

The Rheological and Structural Behavior of Silylcellulosics Derivatives

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ABSTRACT: The trimethylsilylcellulose (TMSC) samples were characterized in solution by osmometry, viscometry, and gel permeation chromatography. The Mark-Houwink-Sakurada (M-H-S) equation coefficients were determined in chloroform, 1,1,1-trichloroethane, and *o*-xylene, in all cases the exponent "a" being higher than unit, this indicating a great stiffness of the macromolecules in solution. Also, the temperature dependence of the limiting viscosity number and M-H-S coefficients respectively for TMSC in *o*-xylene were studied. The exponent from M-H-S equation is also higher than unit, and increases linearly with the temperature. The GPC studies indicates a relative high polydispersity of the studied samples; the polydispersity index being situated between 2 and 3. 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 the molecular weight. The viscous flow parameters for dilute solutions of trimethylsilylcellulose 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 solution's concentration and molecular weight. For preexponential factor no significant dependence on concentration and molecular weight was found. This behavior was attributed to the very great stiffness of the macromolecular chains. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2277–2285, 2001

Key words: trimethylsilylcellulose; dilute solutions; X-ray diffraction; crystallinity; flow parameters

INTRODUCTION

Celluloses, containing an abundance of free hydroxyl groups, are an insoluble compound in water or in organic solvents. Replacement of some or of all hydroxyl groups can radically alter the properties of this polymer. At the same time, the cellulose becomes a meltable polymer by this procedure. The effects of polymer modifications by substitution with triorganosilyl groups (silylation) have been demonstrated 30 years ago; the

increased solubility of silylated polymers in non-polar solvents is particularly note worthy.^{1–3}

The silylcellulose derivatives have various uses; as fibers,⁴ films, or liquid crystals,^{5,6} a search in the literature revealed that rather a small number of studies are devoted to characterization of these compounds, especially in solution, a reduced number of studies are devoted to characterization of these compounds in solution. Most likely, this lack is perhaps determined both by synthesis difficulties and by the fact that in the absence of some peculiar measures of precaution, unstable products are obtained.

Taking into account the fact that both regenerated cellulose properties and liquid crystals prop-

erties of TMSC mainly depend on the dimensions and flexibility of the macromolecules,^{7,8} a detailed characterization of these compounds in different solvents is necessary.

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 these changes, the cellulose support used for synthesis and the cellulose derivatives obtained, were studied by X-ray diffractometry.

In our previous studies,⁹ trimethylsilylcellulose (TMSC) were characterized in solution, determining the Mark-Houwink-Sakurada coefficients in *o*-xylene, chloroform and 1,1,1-trichloroethane at 30°C, and in *o*-xylene over the 30–70°C temperature range.

Two important aspects have been evidenced from these studies: the very high values of the relative viscosities, and the higher than unity value of the M-H-S exponent—both associated with a very rigid chains structure, as rod-like, columnar, or rigid helix. These characteristics can appreciably influence the flow properties of the solutions.

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 filaments and films with vastly improved physical properties.

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

EXPERIMENTAL

The silylation process was realized, in heterogeneous medium, treating a suspension of activated cellulose in *o*-xylene with trimethylchlorosilane. An adequate quantity of pyridine was added in the reaction medium to remove the hydrochloric acid and to prevent the reverse reaction. The silylation was realized at 115–120°C, under nitrogen atmosphere, in a glass reaction vessel, provided with a backflow condenser. Trimethylsilylcelluloses were separated from the reaction medium by precipitation with isopropanol, followed by a few washings, also with isopropanol,

