A Structural–Thermodynamic Study of Triphenylsilylcellulose

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ABSTRACT: The purpose of this article is to report the characterization of a solution of triphenylsilylcellulose (TPSC) in terms of its rheologic properties by osmometry and viscometry to better understand processing parameters and conditions. This work is an extension of previous similar work on trimethylsilylcellulose (TMSC). TPSC was prepared in a medium of dimethylformamide (DMF) plus pyridine, under heterogeneous starting conditions and nitrogen atmosphere, by silylation of activated celluloses with triphenylchlorosilane at 115–120 °C. The isolated and purified ethers were characterized according to their polydispersities and their substitution degrees, by osmometry and viscometry in various solvents. The Mark–Houwink–Sakurada equation coefficients were evaluated in 1,1,1-trichloroethane, chloroform, and *o*-xylene at 30 °C and in *o*-xylene over the 30–70 °C temperature range. The values of 2.12–2.18 obtained for exponent "*a*" correlated with the very low values of pre-exponential factor (of 10^{-12} order), indicating a high stiffness of the macromolecular chains. The viscous flow parameters for dilute solutions of TPSC in *o*-xylene were determined in the temperature range 30–70 °C. The temperature dependence of the dynamic viscosity of the solutions obeys an Arrhenius-type equation in which the apparent activation energy is linearly dependent on both the concentration and molecular weight of the solution. No significant dependence on concentration and molecular weight was found for the pre-exponential factor. This behavior was attributed to the great stiffness of the macromolecular chains. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2875–2884, 2002

Key words: structure; thermodynamics; rheology

INTRODUCTION

To obtain supramolecular structures of Langmuir–Blodgett and spin-coated cellulosic films, the silylcellulose derivatives have been shown to be suitable because they are soluble in common solvents and very easily regenerable.[1] It is well known that trimethylsilylcellulose (TMSC) with substitution degrees >2.5 form well-defined mono- and multi-layered architectures, and, as a consequence, the desilylation of these films is a convenient method to generate oriented hydrophilic films. The precipitation time in isopropyl alcohol at acid pH for triphenylsilylcellulose (TPSC) is known to be smaller than that for TMSC.[2] Silylcellulose derivatives can also be used to obtain regenerated cellulose fiber[3] with some liquid crystal properties.[4–7]

In a previous study,[8] the characterization of TMSC in solution was reported. The aim of the present paper is a similar study of TPSC by osmometry and viscometry.

The understanding of the rheological behavior of the silylcellulose derivatives is essential for establishing the optimal processing of these solutions with a view to regeneration of cellulosic

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Table I Characteristics of the Cellulose Support Samples (C)

Characteristic	Cellulose Sample C_1	C_2	C_3	C_4	C_5
Polymerization degree (DP)	327	588	708	880	1100
Molecular weight Mv (g mol^{-1})[a]	53,300	96,400	116,100	144,300	180,000

[a] Determined by viscometry.

filaments and films with vastly improved physical properties.

For this reason, we studied the dynamic viscosities of TPSC/*o*-xylene dilute solutions at temperatures from 30 to 70 °C and concentrations up to 0.7 g/dL and even lower for higher molecular weight samples.

EXPERIMENTAL

Synthesis and Characterization of Triphenylsilylcellulose (TPSC)

Five samples of cellulose with different polymerization degrees (the same as those used in the earlier study[8]) were used to obtain corresponding TPSC derivatives (Table I).

The silylation of the five cellulose samples was carried out in heterogeneous medium under nitrogen atmosphere. As in previous studies,[9, 10] cellulose with the characteristics presented in Table I was introduced in a reaction bowl made of glass and kept at a constant temperature of 20 °C. Next, acetic acid was introduced over cellulose in a molar ratio of 0.2 to 10 mol of CH_3COOH/mol cellulose and was submitted to an agitation process for 60 min. The resulting activated cellulose (defibrated) was dried in an vacuum stove at 80 °C to eliminate the acetic acid. The activated and dried cellulose was suspended in *N*,*N*-dimethylformamide + pyridine medium and pre-treated at 60 °C for 60 min with triphenylchlorosilane. Then, the temperature was increased to 115 °C and the sample was stirred for another 120 min. Finally, *o*-xylene was added to the reaction, which was stirred for an additional for 60 min at 115–120 °C.

The solution was cooled to 60 °C, and TPSC was separated by precipitation with isopropyl alcohol, washed with isopropyl alcohol, and a finally washing with acetone. The samples were purified by successive precipitations with isopropyl alcohol from benzene and chloroform solutions.

