Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Synthesis and Characterization of Trimethylsilylcellulose in Solution

Nicolae Aelenei[a]; Danut Bontea[b]; Catalina Ioan[b]
[a] Physical Chemistry Department, Technical University "Gh. Asachi" Bulevard Dimitrie Mangeron, Iasi, Romania [b] "Petru Poni" Institute of Macomolecular Chemistry, Iasi, Romania

To cite this Article Aelenei, Nicolae , Bontea, Danut and Ioan, Catalina(1998) 'Synthesis and Characterization of Trimethylsilylcellulose in Solution', Journal of Macromolecular Science, Part A, 35: 10, 1667 — 1680
To link to this Article: DOI: 10.1080/10601329808000978
URL: http://dx.doi.org/10.1080/10601329808000978

J.M.S.—PURE APPL. CHEM., A35(10), pp. 1667–1680 (1998)

SYNTHESIS AND CHARACTERIZATION OF TRIMETHYLSILYLCELLULOSE IN SOLUTION

Nicolae Aelenei
Physical Chemistry Department
Technical University "Gh. Asachi"
Bulevard Dimitrie Mangeron, 71
RO-6600 Iasi, Romania

Danut Bontea and Catalina Ioan
"Petru Poni" Institute of Macomolecular Chemistry
Aleea Gr. Ghica Voda, 41 A
RO-6600 Iasi, Romania

ABSTRACT

Five samples of cellulose, with different polymerization degrees, were used to obtain corresponding trimethylsilylcellulose derivatives by reaction with trimethylchlorsilan. 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 1.0, indicating great stiffness of the macromolecules in solution. Also, the temperature dependence of both the limiting viscosity number and M-H-S coefficients for TMSC in o-xylene were studied. The exponent from M-H-S equation is also higher than 1.0 and increases linearly with the temperature. The GPC studies indicate a relatively high polydispersity of the studied samples; the polydispersity index being situated between two and three.

INTRODUCTION

Celluloses, containing an abundance of free hydroxyl groups, are 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].

Silylations were carried out by suspending cellulose in polar solvents such as dimethylsulfoxide, dimethylformamide, N-methylpyrolidone, and the addition of a bis(trimethylsilyl) acetamide excess and heating the stirred mixture at 100-150°C, under anhydrous conditions. Sometimes, insoluble gels remain in the obtained products, altering the properties, especially the stability, and making the studies extremely difficult to perform. Treatment of cellulose in N-methylpyrolidone with N-trimethylsilylpiperidine or with hexamethyldisilazane, at 140-150°C, gave viscous solutions with some insoluble residues.

Silylation of cellulose with trimethylchlorosilane in pyridine have been conducted on extremely insoluble polymers in organic solvents [3, 4]. Klebe and Finkbeiner explained this fact by both the grade of celluloses, depending on the prior history of them, and the crosslinking of the polymer, as a result of either some secondary reaction mode of the trimethylchlorosilane itself, or the presence of some impurities in the chlorosilane, such as higher clorinated silanes, which are known to be considerably more reactive than trimethylchlorosilane. Using a pure, freshly prepared and anhydrous trimethilchlorosilane a completely soluble product was obtained. It was also found that a complete remove of the pyridine hydrochloride from the product is requested; otherwise TMSC becomes partially insoluble after precipitation and drying. Thus, the insolubilization may be caused by the reverse reaction in which the silyl ether bond are cleaved by the hydrochloride acid.

A thermoplastic TMSC, prepared from chemical cellulose and hexamethyldisilazane in dimethylformamide, using chlorotrimethylsilane/pyridine as catalyst, was reported [5].

Silylated derivatives were also obtained by a homogeneous reaction using a mixture of LiCl and N,N-dimethylacetamide as a solvent for cellulose. The homogeneous reaction provides a uniform substitution distribution [6, 7] and a controlled degree of substitution [8]. Uniformly substituted cellulose derivatives should exhibit predictable properties and enhanced resistance to enzymatic degradation. By this procedure, using an excess of hexamethyldisilazane as silylation agent, trimethylsilyl cellulose was also synthesized [9-11].