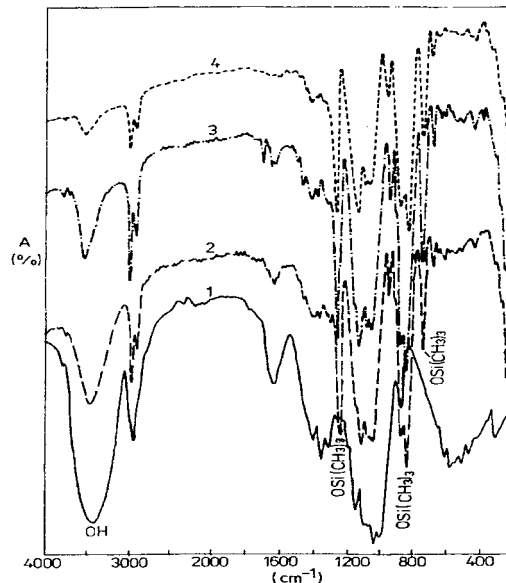


Figure 1 Solid-state IR spectra of cellulose support and TMSC with different substitution degrees: 1—cellulose support; 2—TMSC₂; 3—TMSC₂; 4—TMSC₂.

and a final washup with acetone. These samples showed a pronounced tendency of hydrolysis, becoming partially insoluble. At the same time, preliminary DSC studies indicated a lower thermal stability. To raise the stability degrees of these samples, a supplementary purification was requested, and it was 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 a nitrogen atmosphere. After this supplementary purification, the hydrochloric acid and pyridine hydrochloride were completely removed from the TMSC samples.

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

Five samples of TMSC of different degrees of polymerization were obtained, starting from the same cellulosic support samples. The synthesis conditions and main characteristics of these samples were presented in the earlier studies.⁹

The characterization was performed in *o*-xylene, at 20°C for TMSC and 30°C samples and the number-average molecular weights (M_n), the sec-

Table I The Characterization of TMSC Samples in *o*-Xylene, at 20°C⁴

Sample	TMSC-1	TMSC-2	TMSC-3	TMSC-4	TMSC-5
M_n (g/mol) (a)	92,500	172,900	200,000	271,000	357,000
$10^4 A_2$ (m ³ mol · kg ⁻²) (a)	3.37	5.47	7.55	7.52	6.60
DS(CH) (b)	2.85	2.84	2.82	2.85	2.85
DS(IR) (c)	2.56	2.75	2.60	2.70	2.58
I_p (d)	2.21	2.14	2.18	2.65	3.11
$[\eta]$ dL/g (e)	1.256	4.009	4.993	6.367	8.315

ond virial coefficients (A_2), the polydispersity index (I_p), and limiting viscosity number ($[\eta]$) were determined. Supplementary, the substitution degrees were determinate by chemical analysis, DS(CH), and by IR-spectroscopy, DS(IR). These characteristics of the two series of samples are presented in Table I.

The IR spectra were recorded on a SPECORD M90 Carl Zeiss Jena apparatus using the KBr pellet technique. The unsubstituted OH groups from the three TMSC samples analyzed are evidenced in Figure 1.

These spectra confirm the structural changes produced by the etherification process when the —OH groups were substituted by O—Si(CH₃)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(CH₃)₃); 850 cm⁻¹ (Si—C). The peaks associated with deformation vibrations, as 970 cm⁻¹ (Si—O) and 1470 cm⁻¹ (SiCH₃) can also be identified. The characteristic absorption band associated to the OH valence vibration ($\nu = 3450\text{--}3500$ cm⁻¹) is lower in the silylated compounds, 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 appara-

tus, 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 an X-ray diffractometer Siemens-type D500 working with CuK_α radiation.

The viscosities of the polymer solutions were measured using an Ubbelohde-type viscometer, with dilution and suspended bulb level, for which—due to the high flow times—the kinetic energy corrections were negligible. Temperature was controlled within ±0.02°C. Viscometric measurements were made in chloroform, 1,1,1-trichloroethane, and *o*-xylene. When *o*-xylene was used, the viscosities were determined as a function of temperature in the domain 20–70°C. The maximum concentrations of the solutions were the same as in osmometric measurements.