Step One (I)

The TPSC solution in *N*,*N*-dimethylformamide (DMF) was precipitated in isopropyl alcohol and agitated for 60 min. The precipitated product in a wire (thread) form (bundle) was washed successively with isopropyl alcohol, using one part by weight of TPSC and 30 parts by weight of solvent (3 washes) to remove the xylene and the pyridine chlorhydrate. The product was then dried in a nitrogen current to avoid its degradation.

Step Two (II)

TPSC was dissolved in benzene, and then the washing and a drying procedures from step I were repeated (one part in weight of TPSC with 30 weight parts of solvent).

Step Three (III)

The TPSC obtained is dissolved in chloroform, then it is washed and dried (one part by weight of TPSC with 30 parts by weight of solvent).

Successive dissolution in different solvents was chosen to take into account both the extracting capacity of xylene and pyridine chlorhydrate and the evaporating temperature of the solvent that remained in the polymer.

The characterization was performed in *o*-xylene at 30 °C for TPSC samples, and the number average molecular weights (M_n), the second virial coefficients (A_2), the polydispersity index (I_p), and limiting viscosity number ($[\eta]$) were determined.

The substitution degree was also determined by the acid decomposition method, which consists of heating the TPSC in a porcelain or platinum capsule and then decomposing by adding concen-

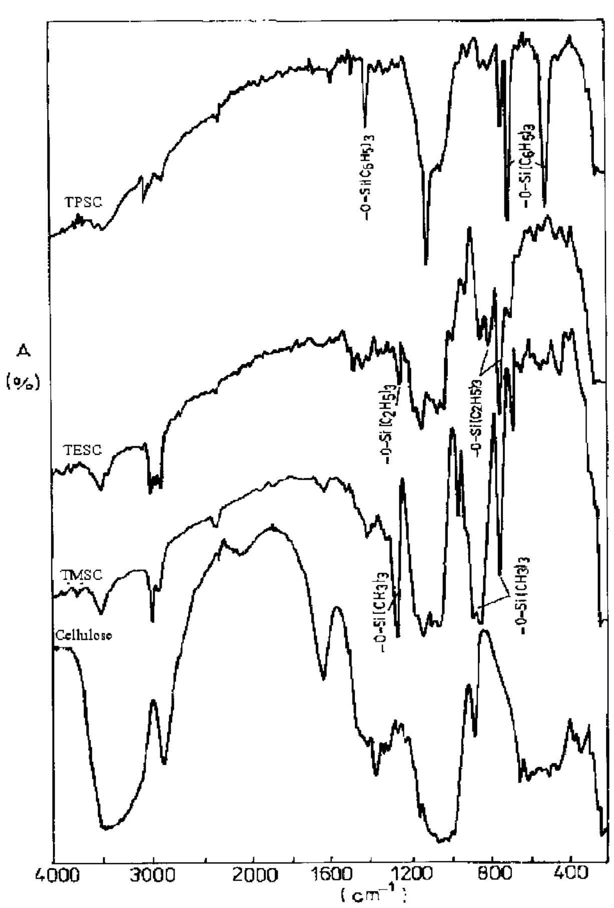

Figure 1 Solid-state IR spectra of cellulose support and silylcellulose.

trated sulfuric acid until the residue becomes bright white.

The sample was weighed, and then the percent of silicon existing and the respective degree of substitution DS(CH) were determined and checked by infrared (IR) spectroscopy [DS(IR)]. The IR spectra were recorded on a SPECORD M90 Carl Zeiss Jena apparatus using the KBr pellet technique.

To characterize the crystallinity of cellulose supports and their silylcellulose derivatives, we used a X-ray diffractometer, SIEMENS type D500, and used CuK_α radiation.

Osmotic measurements were made with an automatic Hewlett-Packard osmometer, at 30 °C, using cellulosic membranes of the PECELL-600 type.

o-Xylene of analytical grade was used as solvent. For each sample, the osmotic pressure was measured for five solutions of concentrations between 0.2 and 1.0 g/dL, obtained by diluting a solution of 1.0 g/dL concentration. In the used concentration range, the (π/c) versus c plots is linear (Figure 1) for all the fractions used. Number average molecular weights (M_n) and the second virial coefficients (A_2) were evaluated from the straight line coefficients, which were estimated by the least squares method.

The viscometric measurements in *o*-xylene, 1,1,1-trichloroethane (TCE), and chloroform were carried out with an Ubbelohde type viscometer, with suspended level and internal dilution and equipped with sintered glass filter.

Because of the very high solution viscosities, the maximum concentration of the used solutions was 0.7 g/dL for all samples.

