstrates the passing from cellulose I (C_5) to cellulose II (regenerated from alkalicellulose C_4-C_1).

The maximum from $2\theta = 23°$ and 15° decrease with the increasing of the treatment time reaching for sample C_1 to be close to that one of amorphous cellulose etalon.

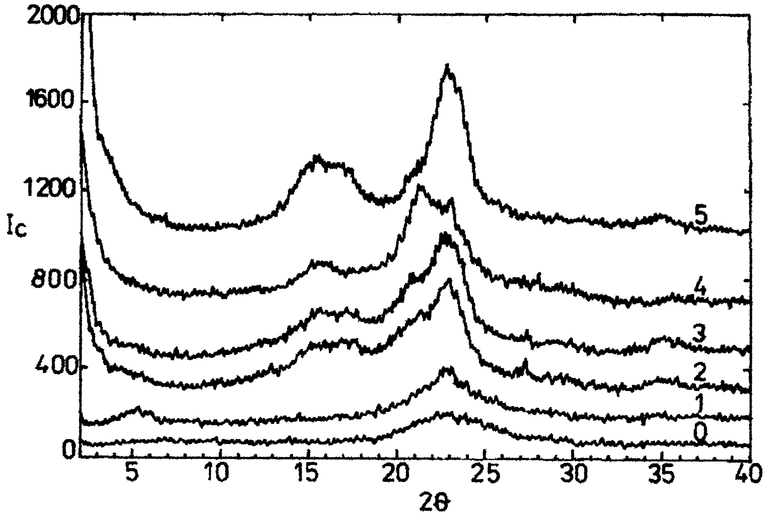


Figure 2. X-ray diffractograms of used cellulose supports: 0 -amorphous standard cellulose; 1 - sample C_1; 2 - sample C_2; 3 - sample C_3; 4 - sample C_4; 5 - sample C_5.

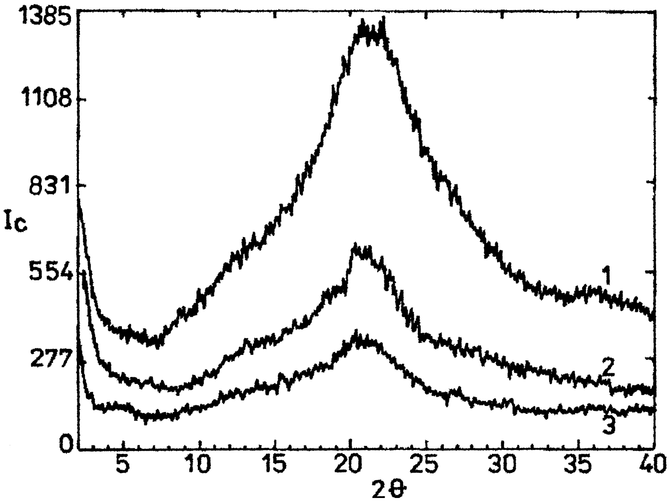


Figure 3. X-ray diffractograms of TMSC function of the substitution degree. 1-$TMSC_2$" (DS = 1.60): 2-$TMSC_2$' (DS = 2.20); 3-$TMSC_2$ (DS = 2.82).

The TMSC diffractograms presented in Figure 3 show a maximum at 2θ = 20.5° that decreases with the increasing of the substitution degree.

From these diffractograms result a maximum at 2θ = 20.5° that decreases with the increasing of the TMSC molecular weight The diffractograms of the triethylsilylcellulose samples present a maximum at 2θ =22° that is moving to low angles starting with $TESC_3$ - the maximum having two peaks at 2θ = 19° respectively 2θ = 14°, simultaneously with the appearance of a maximum at 2θ = 7°.

The diffractograms of TFSC present a maximum at 2θ = 22° angle that decreases and is moving at low angles 2θ = 19° with the increasing of the polymerization degree of used cellulose. These changes correspond to an increasing of cell parameters this being normally because of the higher volume of the substituent that occupy these cells.

The maximum from 2θ = 7° increases with the increasing of the polymerization degree for used cellulose. Using as standard the X-ray diffractogram of the amorphous cellulose (curve 0 from Figure 2) the crystallinity index for the support celluloses and their silyl derivatives were calculated and the results are presented in Tables 4 and 5. The crystallinity index was calculated with the relation indicated in reference [17].