The dynamic viscosities were calculated with the relation:

$$\eta = \eta_0 \frac{\tau \cdot \rho}{\tau_0 \rho_0}$$

where: η_0 is the dynamic viscosity of *o*-xylene, τ_0 and τ —the flow times for pure solvent and solution, ρ_0 and ρ —the densities of pure solvent and

Table II Limiting Viscosity Number $[\eta]$, in dL · g⁻¹, for TMSC Samples in Different Solvents, at 20°C

Solvent	Sample				
	TMSC-1	TMSC-2	TMSC-3	TMSC-4	TMSC-5
Chloroform	1.343	3.222	4.898	6.162	8.120
1,1,1-Trichloroethane	1.526	4.400	5.546	6.530	9.314
<i>o</i> -Xylene	1.256	4.009	4.993	6.367	8.315

Table III The Mark-Houwink-Sakurada Equation Coefficients, at 20°C

Solvent	$10^7 \cdot K$ (dL · g ⁻¹)	a
Chloroform	2.659	1.353
1,1,1-Trichloroethane	5.010	1.316
<i>o</i> -Xylene	1.635	1.399

solution at the same temperature and concentration.

The densities of both *o*-xylene and solution with maximum concentration were determined gravimetrically at 30 and 70°C. Then the densities of the polymer solutions with different concentrations at different temperatures were evaluated assuming a linear dependence of the densities on both the concentration and temperature.

Number-average molecular weights of the TMSC samples were determined with an automatic Hewlett-Packard Model 502 osmometer. The measurements were carried out in *o*-xylene, at 20°C, using membranes from regenerated cellulose of a CR-1 type,¹⁰ which exhibit high-solution retention. Because of the high solutions viscosities, the maximum concentration of the sample in the osmometric studies were: 1 g · dL⁻¹ for samples 1.3; 0.7 g · dL⁻¹ for sample 4 and 0.5 g · dL⁻¹ for sample 5. In all cases, the experimental errors were situated below 1%, and a linear dependence was obtained in $\pi/c - c$ coordinates.

RESULTS AND DISCUSSIONS

The specific viscosities of the TMSC dilute solutions in different solvents are highly dependent on the concentration, so that the Huggins curves, $\eta_{sp}/c = f(c)$, presents high and increasing slope; the Huggins constant values being approximately

10 times higher than that for usual polymers. In these conditions, the Huggins, Fuoss-Mead, or Martin equations for the limiting viscosity number evaluation results in high number errors, and are not applicable for this polymer. For this reason, to determine the limiting viscosity number, the Fedors equation¹¹ was applied:

$$f(\eta_r) = \frac{1}{2(\sqrt{\eta_r} - 1)} = \frac{1}{[\eta]} \left(\frac{1}{c} - \frac{1}{c_m} \right)$$

This equation allows a linear extrapolation in the $f(\eta_r) - (1/c)$ coordinates for the TMSC samples in the three solvents. Experimental results are shown in Table II. First, it is noticed, taking into account the relatively small values of the molecular weights, that the limiting viscosity number values are very high. The very pronounced rise in the limiting viscosity number with molecular weight of the sample should also be noticed. This behavior indicates that the polymer chains of these cellulose derivatives are extremely stiff.

By using the experimental number-average molecular weights and limiting viscosity numbers from Table II, the coefficients K and a , of the Mark-Houwink-Sakurada equation, $[\eta] = K \cdot M^a$, were calculated. The values of these coefficients are presented in Table III.

For many cellulose derivatives the values of the “ a ” exponent of the Mark-Houwink-Sakurada equation are very close to the unity,¹²⁻¹⁴ this is due to the strongly stiffness of the macromolecular chains. In the case of the TMSC in the three solvents the exponent a is higher than unity, indicating a special conformation of the macromolecules in solution compared with the great majority of the polymers. Values higher than unit for the exponent “ a ” have been quoted for carboxymethylcellulose in NaCl-aqueous solutions,¹⁵ cel-

Table IV Limiting Viscosity Number, $[\eta]$ in dL · g⁻¹, for TMSC Samples in *o*-Xylene, as Function of Temperature

t , °C	TMSC-1	TMSC-2	TMSC-3	TMSC-4	TMSC-5
20	1.256	4.009	4.993	6.367	8.315
30	1.175	3.398	4.667	5.600	9.496
40	1.187	3.398	4.530	5.517	9.004
50	1.154	3.228	4.469	5.415	8.823
60	1.120	2.980	4.320	5.353	8.480
70	1.049	2.844	4.306	5.204	8.233

