

Solution Properties of Triphenylsilyl Cellulose

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ABSTRACT: Five samples of triphenylsilyl cellulose (TPSC) are characterized in solution by osmometry, viscometry, and size exclusion chromatography. The isolated and purified cellulose ethers are prepared in a *N,N*-dimethylformamide and pyridine medium under heterogeneous starting conditions and a nitrogen atmosphere by silylation of activated celluloses with triphenylchlorosilane at 115–120°C. TPSCs are characterized by their polydispersities and degrees of substitution by osmometry and viscometry in various solvents. The Mark–Houwink–Sakurada equation

coefficients are evaluated in 1,1,1-trichloroethane, chloroform, and *o*-xylene at 30°C and in *o*-xylene over a temperature range of 30–70°C. Values of 2.12–2.18 are obtained for exponent *a*. This indicates, in combination with low values of the preexponential factor (on the order of 10^{-12}), strong stiffness of the macromolecular chains. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1257–1261, 2007

Key words: triphenylsilyl cellulose; Mark–Houwink–Sakurada coefficients; osmometry; viscometry

INTRODUCTION

Cellulose, which contains an abundance of free hydroxyl groups, is insoluble in water or organic solvents. The effects of polymer modifications by substitution with triorganosilyl groups (silylation), which were increased solubility of silylated polymers in nonpolar solvents, were demonstrated 30 years ago. To obtain supramolecular structures of Langmuir–Blodgett and spin-coated cellulosic films, silylcellulose derivatives were shown to be suitable, because these compounds are soluble in common solvents and easily regenerated.^{1–5} It is well known that trimethylsilyl cellulose (TMSC), having a degree of substitution (DS) higher than 2.5, forms well-defined mono- and multilayered architectures; as a consequence, desilylation of these films is a convenient method to generate oriented hydrophilic films.⁶ Silylcellulose derivatives can also be used for obtaining regenerated cellulose fibers,^{7,8} and some of their liquid crystal properties were evidenced.^{9,10} Taking into account that both the regenerated cellulose properties and the liquid crystal properties depend mainly on the solution properties of the silylated celluloses,^{11–13} their characterization in solution should be the main issue of the studies devoted to these compounds. Unfortunately, difficulties in synthesis and a pronounced instability of these compounds make a systematic analysis in this field quite diffi-

cult, so the literature in the field provides only an insignificant number of such studies.

The characterization of TMSC in solution was reported in a previous study.¹⁴ A similar study performed on triphenylsilyl cellulose (TPSC) by means of osmometry and viscometry is presented here.

EXPERIMENTAL

Synthesis and characterization of TPSC

The silylation process was realized in a heterogeneous medium, comprising *N,N*-dimethylformamide (DMF) plus pyridine, by treating a suspension of activated cellulose with triphenylchlorosilane. Five samples of chemically purified cellulose with different degrees of polymerization (the same as those used in an earlier study^{14,15}) were used to obtain corresponding TPSC derivatives.

The activated and dried cellulose was suspended in DMF and pyridine medium and pretreated at 60°C for 60 min with triphenylchlorosilane. Then, the temperature was raised to 115°C and the sample was stirred for other 120 min. Finally, *o*-xylene p.a. was added in the reaction medium with stirring for 60 min at 115–120°C. All operations were carried out under a nitrogen atmosphere. The reaction medium was cooled to 60°C. Then, the TPSC was separated by precipitation with isopropanol p.a., washed with isopropanol, and washed with acetone. The samples were purified by successive precipitations with isopropanol from benzene and chloroform solutions.

The TPSC samples were characterized by their DS and polydispersity. The DS was calculated by

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TABLE I
Main Characteristics of TPSC Samples

	Sample				
	TPSC-1	TPSC-2	TPSC-3	TPSC-4	TPSC-5
M_n^a (g/mol)	93,130	137,100	164,130	172,500	169,800
M_w^a (g/mol)	202,900	317,710	396,200	460,500	580,500
M_w/M_n^a	2.18	2.32	2.41	2.67	3.42
DS	2.89	2.81	2.75	2.75	2.70

^a Determined by size exclusion chromatography against polystyrene standards.

determining the silicon content by applying the acid decomposition method.¹⁶ A PL-EMD 950-type gel permeation chromatography (GPC) chromatograph was used for polydispersity measurements. All measurements were carried out at 25°C with *o*-xylene as the eluent at a flow rate of 0.5 mL/min. The apparatus was calibrated according to narrow distribution polystyrene standards.