Due to the fact that silylated celluloses are suitably soluble, and very easily regenerable, these derivatives have been used to design supramolecular structures in Langmuir-Boldgett and spin-coated films [12, 13]. Thus, trimethylsilyl cellulose, having substitution degrees higher than 2.5, form well-defined mono and multi-layered architectures; the desilylation of these films being a convenient method to generate oriented hydrophilic films [9].

Although the silylcellulose derivatives have various uses; as fibers [14], films, or liquid crystals [15, 16] , a search in the literature revealed that rather a small number of studies are devoted to characterization of these compounds, especially in solution. Most likely, this lack is perhaps determined both by the 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 the regenerated cellulose properties and the liquid crystals properties of TMSC mainly depend on the dimensions and flexibility of the macromolecules [17, 18], a detailed characterization of these compounds in different solvents is necessary.

EXPERIMENTAL

Synthesis of TMSC

The trimethylsilylcellulose samples were obtained from activated celluloses and trimethylchlorsilane in o-xylene+pyridine medium, under nitrogen atmosphere at normal pressure [8]. For synthesis, five samples of cellulose with different molecular weight were used. These samples were obtained from resinous cellulose by depolymerization in NaOH medium (17.5 %), in two steps: 60 minutes at 20°C and 30-300 minutes at 40°C. The polymerization degree and the molecular weights of cellulose supports were determined by a viscometric method, in cupriethylenediamine solutions, at 25°C [20]. The obtained values are presented in Table 1.

The activation of the cellulose samples was achieved in acetic acid, at 25°C, for 60 minutes, followed by heating at 120°C, till the complete elimination of water and acetic acid. By activation, the celluloses are turned to a anhydrous form, being also grinded; as a result, a uniform substitution was achieved.

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 hydro-

TABLE 1. The Polymerization Degree (DP) and Viscometric Molecular Weight (M_V) of the Cellulose Samples as Function of Treatment Times

SAMPLE	**C1**	**C2**	**C3**	**C4**	**C5**
Treatment time (min)	**300**	**240**	**180**	**60**	**0**
DP	**327**	**588**	**708**	**880**	**1100**
M_v (g mol^{-1})	**53,300**	**96,400**	**116,100**	**144,300**	**180,000**

chloric acid and to prevent the reverse reaction. The silylation was realized at 115-120°C, under nitogen atmosphere, in a glass reaction vessel, provided with a back-flow condenser. Trimethylsilylcelluloses were separated from the reaction medium by precipitation with isopropanol, followed by a few washings, also with isopropanol, and a final wash-up 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. In order 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.

Characterization

The five purified samples of TMSC were characterized by IR spectroscopy, gel permeation chromatography (GPC), and chemical analysis. The IR spectra were recorded on a SPECORD M90 Carl Zeiss Jena spectrophotometer, using a KBr pellet technique. The polydispersities of the samples were determined by GPC, using a PL-EMD Evaporative Light Scattering Detector Instrument of 950 type, o-xylene as eluent, a flow rate of 0.5 mL/min^{-1} and 25°C. Polystyrene standards with narrow distribution were used to calibrate the apparatus. The degrees of substitution (DS) were determined measuring the content by means of the acid decomposition method [21].

Solid state IR spectra of both TMSC (sample TMSC-3) and the corresponding cellulose support (sample C3) are presented in Figure 1. These spectra