Table V Temperature Dependence of the M-H-S Equation Coefficients for TMSC in *o*-Xylene

t (°C)	20	30	40	50	60	70
$10^8 K$ (dL · g ⁻¹)	16.350	11.670	6.865	5.886	5.221	3.534
a	1.399	1.424	1.464	1.474	1.481	1.510

lulose xanthate in aqueous solution of glycerine,¹⁶ for some polypeptides in different solvents,¹⁷ etc.^{18,19}

The peculiar behavior is always associated with a rigid structure of the polymer chain, with the formation of some associations or with the transition from a flexible macromolecular coil to a rigid helix, a rod-like or a "columnar" structure. This kind of structure in the case of the TMSC is due perhaps to the increasing of the chain stiffness caused by the presence of the trimethylsilyl groups having a great volume, and which exhibit short-range repulsion forces against the cycles from the principal chain, but can also be due to the tendency of the TMSC solutions for tixotropic gel formation.

The temperature dependence of the limiting viscosity number and respective of the M-H-S equation, coefficients for TMSC in *o*-xylene were also analyzed and the results are presented in Tables IV and V.

Although the dynamic viscosities of the TMSC in xylene present a pronounced decrease with the temperature, the decreasing of the limiting viscosity number is less pronounced. The variation of the limiting viscosity number is almost linear for the entirely domain considered, except for the TMSC-5 sample, which exhibits a maximum at

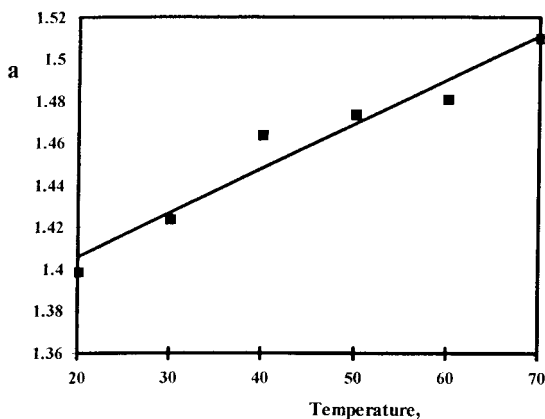
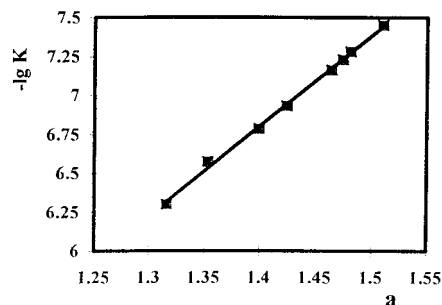
30°C. This maximum can be related to a conformational transition, which can occur at a certain temperature and/or molecular weight of the polymer. Based on the data from Table IV, and using the experimental number-average molecular weights, the M-H-S equation coefficients were calculated, and obtained values are shown in Table V.

Even at high temperatures the values of exponent "a" from the M-H-S equation are higher than the unit, and, much more, its value increases linearly with the temperature increasing (Fig. 2). A linear regression analysis gives:

$$a = 1.364 \pm 0.0021 \cdot t$$

In accordance with the very high values of the exponent "a" the preexponential factor is extremely low, and decreases with the increasing temperature. The exactness of these data can be verified analyzing the correlation between the two coefficients of the M-H-S equation, correlation that appears at any type of equation expressing an exponential dependence between two quantities.

In the case of the M-H-S equation, a correlation of the type: $\log K = A + Ba$ should be satisfied. The values of coefficients K and a obtained for TMSC in the three solvents and in *o*-xylene at different temperatures are represented in Figure 3, in $\log K - a$ coordinates.

**Figure 2** Temperature dependence of the exponent "a" from the M-H-S equation.**Figure 3** Graphical representation of the compensation effect for the two coefficients of the M-H-S equation.