RESULTS AND DISCUSSION

The unsubstituted OH groups from the TMSC, TESC, and TPSC samples analyzed are shown in Figure 1. These spectra confirm the structural changes produced by the etherification process when the —OH groups were substituted by O—Si(R)$_3$ groups (R = CH_3, C_2H_5, C_6H_5). Thus, in the TMSC spectrum, several new pronounced peaks appear that are characteristic of the valence vibrations in the substituted groups; namely, 750–760 cm^{-1} ($Si(CH_3)_3$) and 850 cm^{-1}

Table II Characterization of TPSC Samples in *o*-Xylene at 30 °C

Characteristic	TPSC-1	TPSC-2	TPSC-3	TPSC-4	TPSC-5
DS(CH)[a]	2.82	2.83	2.85	2.82	2.72
DS(IR)[b]	2.71	2.76	2.67	2.60	2.52
I_p[c]	2.18	2.32	2.41	2.67	3.42
[η], dL g^{-1}[d]	0.911	1.344	1.616	2.106	2.509

[a] Determined by chemical analysis.
[b] Determined by IR spectroscopy.
[c] Determined by gel permeation chromatography.
[d] Determined by viscometry.

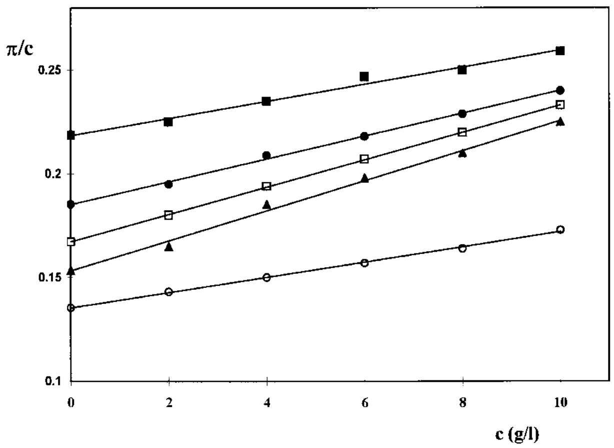

Figure 2 Osmometric curves for the triphenylsilylcellulose (TPSC) samples. Key: (○) $TPSC_1$; (▲) $TPSC_2$; (□) $TPSC_3$; (●) $TPSC_4$; (■) $TPSC_5$.

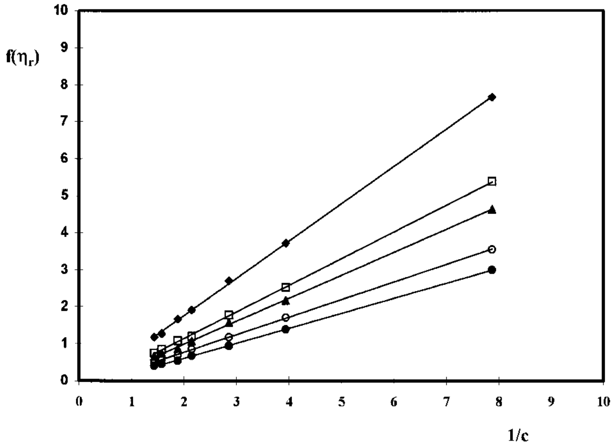

Figure 3 Fedors-type curves for the triphenylsilylcellulose (TPSC) samples in *o*-xylene at 30 °C. Key: (♦) $TPSC_1$; (□) $TPSC_2$: (▲) $TPSC_3$;(○) $TPSC_4$; (●) $TPSC_5$.

(Si—C). The peaks associated with deformation vibrations, such as 970 cm^{-1} (Si—O) and 1470 cm^{-1} ($SiCH_3$) can also be identified (Figure 1). The absorption bands for the triethylsilyl group have the same wavelengths as those for the trimethylsilyl group. In comparison with the latter, the absorption bands for the triphenylsilyl group have the following wavelengths: 1300, 700, and 625 cm^{-1}. The characteristic absorption band associated with the OH valence vibration ($\nu = 3450–3500\ cm^{-1}$) is lower in the silylated compounds than in the corresponding band in the cellulose spectrum. This decrease is proportional to the substitution degree and can be used as a rather qualitative determination of the degree of substitution Because the pellet composition and thickness, as well as the amplification factor of the apparatus, are less controllable parameters, a relative method is recommended. For this purpose, the peak that stayed at 1120–1130 cm^{-1}, corresponding to the C—O—C vibration and present in the all spectra, was used as a reference band.