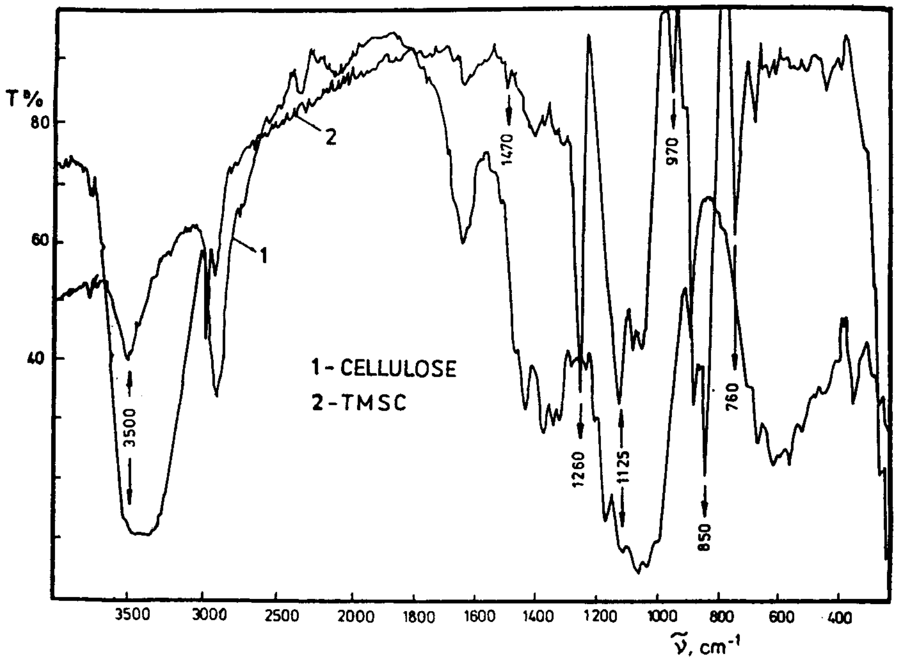

Figure 1. Solid state IR spectra for TMSC and cellulose support samples.

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, and these were characteristic to the valence vibrations in the substituted groups, namely: 750-760 cm^{-1} and 1260 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 absorbtion band associated to the OH valence vibration (v= 3450-3500 cm^{-1}) is lower in the silylated compound, 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 controllable quantities, a relative method is recommended. For this purpose, the peak stayed at 1120-1130cm^{-1}, corresponding to the C-O-C vibration, and present in both spectra, was used as reference band.

TABLE 2. The Results of the IR, GPC and Chemical Characterization of the TMSC Samples

SAMPLE	TMSC-1	TMSC-2	TMSC-3	TMSC-4	TMSC-5
DS (IR)	2.56	2.75	2.60	2.70	2.58
DS (CH)	2.85	2.84	2.82	2.85	2.85
M_n (g.mol^{-1})	48,490	134,130	149,670	165,350	205,500
M_w (g.mol^{-1})	107,140	286,860	420,992	438,900	639,980
M_v (g.mol^{-1})	97,270	257,240	366,100	383,900	550,970
$I_p = M_w/M_n$	2.21	2.14	2.18	2.65	3.11

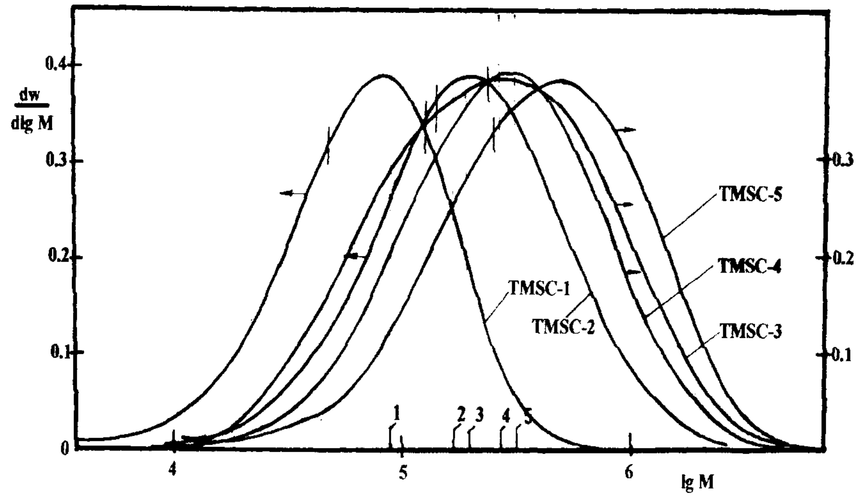

Figure 2. Differential distribution curves for the five TMSC samples.

The substitution degrees presented in Table 2, and denoted as DS (IR) were evaluated by this procedure. The substitution degree determined by chemical analysis of silicon content, and denoted as DS(CH), is also presented in Table 2.

Figure 2 shows the differential distribution curves obtained by GPC for the TMSC samples in o-xylene.