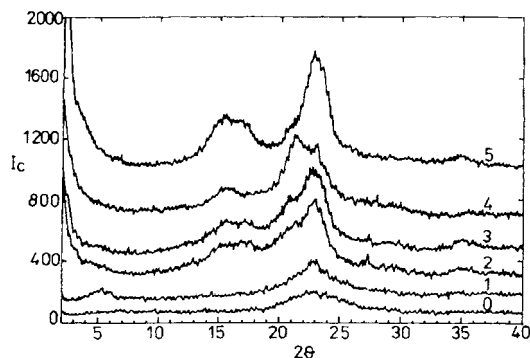


Figure 4 X-ray diffractograms of used cellulose supports: 0—amorphous standard cellulose; 1—sample C₁; 2—sample C₂; 3—sample C₃; 4—sample C₄; 5—sample C₅.

This figure clearly show that the equation of compensation satisfy the experimental data very well. With these data the following equation of compensation is obtained:

$$\log K = 1.408 - 5.857 \cdot a$$

Using a standard the X-ray diffractogram of the amorphous cellulose (curve 0 from Fig. 4) the crystallinity index for the support celluloses and their silyl derivatives were calculated, and the results are presented in Tables VI and VII. The crystallinity index was calculated with the relation indicated in ref. 20.

From the values presented in Table VII, 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-4 sample we obtained an orthorhombic symmetry, with the lattice parameters closed to $a = 23.08(6) \text{ \AA}$, $b = 14.06(2) \text{ \AA}$, and $c = 3.69(1) \text{ \AA}$.

Table VI The Crystallinity Index for Trimethylsilylcellulose

Sample No.	DP Cellulose Support	Crystallinity Index for TMSC (%)
1	337	60,0
2	588	57,2
3	708	37,9
4	880	31,4
5	1100	11,0

Table VII 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

Several studies were devoted to the temperature dependence of the dilute polymer solution dynamic viscosities.²¹⁻²⁶ This dependence was found to be of an Arrhenius-type law, and can be expressed by the equation proposed by Guzman and Andrade:

$$\eta = A \exp \cdot (Q/RT) \quad (1)$$

where η is the dynamic viscosity of the solution; Q is the apparent activation energy of the viscous flow; and A is the preexponential factor, 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:

$$Q = Q_0 + k_e \cdot c \quad (2)$$

Q_0 being the activation energy of the viscous flow of the pure solvent and k_e a coefficient, depending on the molecular weight of the polymer.

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

$$k_e = K_e \cdot Mn \quad (3)$$

The analysis of many data indicates that K_e value depends on the flexibility of the polymer chains in solution; for flexible polymers in good solvents K_e being by one to two orders lower than for stiff chain polymers, as cellulosic derivatives.

The dependence of the preexponential factor A , on concentration and molecular weight is strongly correlated with the chain flexibility in solution, being interpreted by Moore²⁷ in terms of the activation entropy change of viscous flow. Thus, for flexible chain polymers in dilute solutions:

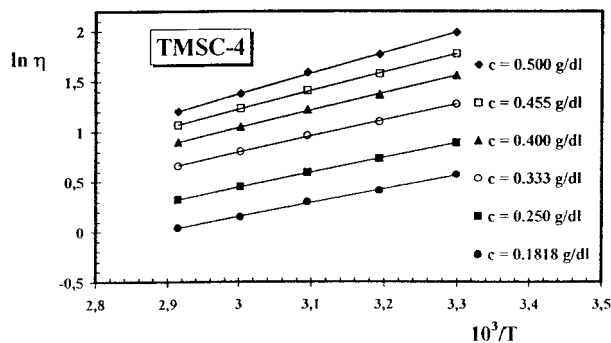


Figure 5 Typical diagram ($\ln \eta$) vs. ($1/T$) for TMSC-4/*o*-xylene at various concentrations. Sample: TMSC-4; $M_n = 271,000$ g/mol.

$$A = A_0 + K_a \cdot M^\alpha \cdot c \quad (4)$$

while, for stiff chain polymers:

$$A = A_0 \exp(-K_b \cdot M^\beta \cdot c^2) \quad (5)$$

where: A_0 represents the preexponential factor of the pure solvent and K_a , K_b , α and β are constants, depending on the nature of the polymer/solvent system.