The number-average molecular weights (M_n), weight-average molecular weights (M_w), and polydispersity index (M_w/M_n) obtained by GPC and the DS are listed in Table I.

As in the case of TMSC, the TPSC-5 sample, which was prepared from the highest molecular weight cellulose support, shows a large polydispersity and the lowest DS.

Osmotic measurements were made with an automatic Hewlett-Packard model 502 osmometer at 30°C using cellulosic PECELL-600 type membranes. Analytical grade *o*-xylene was used as a solvent. For each sample, the osmotic pressure was measured for five different concentrations, ranging between 0.2 and 1.0 g/dL, which were obtained by diluting a 1.0 g/dL concentrated solution. Within the concentration range applied, the (π/c) versus c plots are

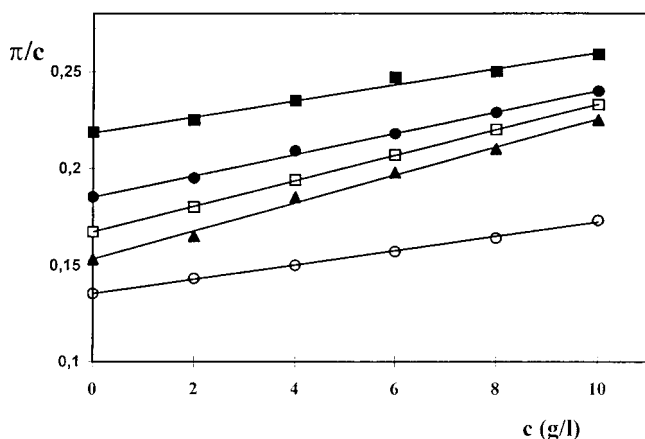


Figure 1 Osmometric curves for the TPSC samples: (■) TPSC-1, (●) TPSC-2, (□) TPSC-3, (▲) TPSC-4, and (○) TPSC-5.

linear (Fig. 1) for all the TPSC samples used. The M_n and second virial coefficients (A_2) were evaluated with the straight line coefficients using the least squares method.

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

RESULTS AND DISCUSSION

Due to the very high solution viscosities, the maximum concentration of the solutions was 0.7 g/dL for all samples. The values of the limiting viscosity number ($[\eta]$) were obtained according to the Fedor equation,¹⁷ which allows a linear extrapolation of the $f(\eta_r) = [2(\eta_r - 1)]^{-1}$ versus ($1/c$) graph, as can be seen in Figure 2. The $[\eta]$ was also evaluated by the least squares method.

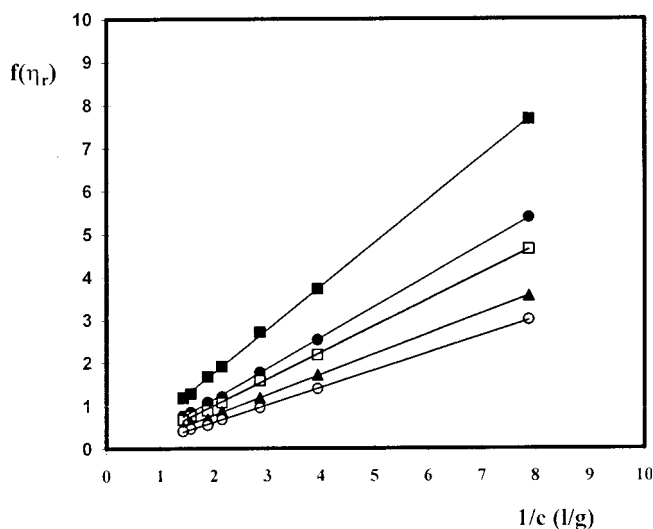


Figure 2 Fedors-type curves for the TPSC samples in *o*-xylene at 30°C: (■) TPSC-1 ($M_n = 128,200$ g/mol), (●) TPSC-2 ($M_n = 152,400$ g/mol), (□) TPSC-3 ($M_n = 167,900$ g/mol), (▲) TPSC-4 ($M_n = 188,000$ g/mol), and (○) TPSC-5 ($M_n = 207,400$ g/mol).

TABLE II
Results Obtained from Osmometry and Viscometry for Triphenylsilyl
Cellulose at 30°C

	Sample				
	TPSC-1	TPSC-2	TPSC-3	TPSC-4	TPSC-5
M_n (g/mol)	128,200	152,400	167,900	188,000	207,400
$10^4 A_2$ (m ³ mol/kg)	1.38	1.95	2.31	2.66	1.28
Trichloroethane	0.839	1.255	1.553	1.941	2.401
$[\eta]$ (dL/g)					
CHCl ₃	0.886	1.301	1.611	1.986	2.518
<i>o</i> -Xylene	0.911	1.344	1.616	2.106	2.509

In both the osmometric and viscometric graphs, a very good linearity can be noticed, in which the R^2 coefficients exceed 0.995.