As can be seen, the studied samples exhibited a relatively high polydispersity. From GPC data, the number average molecular weights (M_n), weight

TABLE 3. Number Average Molecular Weights (M_n) and the Second Virial Coefficient (A_2) for the TMSC Samples, at 20°C

SAMPLE	TMSC-1	TMSC-2	TMSC-3	TMSC-4	TMSC-5
M_n , $g.mol^{-1}$	92,500	172,900	200,000	271,000	357,000
$10^4.A_2$, $m^3mol.kg^{-2}$	3.37	5.47	7.55	7.52	6.60
M_v(calc), $g.mol^{-1}$	73,800	133,400	160,700	199,700	249,000

average molecular weights (M_w), the viscometric average molecular weights (M_v), and the polydispersity index (Ip) were also obtained. These results are listed in Table 2.

Measurements

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 CR-1 type [22] which exhibit a 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 π/c - c coordinates.

The viscometric measurements were carried out on an Ubbelohde type viscometer with internal dilution, equipped with a sintered glass filter. The temperature was kept constant with a precision of ± 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.

RESULTS AND DISCUSSION

The osmometric results, obtained in o-xylene at 20°C, are presented in Table 3.

The last line of Table 3 shows the viscometric average molecular weights, calculated on the basis of the molecular weights of the support celluloses (from

Table 1), taking into account the substitution degree of the TMSC samples determined by chemical method. It can be observed that the experimental molecular weights are with 20-30% greater than those calculated, although, considering the theory, they should be smaller ($M_n<M_v$). This can be explained as a result of the fact that during the repeated purification, the fractions with very small molecular weights, have been removed from the samples.

Another observation which can be made, is the fact that osmometric number average molecular weights have 30-90% higher values than those determined by GPC. This is due perhaps to the fact that the GPC apparatus calibration was made with standard polystyrene, which is a flexible chain polymer

Although the values of the second virial coefficient are stated in the common limits encountered for the nonpolar polymers in good solvents, an abnormal dependence $A_2 = f(M_n)$ was found, since A_2 increases with M_n instead of a decreasing dependence. Such abnormal behavior was also found for the other cellulose derivatives and for rigid polymers, and have been attributed to the fact that the theories of the flexible polymers are not applicable to the polymers having a rodlike structure in solution.

The specific viscosities of the TMSC dilute solutions in different solvents are highly dependent on the concentration, so that the Huggins curves, $\frac{\eta_{sp}}{c} = f(c)$, present high and increasing slopes; the Huggins constant values being approximately ten times higher than that for usual polymers. Under these conditions, the Huggins, Fuoss-Mead or Martin equations for the limiting viscosity number evaluation results in a high number of errors, and are not applicable for this polymer. For this reason, in order to determine the limiting viscosity number, the Fedors equation [23] was applied:

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

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 4. First of all, 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.

TABLE 4. Limiting Viscosity Number [η]in dl.g^{-1}, TMSC Samples in Different Solvents, at 20°C

SAMPLE SOLVENT	TMSC-1	TMSC-2	TMSC-3	TMSC-4	TMSC-5
CHLOROFORM	1.343	3.222	4.898	6.162	8.120
1,1,1TRICHLORETHANE	1.526	4.400	5.546	6.530	9.314
o-XYLENE	1.256	4.009	4.993	6.367	8.315

TABLE 5. The Mark-Houwink-Sakurada Equation Coefficients, at 20°C

SOLVENT	10^7.K (dl.g^{-1})	a
CHLOROFORM	2.659	1.353
1,1,1-TRICHLOROETHANE	5.010	1.316
o-XYLENE	1.635	1.399

By using the experimental number average molecular weights and limiting viscosity numbers from Table 4, the coefficients **K** and **a**, of the Mark-Houwink-Sakurada equation, $[\eta] = K.M^a$, were calculated. The values of these coefficients are presented in Table 5.

For many cellulose derivatives, the values of the "a" exponent of the Mark-Houwink-Sakurada equation are very close to the unity [24-26], this is due to the strong 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 as 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 [27], cellulose xanthate in aqueous solution of glycerine [28], for some polypeptides in different solvents [29], etc. [30, 31].

TABLE 6. 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 7. 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

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 rodlike 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 6 and 7.