The crystallinity index for the silylcellulose derivatives decreases with the increasing of the polymerization degree, because of the fact that the long

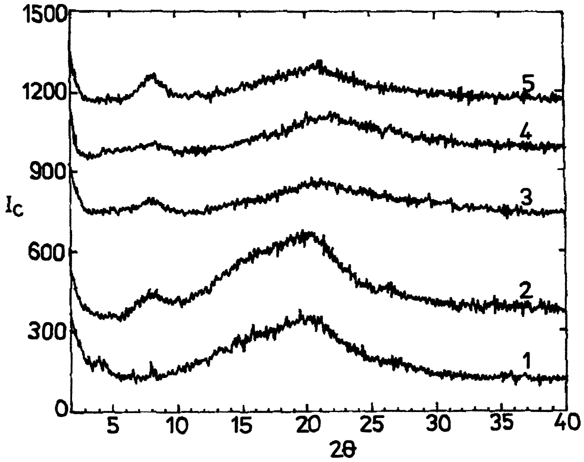


Figure 4. X-ray diffractograms for TMSC samples as function of molecular weight. 1-$TMSC_1$; 2-$TMSC_2$; 3-$TMSC_3$; 4-$TMSC_4$; 5-$TMSC_5$.

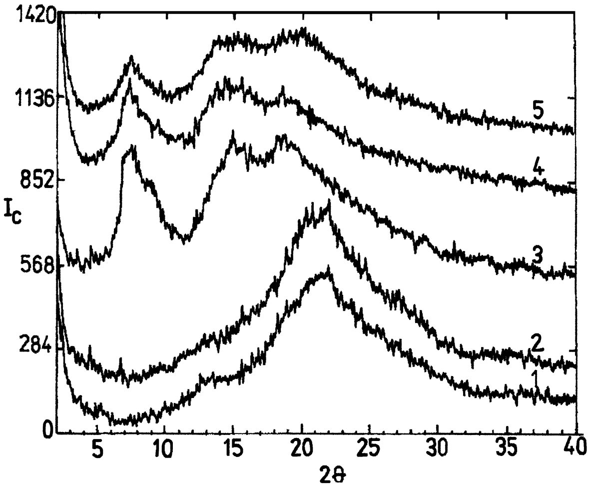


Figure 5. X-ray diffractograms for TESC function of molecular weight. 1-TESC$_1$; 2-TESC$_2$; 3- TESC$_3$; 4 -TESC$_4$; 5 -TESC$_5$.

macromolecular chain is difficult to be oriented on long distances. The crystallinity index increases with the volume of the substituted group (methyl< ethyl<phenyl), the highest crystallinity index being obtained for TFSC$_1$. The crystallinity index for TMSC decreases much more with the increasing of molecular weight than for TESC and TFSC, this probable due to the fact that the variation domain of the molecular weight is higher in case of the TMSC samples than for the other derivatives.

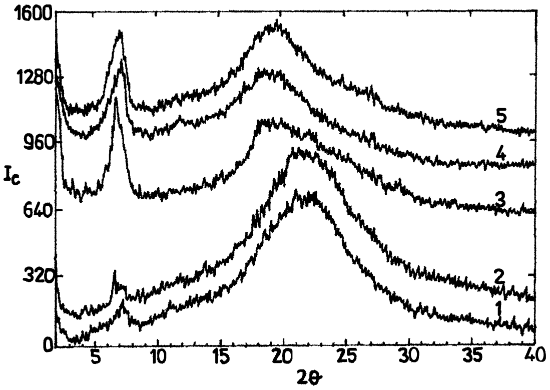


Figure 6. X-ray diffractograms for TFSC as function of the molecular weight. 1-TFSC$_1$; 2-TFSC$_2$; 3-TFSC$_3$; 4-TFSC$_4$; 5-TFSC$_5$.