The M_n , A_2 , and $[\eta]$ in TCE, chloroform, and *o*-xylene at 30°C are presented in Table II.

Taking into account the DS of TPSC and the degree of polymerization of the cellulosic supports, the molecular weights of TPSC should range between 132,000 and 415,000 g mol⁻¹, whereas the experimental values should be between 128,000 and 207,000 g mol⁻¹. The substantially diminished values obtained for the high molecular weights samples are probably the result of the more vigorous conditions of the applied TPSC synthesis, as compared with those of the TMSC synthesis.¹⁴ In contrast, except for sample TPSC-5, the uniformity of the samples, regarding both the DS and polydispersity, was much higher, which can be explained by taking into account the repeated purifications during which the less soluble molecules (fractions with a lower DS) and the small molecular weight fractions were removed.

As in the case of the TMSC samples, the A_2 shows an abnormal dependence on the molecular weight and it increases with increasing molecular weight, with the exception of sample TPSC-5. This behavior

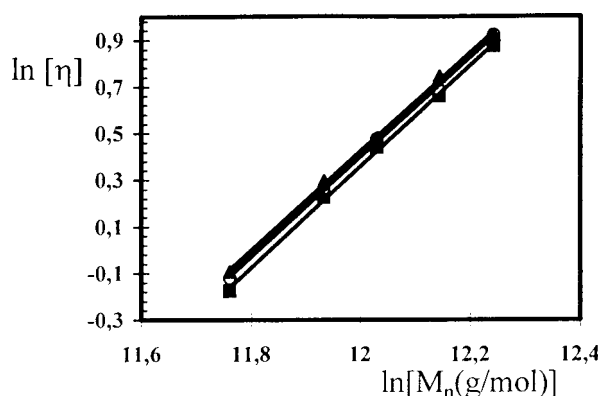


Figure 3 The limiting viscosity number and molecular weight correlation according to the MHS equation for the TPSC samples in different solvents: (▲) trichloroethane, (○) chloroform, and (■) *o*-xylene.

can be attributed to the largest polydispersity of this sample.

By using the experimental values of the average molecular weights and the limiting viscosity number (data from Table II), the coefficients of the Mark-Houwink-Sakurada (MHS) equation, K and a , were calculated. The graph $\ln [\eta]$, in correlation with $\ln M_n$, presented in Figure 3 shows a very good linearity between the two variables for all three solvents. The linear correlation coefficients exceed 0.995.

The obtained K and a coefficient values are presented in Table III. Compared with the TMSC derivatives (for which $a = 1.3$ – 1.4) the higher exponent a values obtained in the three solvents indicate increased stiffness of the polymeric chains. In the case of TPSC, this observation can be explained by the higher bulkiness of the $-\text{Si}(\text{C}_6\text{H}_5)_3$ groups compared to the $-\text{Si}(\text{CH}_3)_3$ groups. Corresponding to the very high values of exponent a , the preexponential 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 IV.

Table V provides coefficients K and a , which were evaluated for the MHS equation on the basis of the data from Table IV.

Of interest, unlike the results obtained for TPSC samples, the MHS exponent decreases when the temperature increases (except at 70°C). This decrease is very pronounced and is accompanied by a strong increase of the preexponential factor.

Except for the value found for a temperature of 70°C, a linear dependence on the temperature is

TABLE III
Coefficients of Mark-Houwink-Sakurada Equation for
TPSC Samples

	Solvent		
	1,1,1-Trichloroethane	Chloroform	<i>o</i> -Xylene
$10^{12} K$ (dL/g)	6.67	9.82	14.06
a	2.174	2.145	2.118

TABLE IV
Limiting Viscosity Number [Z] (dL/g) for TPSC
Samples in *o*-Xylene

<i>t</i> (°C)	Sample				
	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

obtained. This dependence can be expressed by the following equation:

$$a = 2.591 - 0.165t$$

where *t* is the temperature (°C) and *a* is the exponent from the MHS equation.