For a moderate stiff polymer, as PVC in tetrahydrofuran, the correlation of A with M and c was found to be of the type.²⁵

$$A = A_0 - K_c M^\gamma c^2 \quad (6)$$

which, in fact, is equivalent with (6) arising from this by expanding in series the exponential factor and retaining no terms beyond those in the square of the concentrations. All these equations confirm the complicated dependence of the preexponential factor on chain flexibility.

According with eq. (1), Figure 5 presents the representative curves in ($\ln \eta$) – ($1/T$) coordinates for different concentrations of the solution.

These figures showed the classical linear dependence in logarithmic-hyperbolic coordinates for the concentration interval analyzed. This dependence is preserved for the all studied fractions.

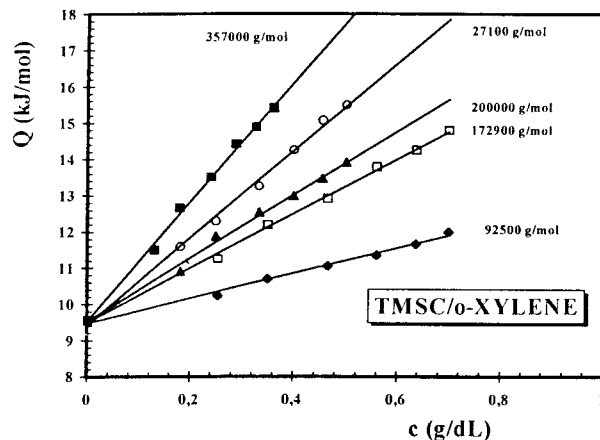


Figure 6 Dependence of the apparent activation energy, Q , on concentration and molecular weight for the TMSC.

The apparent activation energy and preexponential factor for the representative samples, at different concentrations of the solution, were evaluated by the least-squares method, and are presented in Table VIII.

It can be seen that, for both samples, the apparent activation energy of viscous flow increases with concentration; while, unexpectedly, the preexponential factor does not show a regularly variation with solution's concentration, but, contrary, dissimilar values were obtained. For this reason, the mean values of this factor were calculated: $A = 15.73 \cdot 10^{-3}$ cP for the TMSC-4 sample.

The concentration dependence of the apparent activation energy for different molecular weight samples are presented in Figure 6—for TMSC. For the pure *o*-xylene the value $Q_0 = 9.566 \cdot 10^3$ J/mol was chosen. This value was evaluated on the basis of the literature data for *o*-xylene.

As can be seen, a good linearity is obtained in all the cases. According to eq. (2) the k_e values were evaluated from the slopes of these straight lines.

The dependence of the k_e coefficient on the molecular weight of the polymer samples is illustrated in Figure 7 for the two types of silylated compounds.

Table VIII The Guzman-Andrade Coefficients for the TMSC-4 Sample in *o*-Xylene ($M_n = 271,000$ g/mol)

c (g/dL)	0.182	0.250	0.333	0.400	0.455	0.500
$10^{-3} Q$ (J/mol)	11.424	12.301	13.263	14.259	15.271	15.499
$10^3 A$ (cP)	18.93	18.48	18.55	16.53	13.83	15.08

In accordance with eq. (3), from the slopes of these two straight lines were calculated the constants K_e for the polymer in *o*-xylene $K_e(\text{TMSC}) = 0.0451 \text{ J} \cdot \text{dL/g} \cdot \text{mol}$.

Generally, the preexponential factor, A , depends also on the concentration and the molecular weight of the polymer but, compared to Q , it is much more sensitive to chain flexibility, polydispersity of polymers and, especially, to experimental errors.

The mean values of the preexponential factor obtained, taking into account the values found for the various concentration used—as a function of molecular weight, are presented in Table IX for TMSC.

As in the case of the concentration dependence of A , the dependence on molecular weight of the preexponential factor is also unconvincing; the obtained values are very dispersed, and do not exhibit an evident variation to a certain sense.