These characteristics of the series of samples are presented in Table II. Values of the limiting viscosity number (intrinsic viscosity $[\eta]$) were obtained with Fedors equation,[11] which allows a linear extrapolation in the $f(\eta_r) = [2(\eta_r - 1)]^{-1}$ versus ($1/c$) graph, as shown in Figures 2 and 3. The limiting viscosity number was also evaluated by the least squares method. In the cases of both osmometric and viscometric graphs, there is very good linearity ($r^2 > 0.995$).

The number average molecular weight (M_n), the second virial coefficient (A_2), and limiting viscosity number ($[\eta]$) in 1,1,1-trichloroethane (TCE), chloroform, and *o*-xylene at 30 °C are presented in Table III. Taking into account the substitution degrees of the samples and the polymerization degrees of the cellulosic supports, the molecular weights of the substituted samples must to be within 132,000 and 415,000 g mol^{-1}, whereas the measured experimental values lie between 128,000 and 207,000 g mol^{-1}. On the other hand, excepting sample TPSC-5, much more uniformity of samples with regard to both

Table III Osmometric and Viscometric Results for Triphenylsilylcellulose Samples (TPSC) at 30 °C

Characteristic	TPSC-1	TPSC-2	TPSC-3	TPSC-4	TPSC-5
M_n, g mol^{-1}	128,200	152,400	167,900	188,000	207,400
$A_2 \times 10^4$, m^3 mol kg^{-2}	1.38	1.95	2.31	2.66	1.28
$[\eta]$, dL g^{-1} TCE	0.839	1.255	1.553	1.941	2.401
$[\eta]$, dL g^{-1} $CHCl_3$	0.886	1.301	1.611	1.986	2.518
$[\eta]$, dL g^{-1} *o*-Xylene	0.911	1.344	1.616	2.106	2.509

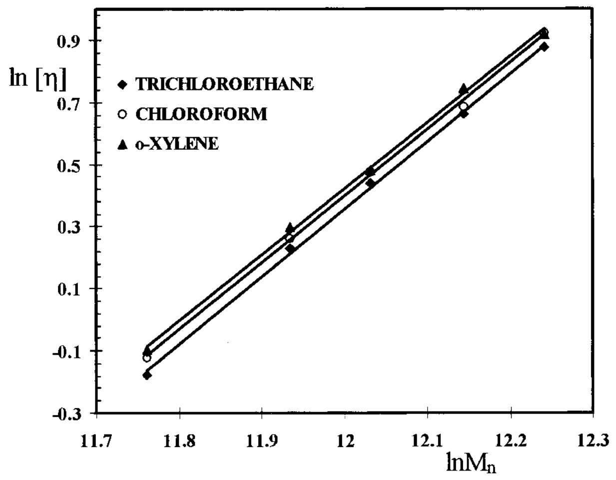

Figure 4 Limiting viscosity number − molecular weight correlation according to the Mark–Houwink–Sakurada (M–H–S) equation for the triphenylsilylcellulose (TPSC) samples in different solvents.

the uniformity of substitution degree (DS = 2.82–2.85) and polydispersity (I_p = 2.18–2.67) is observed. This fact can be explained by taking into account the repeated purifications during which the less soluble molecules (the fractions with lower substitution degree) and small molecular weight fractions were removed.

As in the case of the TPSC samples, the second virial coefficient (A_2) shows an abnormal dependence on molecular weight; A_2 increases with the molecular weight increase, with sample TPSC-5 being an exception again. This behavior can be attributed to the larger polydispersity of this sample.

By using the experimental values of the number average molecular weights and limiting viscosity number (data from Table III) the coefficients of the Mark–Houwink–Sakurada (M–H–S) equation, K and a, were calculated. The graph ln $[\eta]$ − ln M_n, presented in Figure 4, indicates a very good linearity between the two variables for all three solvents, with the linear correlation coefficients >0.995 (Figure 5).

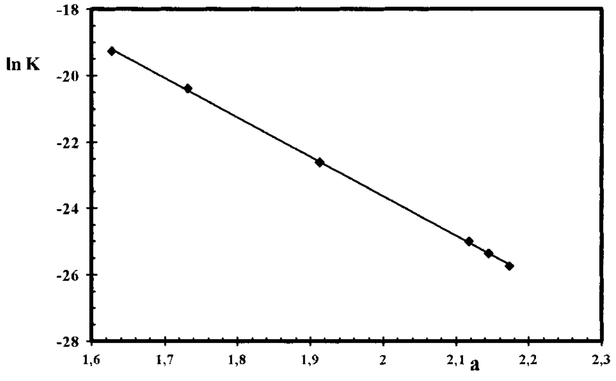

Figure 5 Graphical representation of the compensation effect for the two coefficients of the Mark–Houwink–Sakurada (M–H–S) equation.