TABLE 4. The Crystallinity Index for Silyl Cellulose Derivatives

Sample no.	DP cellulose support	Crystallinity Index (%)		
		TMSC	TESC	TFSC
1	337	60.0	80.9	82.2
2	588	57.2	80.8	81.6
3	708	37.9	75.5	77.8
4	880	31.4	71.9	73.0
5	1100	11.0	70.7	71.4

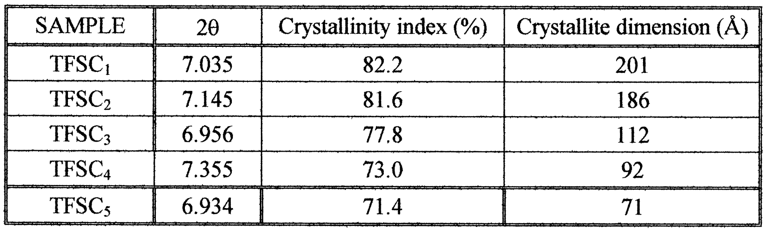
From the values presented in Table 5, we can observe that the crystallinity index increases with the decreasing of substitution degree, having a value of 89% at DS=1.60, a higher value than for the corresponding cellulose support. For example, by indexing the X-ray diffractogram for the $TMSC_3$ sample we obtained an orthorhombic symmetry, with the lattice parameters closed to a=23.08(6) Å b=14.06(2) Å and c=3.69(1) Å. For the triphenylsilylcellulose the average crystallite dimensions were evaluated with the relationship [18]. We have employed for the measurement of the crystallites dimensions the (110) lattice plane. The results are presented in the Tables 6-7. The crystallites size decreases by increasing of molecular weight and with decreasing the crystallinity index.

Qualitative attempts about the solubility of the three types of derivatives in o-xylene, 1,1,1-trichloroethane and chloroform evidenced that the solubility decreases with increasing of the crystallinity index and with volume of the grafted substituent to the cellulosic chain. The decreasing of solubility is associated with a gelation tendency of the solutions in time.

TABLE 5. The Crystallinity Index for TMSC as Function of the Substitution Degree

Sample	$TMSC_2$	$TMSC_2'$	$TMSC_2''$
Cellulose support (DP)	588	588	588
Substitution degree (DS)	2.82	2.20	1.60
Crystallinity index (%)	57.2	74.0	89.0

TABLE 6. The Dimension of Crystallites for TFSC Samples



SAMPLE	2θ	Crystallinity index (%)	Crystallite dimension (Å)
TFSC$_1$	7.035	82.2	201
TFSC$_2$	7.145	81.6	186
TFSC$_3$	6.956	77.8	112
TFSC$_4$	7.355	73.0	92
TFSC$_5$	6.934	71.4	71

CONCLUSION

The crystallinity index for cellulose decreases with the increasing of thermal treatment time.

The crystallinity index for silylcellulose derivatives is independent on the nature of the cellulose used.

The crystallinity index for silylcellulose derivatives increases with the volume of grafted substituent on the cellulose chain.

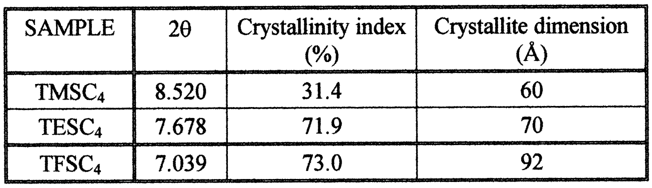
The crystallinity index depends on the substitution degree of the silylcellulose derivative.

The solubility of silylcellulose derivatives studied decreases with the crystallinity, respectively with the dimension of grafted substituent volume on cellulosic chain.

For the triphenylsilylcellulose, the average crystallite size decreases with the increasing of the molecular weight and with decreasing of the crystallinity index.

For a trimethilsilylcellulose sample the powder X-ray diffractogram indexation revealed an orthorhombic symmetry with lattice parameters closed to a=23.08(6) Å, b=14.06(2) Å and c=3.69(1) Å.

TABLE 7. The Dimension of Crystallites for Sylilcellulose Samples in Function of Substituent Type



SAMPLE	2θ	Crystallinity index (%)	Crystallite dimension (Å)
TMSC$_4$	8.520	31.4	60
TESC$_4$	7.678	71.9	70
TFSC$_4$	7.039	73.0	92

For the silylcellulose derivatives, the average crystallite size obtained employing the (110) lattice plane decreases with the increasing of the volume of grafted substituent on the cellulose chain.

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