A correlation of $\ln K = A + B \times a$ between the MHS coefficients is verified in Figure 4 using the data obtained in TCE, CHCl₃, and *o*-xylene at different temperatures. The equation obtained is

$$\ln K = 0.0793 - 11.854a$$

Generally, the stiffness of a macromolecular chain can be due both to long-range interactions between chain segments separated by a large number of skeletal bonds and to a large volume of lateral 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 units of cellulose, TMSC, and TPSC were considered. The calculus of molecular mechanics (MM+, HYPERCHEM 5.02 program) was performed to find the minimum energy configuration. The glucosidic bond angle was found at around 116° for all considered molecules. Then, the C—O—C bond angle between the central structural units (θ) was modified and the energies were calculated, without a new optimization. For the three derivatives considered here, the calculated energies are presented in Figure 5 versus the deformation angle.

These curves entirely confirm the chain stiffness, which was previously appreciated qualitatively by the value of the MHS equation exponent. The chain

TABLE V
Mark-Houwink-Sakurada Coefficients for TPSC
in *o*-Xylene as Function of Temperature

	<i>t</i> (°C)				
	30	40	50	60	70
10 ¹² K (dL/g)	14.06	152.3	1384	4505	4.58
<i>a</i>	2.118	1.913	1.731	1.628	2.195

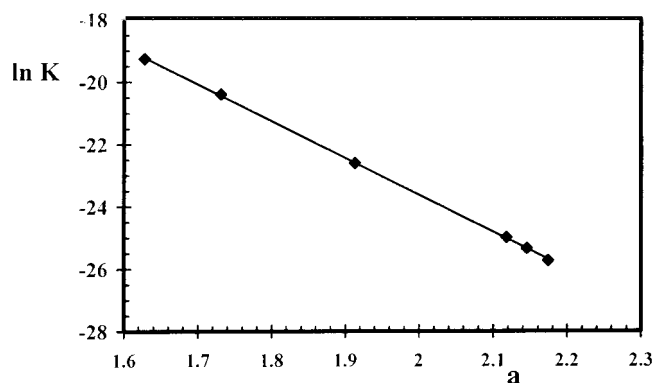


Figure 4 A representation of the compensation effect for the two coefficients of the MHS equation.

stiffness increases in the order cellulose < TMSC < TPSC.

CONCLUSIONS

1. Coupling of the triphenylsilyl groups to the cellulosic chains was realized, with a 95% DS, by the reaction between activated celluloses and triphenylchlorosilane in DMF-pyridine medium under heterogeneous starting conditions and a nitrogen atmosphere. The stability of the obtained samples was improved by successive solving/precipitating operations until a complete elimination of pyridine.
2. The well-purified samples were characterized by their DS (Si determinations of content) and polydispersities (determinations by GPC) and osmometry and viscometry in various solvents.

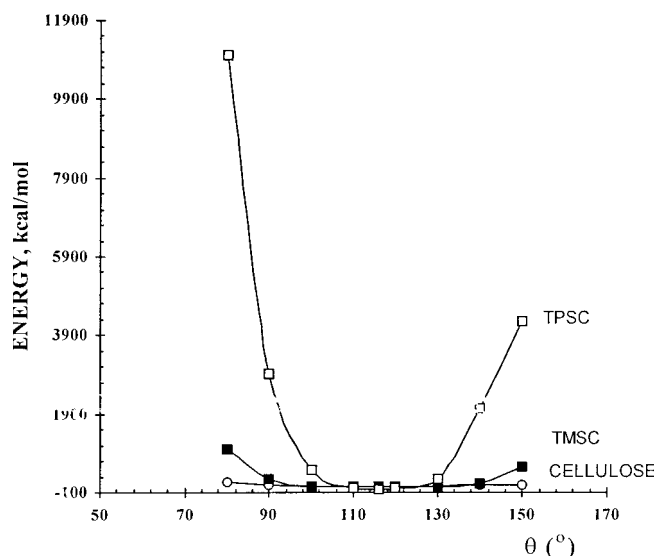


Figure 5 The variation of the total energy as a function of the glucosidic bond angle for (□) cellulose, (■) TMSC, and (○) TPSC.

3. The exponent a value of the MHS equation in TCE, chloroform, and *o*-xylene was extremely high, having values between 2.12 and 2.18, which was similar for all three solvents. In accordance with these high values, the preexponential factor had very low values (on the order of 10^{-12}), indicating strong stiffness of the macromolecular chains in solution. Qualitatively, this stiffness was confirmed by molecular mechanics calculus.
4. Contrary to the behavior of TMSC samples, the exponent a for *o*-xylene was significantly decreased with increasing temperature, indicating a relative increase of chain flexibility.
5. The two coefficients of the MHS equation were correlated by a compensating equation.

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