Table IV Coefficients of the Mark–Houwink–Sakurada Equation

	Solvent		
Coefficient	1,1,1-Trichloroethane	Chloroform	*o*-Xylene
$K \times 10^{12}$, dL g^{-1}	6.67	9.82	14.06
a	2.174	2.145	2.118

By statistical processing of these data, the K and a coefficients values presented in Table IV were obtained. As compared with TMSC derivatives (for which a = 1.3–1.4),[8] the higher values obtained in the three solvents for the a exponent indicate an increased stiffness of the polymeric chains. This observation can be explained if the greater difference of volume between —$Si(CH_3)_3$ and —$Si(C_6H_5)_3$ groups is considered. Corresponding to the very high values of the exponent a, the pre-exponential factor is extremely low.

The temperature dependence of the limiting viscosity number for TPSC in *o*-xylene was also analyzed and the experimental results are presented in Table V. The coefficients K and a for the M–H–S equation, evaluated on the basis of the data in Table V, are listed in Table VI. Except for the value that was found for 70 °C, a linear dependence on temperature is obtained. This dependence can be expressed by the equation:

$$a = 2.591 - 0.165t \tag{1}$$

Table V Limiting Viscosity Number, $[\eta]$ (dL g^{-1}), for TPSC Samples in *o*-Xylene

	$[\eta]$, dL g^{-1}				
t, °C	TPSC-1	TPSC-2	TPSC-3	TPSC-4	TPSC-5
30	0.911	1.344	1.616	2.106	2.509
40	0.897	1.258	1.528	1.906	2.230
50	0.961	1.297	1.557	1.883	2.197
60	0.841	1.205	1.454	1.751	2.035
70	0.749	1.060	1.349	1.702	2.047

Table VI Mark–Houwink–Sakurada Coefficients for TPSC in *o*-Xylene as Function of Temperature

	t, °C				
Coefficient	30	40	50	60	70
$K \times 10^{12}$ dL g^{-1}	14.06	152.3	1384	4505	4.58
a	2.118	1.913	1.731	1.628	2.195

where t is temperature in degrees Celsius and a is the exponent from the M–H–S equation.

A correlation of $\ln K = A + B \cdot a$ type between the M–H–S coefficients is verified in Figure 5 using the data obtained in TCE, $CHCl_3$, and, *o*-xylene at different temperatures. The obtained equation of compensation is:

$$\ln K = 0.0793 - 11.854a \qquad (2)$$

The stiffness of a macromolecular chain can generally be due both to the long-range interactions between chain segments separated by a large number of skeletal bonds and to a great volume of laterally substituents.

A qualitative image with regard to the stiffness of the silylated cellulose can be obtained by simple calculus of molecular mechanics. For simplification, four structural unities of cellulose, TMSC, or TPSC were considered. The calculus of molecular mechanics (MM+, HYPERCHEM 5.02 programme) was used to find the minimum energy configuration. The glycosidic C—O—C bond angle was found around 116° for all considered molecules. Then, the C—O—C bond angle between central structural unities, θ , was modified and, without a new optimization, the energies were calculated. For the three considered derivatives, the calculated energies are presented versus the deformation angle in Figure 6. These curves entirely confirm the chain stiffness that before was appreciated qualitatively through the value of the M–H–S equation exponent (a), with the chain stiffness increasing in the order cellulose < TMSC < TPSC.

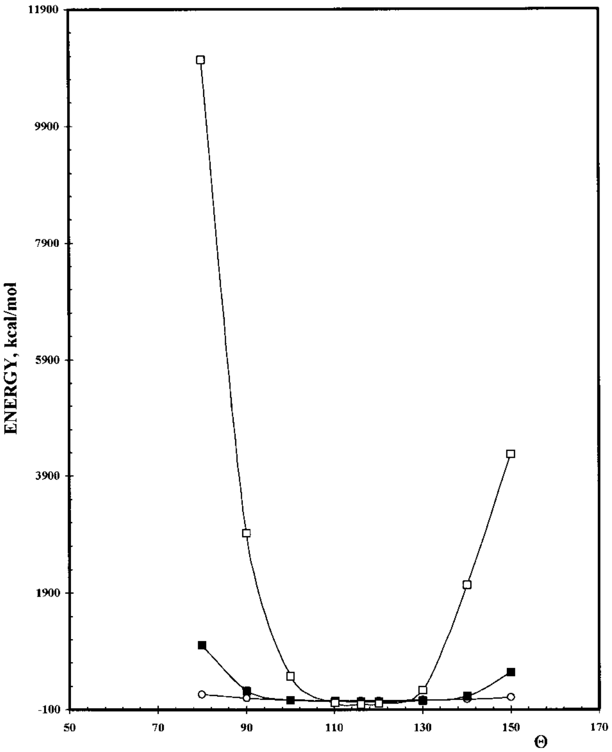

Figure 6 Variation of the total energy as a function of the glucosidic bond angle for cellulose and silylcellulose derivatives. Key: (○) cellulose; (■) trimethylsilylcellulose (TMSC); (□) triphenylsilylcellulose (TPSC).