Although the dynamic viscosities of the TMSC in xylene present a pronounced decrease with the temperature, the decreasing of the limiting viscosity

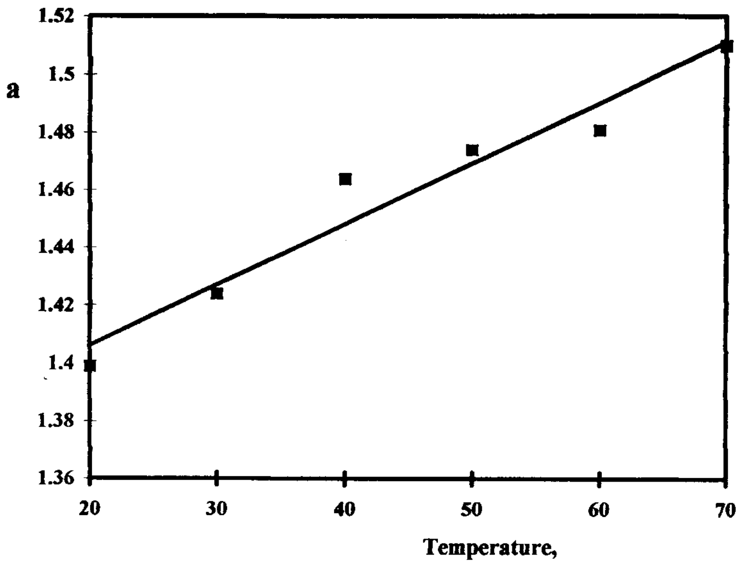

Figure 3. Temperature dependence of the exponent "a" from M-H-S equation.

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 a molecular weight of the polymer. Based on the data from Table 6, and using the experimental number average molecular weights, the M-H-S equation coefficients were calculated, and obtained values are shown in Table 7.

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 (Figure 3). A linear regression analysis gives:

$$a = 1.364 \pm 0.0021 . t \qquad (2)$$

In accordance with the very high values of the exponent "a", the pre-exponential 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 which appears at any type of equation expressing an exponential dependence between two quantities.

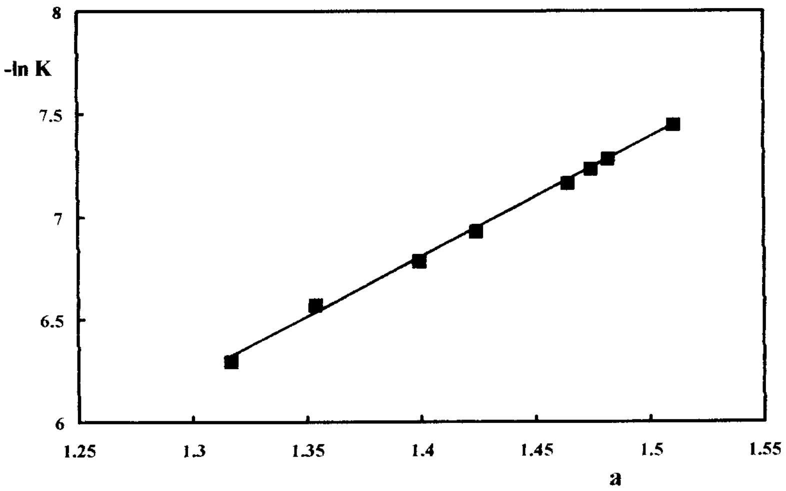

Figure 4. Graphical representation of the compensation effect for the two coefficients of the M-H-S equation.

In the case of the M-H-S equation, a correlation of the type: log K = A + B.a 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 4 , in log **K** - **a** coordinates.

This figure clearly shows that the equation of compensation agrees with the experimental data. With these data, the following equation of compensation is obtained:

$$\log \mathbf{K} = 1.408 - 5.857\ \mathbf{a}$$

CONCLUSION

The coupling of the trimethylsilyl groups to the cellulosic chains can be realized, within a 95% substitution degree, by the 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 till the complete elimination of the hydrochloric acid and pyridine hydrochloride.

The TMSC derivatives are very rigid polymers, having a rodlike structure in chloroform, 1,1,1-trichloroethane and o-xylene; in these solvents, the exponent values in the Mark-Houwink-Sakurada equation being higher than 1.0 In o-xylene, this rigidity increases with the temperature increase.