This behavior differs on that of the other cellulose derivatives²⁴ or polymers with moderate chain stiffness,^{22,25} and can be attributed to the very strong stiffness of the macromolecular chains of these compounds, which was pointed out in the earlier studies⁹ by the more than unity values of the Mark-Houwink-Sakurada exponent ($\alpha = 1.4 \dots 1.5$ for TMSC *o*-xylene in the temperature range 30–70°C), and confirmed qualitatively by the molecular mechanics calculus.

Another reasons for this behavior may be attributed to the high and dissimilar polydispersities of the used samples.

Using these data the mean values of the preexponential factor were calculated as: $A = 17.97 \cdot 10^{-3} \text{ cP}$ for TMSC/*o*-xylene. For pure *o*-xylene the preexponential factor is $A_0 = 15.86 \cdot 10^{-3} \text{ cP}$.

Thus, the following relations can express the flow equations of the dilute solutions of trimethylsilylcellulose:

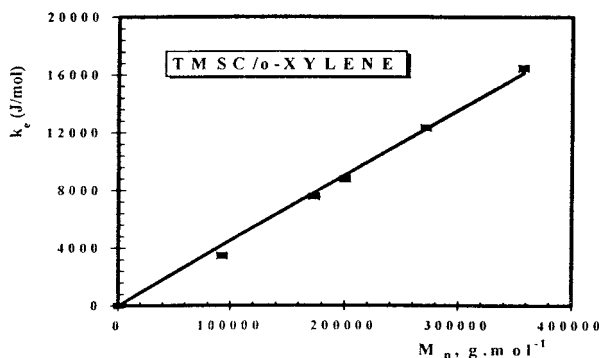


Figure 7 Dependence of the k_e coefficient on molecular weight for TMSC.

Table IX The Mean Value of the Preexponential A as Function of Molecular Weight for TMSC

M_n (g/mol)	92,500	172,900	200,000	271,000	357,000
$10^3 A$ (cP)	17.04	16.71	19.05	15.73	21.10

For TMSC/*o*-xylene:

$$\eta = 1.797 \cdot 10^{-2} \times \exp\left[\frac{1}{RT} (9.566 + 0.0451 \cdot M_n \cdot c)\right] \text{ cP}$$

CONCLUSIONS

1. The coupling of the trimethylsilyl groups to the cellulosic chains can be realized, within a 95% degree of substitution, by reaction between activated celluloses and trimethylchlorosilane in xylene/pyridine medium, at 120°C, under inert atmosphere. The stability of the obtained samples can be improved by successive solving/precipitating operations until the complete elimination of the hydrochloric acid.
2. The TMSC derivatives are very rigid polymers, having a rod-like structure in chloroform, 1,1,1-trichloroethane, and *o*-xylene; in these solvents the exponent values in the Mark-Houwink-Sakurada equation was higher than unity. In xylene, this rigidity increases with the temperature increase.
3. For the K and α coefficients of the M-H-S equation obtained in the three solvents and at different temperatures, there was a compensation relation in agreement.
4. The polydispersity index of the five samples, evaluated by GPC, is relatively high, and ranges between two and three, the higher value being found for the higher molecular sample.
5. The crystallinity index for silylcellulose derivative is independent on the nature of the cellulose used.
6. The crystallinity index depends on the substitution degree of the silylcellulose derivative.

7. For a trimethylsilylcellulose 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.
8. Trimethylsilylcellulose is a cellulosic derivative with very strong chain stiffness and with very big substituted groups. These two characteristics have had a considerable influence on the flow properties of the dilute solutions of these compound.
9. The temperature dependence of the solution's viscosities obeys an Arrhenius-type law, and can be expressed by the Guzman-Andrade equation.
10. The apparent activation energy of viscous flow is linear, 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 being: $4.51 \cdot 10^{-2} \text{ J} \cdot \text{dL/g} \cdot \text{mol}$ for silylated derivatives in *o*-xylene.
11. For the preexponential factor, the dependence on concentration and molecular weight is insignificantly, and this peculiar behavior can be attributed to the great stiffness of the macromolecular chains whose structure is that one of a macromolecular coil, but rather a rod-like or a columnar rigid structure.
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