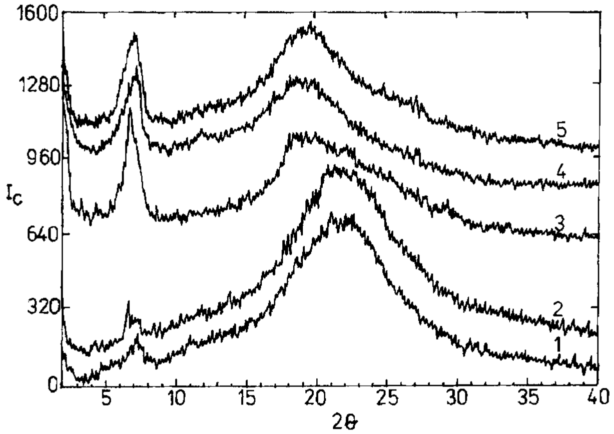

Figure 7 X-ray diffractograms of triphenylsilylcellulose (TPSC) as a function of molecular weight. Key: (1) $TPSC_1$; (2) $TPSC_2$; (3) $TPSC_3$; (4) $TPSC_4$; (5) $TPSC_5$.

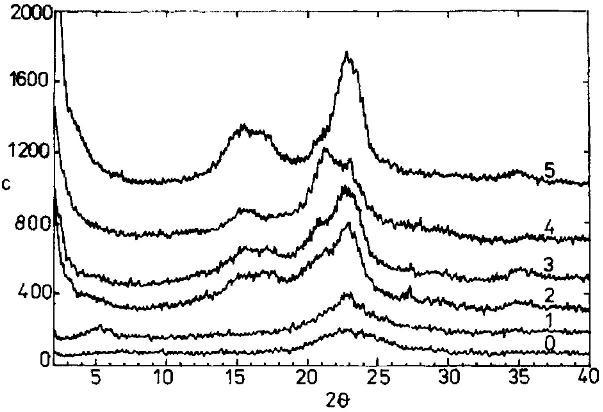

Figure 8 X-ray diffractograms of cellulose supports. Key: (0) amorphous standard cellulose; (1) sample C_1; (2) sample C_2; (3) sample C_3; (4) sample C_4; (5) sample C_5.

The diffractograms of TPSC present a maximum at $2\theta = 22°$ angle that decreases and is moving at low angles $2\theta = 19°$ with the increasing of the polymerization degree of used cellulose[12, 13] (Figure 7). These changes correspond to an increasing of cell parameters that is usually because of the higher volume of the substituent that occupy these cells.

From $2\theta = 7°$, the maximum 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 8), the crystallinity index for the support celluloses and their silyl derivatives were calculated with the relation indicated in the work of Dumbleton and Bowles.[14]

For the TPSC, the average crystallite dimensions were evaluated with a previously published relationship.[15] We have employed for the measurement of the crystallites dimensions the (110) lattice plane. The results are presented in Table VII.

Several studies were focused on the temperature dependence of the dilute polymer solution dynamic viscosities.[16–21] This dependence was of an Arrhenius type law and can be expressed by the equation proposed by Guzman and Andrade as follows:

$$\eta = A \exp(Q/RT) \tag{3}$$

where η is the dynamic viscosity of the solution, Q is the apparent activation energy of the viscous flow, and A is the pre-exponential factor, which is correlated with the activation entropy.

The apparent activation energy of viscous flow is a function of the nature of polymer/solvent system of the solution concentration and of the molecular weight of the polymer. A linear dependence of the apparent activation energy on concentration was found for all polymer/solvent systems studied:

$$Q = Q_0 + k_e c \tag{4}$$

where Q_0 is the activation energy of the viscous flow of the pure solvent and k_e is a coefficient that depends on the molecular weight of the polymer.