For the **K** and **a** , coefficients of the M-H-S equation obtained in the three solvents and at different temperatures, a compensation relation is in agreement

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.

REFERENCES

[1] J. F. Klebe, *J. Polym. Sci., B, 2,* 1097 (1964).
[2] S. Murahoshy, S. Nozakura, and M. Sumi, *J. Polymer Sci., B, 3*, 245 (1965).
[3] J. F. Klebe and H. L.Finkbeiner, *J. Polymer Sci., A1, 7,* 1947 (1969).
[4] H. A. Schuiten, J. W. Weaver, and J. D. Reid, U.S. Pat. 2,562,955 (1951).
[5] G. R. Cooper, K. R. Sandberg, and J. F. Hink, *J. Appl. Polym. Sci., 26*, 3836 (1981).
[6] S. Takahashi, T. Fujimoto, T. Miyamoto, and H. Inagaki, *J. Polym Sci., Part A, Polymer Chem., 25*, 987 (1987).
[7] U. Schuldt, B. Philipp, D. Klemm, A. Stein, H. Jencke, and I. Nehls, *Papier* (Darmstadt), *48 (1)*, 3 (1994).
[8] C. McCormick and P. A. Callais, *Polymer, 28*, 2317 (1987).
[9] W. Schempp, Th. Krause, U. Seifried, and A. Koura, *Papier, 35,* 547 (1981).
[10] D. Klemm and A. Stein, *Journ. Mac. Sci.- Pure & Appl. Chem., A32, 6* , 899 (1995).
[11] I. Nagy, A. Borbely-Kuszmann, K. Becker-Palossy, and E. Zimonyi-Hegedus, *Hung. Period Polytech., Chem. Eng., 18(1)*, 91 (1974).
[12] M. Schaub, G. Wenz, G. Wegner, A. Stein, and D. Klemm, *Adv. Mater., 5,* 919 (1993).
[13] V. Buchholz, P. Adler, M. Baecker, W Hoelle, A. Simon, and G. Wegner, *Langmuir, 13 (12)*, 3206 (1997).
[14] P. Weigel, J. Gensrich, and W. Wagenknecht, *Papier* (Darmstadt), *56 (9)* 483 (1996).
[15] T. Fukada, *Macromolecules, 9*, 28 (1995).
[16] S. K. Kim, S. J. Hong, and T. J. Kang, *Cellulose*, 361 (1990).

[17] R. W. Lenz, *Macromol. Chem. Rapid Comm., 4*, 49 (1983).
[18] P. Keller, *Macromol. Chem. Rapid Comm., 6,* 255 (1985).
[19] D. Bontea and T. Rusu, RO. Pat. 109081 (1996).
[20] R. J. C. Cummerbirch and W. G. Harald, *J. Textile Inst., 49* , 644, 679 (1958); RO- STAS 6485 (1976).
[21] J. Haslam and H.A. Willis, *Identification and Analysis of Plastics*, London, Ilife Books, 1965, p. 253; RO- STAS 167/4 (1970).
[22] N. Aelenei, *Eur. Polym. J, 17,* 533 (1981).
[23] R. F. Fedors, *Polymer J., 20,* 225 (1979).
[24] M. L. Hunt, S. Newman, H. H. Sheraga, and P. J. Flory, *J. Phys. Chem., 60,* 1278 (1956).
[25] H. J. Phylips and C. F. Bjork, *J. Polym. Sci., 6*, 549 (1951).
[26] G. Sitoramaian and D. A. Goring, *J. Polym. Sci., 58,* 1107 (1962).
[27] W. Taite, J. M. Vetter, J. M. Swanson, and P. Debye, *J. Polym. Sci., 7,* 261 (1951).
[28] W. Burchard, *Makromo.l Chem., 57*, 67 (1963).
[29] K. Okita, A. Teramoto, and M. Gujita, *Biopolymers, 9*, 717 (1970).
[30] A. J. Burr and L. J. Fetters, *Macromolecules, 6,* 876 (1973).
[31] H. Murakomi, T. Norisuye, and H. Fujita, *Macromolecules, 13*, 345 (1980).

Received February 10, 1998
Revision received April 10, 1998