The k_e coefficient generally increases with molecular weight increase according to the following linear equation:

$$k_e = K_e M_n \tag{5}$$

The analysis of many data indicates that the K_e

Table VII Crystallinity and Dimension of Crystallites for Cellulose and TPSC Samples

Sample	Cellulose (C) DP	Triphenylsilylcellulose (TPSC) 2θ	Crystallinity Index (%)	Crystallite Dimension (Å)
1	337	7.035	82.2	201
2	558	7.145	81.6	186
3	708	6.956	77.8	112
4	880	7.355	73.0	92
5	1100	6.934	71.4	71

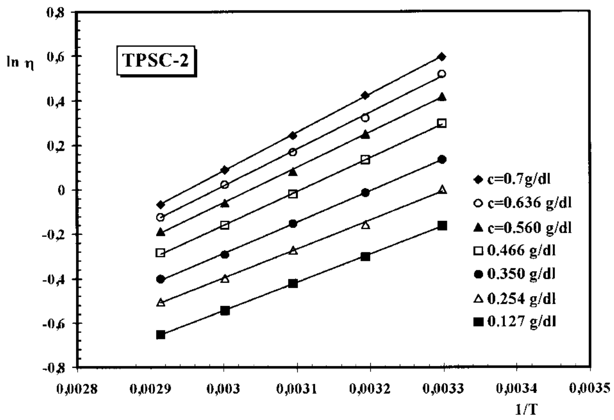

Figure 9 Typical diagram (ln η) versus ($1/T$) for triphenylsilylcellulose (TPSC)/*o*-xylene at various concentrations (sample: TPSC-2; M_n = 152,400 g/mol).

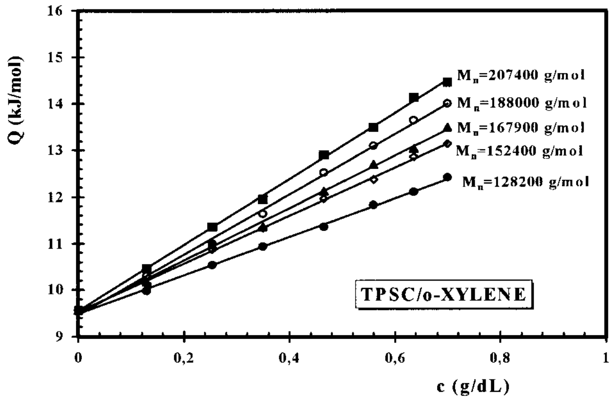

Figure 10 Dependence of the apparent activation energy on concentration and molecular weight for triphenylsilylcellulose (TPSC). Key: (●) TPSC$_1$; (◇) TPSC$_2$; (▲) TPSC$_3$; (○) TPSC$_4$; (■) TPSC$_5$.

value depends on the flexibility of the polymer chains in solution; that is, for flexible polymers in good solvents, K_e is 1–2 orders lower than for stiff chain polymers, as cellulosic derivatives.

The dependence of the pre-exponential factor *A* on concentration and molecular weight is strongly correlated with the chain flexibility in solution, being interpreted by Moore[22] in terms of the activation entropy change of viscous flow.

According to eq.3, the representative curves in (ln η) − ($1/T$) coordinates for different concentrations of the solution are shown in Figure 9.

This figure shown the classical linear dependence in logarithmic–hyperbolic coordinates for the concentration interval analyzed. This dependence is preserved for the all studied fractions.

The apparent activation energy and pre-exponential factor for the two representative samples, at different concentrations of the solution, were evaluated by the least squares method and are presented in Table VIII. The concentration dependence of the apparent activation energy for different molecular weight samples are presented in Figure 10 for TPSC. For the pure *o*-xylene, the value $Q_0 = 9.566 \cdot 10^3$ J/mol was chosen. Good linearity is obtained in all the cases. The k_e values were evaluated from the slopes of these straight lines according to eq. 4. The dependence of the k_e coefficient on the molecular weight of the polymer samples is illustrated in Figure 11 for silylated compounds. Generally, the pre-exponential factor, *A*, depends also on the concentration and the molecular weight of the polymer but, as compared with *Q*, it is much more sensitive to chain flexibility, polydispersity of polymers and, especially, to experimental errors.

The average values of the pre-exponential factor obtained, taking into account the values found for the various concentration used as a function of molecular weight, are presented in Table IX. As in the case of the concentration dependence of *A*, the dependence on molecular weight of the pre-exponential factor is also unconvincing; the obtained values are very dispersed and do not exhibit an evident variation to a certain sense.

This behavior differs from that of the other cellulose derivatives[19] or polymers with moderate chain stiffness,[17, 20] and can be attributed to the high stiffness of the macromolecular chains of

Table VIII The Guzman–Andrade Coefficients for TPSC-2 Sample in *o*-Xylene (M_n = 152400 g/mol)

	Concentration (g/dL)						
Coefficient	0.127	0.254	0.350	0.466	0.560	0.600	0.700
$Q \times 10^{-3}$ (J/mol)	10.143	10.870	11.330	11.970	12.380	12.867	13.143
$A \times 10^{3}$ (cP)	12.92	13.60	13.26	11.27	12.33	11.35	11.12

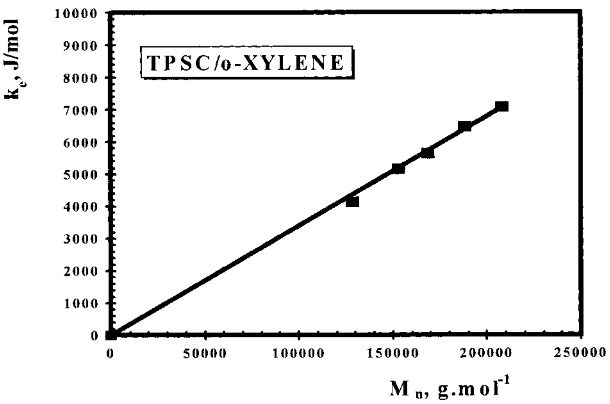

Figure 11 Dependence of the k_e coefficient on molecular weight for triphenylsilylcellulose (TPSC).

these compounds. The latter was pointed out in the earlier studies[8] by values of >1 for the M–H–S exponent (a = 1.628–2.118 for TPSC in *o*-xylene, at 30–70 °C) and confirmed qualitatively by molecular mechanics calculus.

Another reason for this behavior may be attributed to the high and dissimilar polydispersities of the samples studied. Using these data, the average values of the pre-exponential factors were calculated as $A = 15.93 \cdot 10^{-3}$ cP for TPSC/*o*-xylene, and $A_0 = 15.86 \cdot 10^{-3}$ cP for pure *o*-xylene.

Thus, the following relations can express the flow equations of the dilute solutions of TPSC in *o*-xylene:

$$\eta = 1.593 \cdot 10^{-2}\exp\left[\frac{1}{\mathrm{RT}}(9.566 + 0.0339\mathrm{M_n}c)\right] \mathrm{cP} \qquad (6)$$

CONCLUSIONS

Five TPSC esters, with substitution degrees of 2.7–2.8, were prepared in DMF + pyridine medium, under heterogeneous starting conditions and nitrogen atmosphere, by silylation of the activated celluloses with triphenylchlorosilane at 115–120 °C. The purified samples were characterized by their degrees of substitution, which were determined by the acid decomposition method (Si content determinations), by their polydispersities (gel permeation chromatography determinations), by osmometry, and by viscometry in various solvents.

The exponents a of M–H–S equation in 1,1,1-trichloroethane, chloroform, and *o*-xylene are extremely high, with values between 2.12 and 2.18, and very close for all the three solvents. In accordance with these high values of the exponent a, the pre-exponential factor (K) shows very low values (on the order of 10^{-12}), indicating a strong stiffness of the macromolecular chains in solution. Qualitatively, this stiffness was confirmed by molecular mechanics calculus. The two coefficients of the M–H–S equation can be correlated by a compensation equation.

The crystallinity index for silylcellulose derivatives is independent of the nature of the cellulose used. For TPSC, the average crystallite size decreases with the increasing molecular weight and with decreasing crystallinity index

TPSC are cellulosic derivatives with very strong chain stiffness and with very large substituted groups. These two characteristics have a considerable influence on the flow properties of the dilute solutions of these compounds. The temperature dependence of the solution viscosities obeys an Arrhenius-type law, and can be expressed by the Guzman– Andrade equation.

The apparent activation energy of viscous flow is linearly dependent on both the concentration of the solution and molecular weight of the polymer sample. The K_e coefficient, expressing the molecular weight dependence of the dynamic viscosity, is placed in the range of specific values for macromolecular coils with rigid chains; that is, $3.39 \cdot 10^{-2}$ J · dL/g · mol for silylated derivative in *o*-xylene.

The dependence on concentration and molecular weight of the pre-exponential factor is insignificant, and this peculiar behavior can be attributed to the great stiffness of the macromolecular chains whose structure is a rodlike or a columnar rigid macromolecular structure.[17–20]

Table IX Mean Value of the Pre-exponential *A* as Function of Molecular Weight for TPSC

M_n (g/mol)	128,200	152,400	167,900	188,000	207,000
A × 10^3 (cP)	13.47	12.42	12.65	15.58	9.59

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