The Rheology of Silylcellulosic Derivatives Solutions Used for Tissue Regeneration

II. Triphenylsilylcellulose

DANUT BONTEA[1], ION SANDU[2, 3], CONSTANTIN IORDACHE[4], AMALIA MARIA BONTEA[5], IOAN GABRIEL SANDU[3, 6]*, ALINA LUCA[4]
[1] „P. Poni" Institute of Macromolecular Chemistry, 41A Aleea Grigore Ghica Vodă, 700487, Iaşi, Romania
[2] „Al.I.Cuza" University, ARHEOINVEST Interdisciplinary Platform, 22 Blvd. Carol I, 700506, Iaşi, Romania
[3] Romanian Inventors Forum, 3 Sf. Petru Movilă, Bl. L11, Sc.A, III/3, 700089, Iaşi, Romania
[4] „Gr.T. Popa" University of Medicine and Pharmacy, 16 Universităţii Str., 700115, Iaşi, Romania
[5] „Sf. Maria" Clinical Pediatric Hospital, 62 Vasile Lupu Str., 700309, Iaşi, Romania
[6] „Gheorghe Asachi" Technical University of Iaşi, Faculty of Materials Science and Engineering, 67 Blvd. D. Mangeron, 700050, Iaşi, Romania

We studied five samples of cellulose with various polymerization degrees, which were employed for the preparation of triphenylsilylcellulosic derivatives, by the reaction of cellulose with triphenylchlorosylan, in the presence of pyridine and dimethylformamide. The triphenylsilylcellulose samples were studied in solution, through Osmometry, Viscosimetry and Permeable Gel Chromatography techniques. Their behaviour in solution was studied at different temperatures, with chloroform, o-xylene and 1,1,1-trichlorethane as solvents. The Permeable Gel Chromatography studies indicated a relative polydispersity of the triphenylsilylcellulose samples, varying between 2 and 3. In previous studies, the triphenylsilylcellulose was characterized in solutions of o-xylene, chloroform and 1,1,1-trichloroethan, at 30°C, and in o-xylene, too, at a temperature range between 30 and 70°C. The characterization of its behavior in o-xylene was performed at 30°C, for triphenylsilylcellulose, while intrinsic viscosity was determined as a function of molar mass weight.

Keywords: Triphenylsilylcellulose, Osmometry, Viscometry, Intrinsic viscosity

As known, cellulose contains free hydroxyl groups in extremely high amounts, which makes it insoluble in water and organic solvents. Substitution of the hydroxyl groups with triphenylsilyl radicals modifies the properties of this natural polymer, especially its solubility in non-polar organic solvents [1-5].

Silylcellulosic derivatives have various utilizations in which partially-substituted products are involved, such as: obtaining of fibers [6-7], nanofibers [8-11], films [12], liquid crystals [13] and precursors for mixed compounds [14-16].

In a previous note [17], we performed a similar study on trimethyl-silylcellulose, which is used for healing open wounds at the tegument level.

The properties of cellulose regenerated from triphenylsilylcellulose and the liquid crystal character of the triphenylsilylcellulose depend on the size and flexibility of the molecular chain in various solvents [13].

The above – cited studies make mention of two aspects, namely: the high value of relative viscosity and the extremely high rigidity of the macromolecular chain, occurring as a rigid helix. These characteristics have a significant influence on the properties and behaviour of such derivatives in solution.

The rheological behaviour of triphenylsilylcellulose in solution is essential in establishing the optimum conditions for obtaining of yarns, fibers and foils of regenerated cellulose.

Experimental part

The silylation process was realized in heterogeneous medium (dimethylformamide and 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 the first part of the study), were used to obtain corresponding triphenylsilylcellulose derivatives (TPSC).

The activated and dried cellulose was suspended in a mixture of N,N-dimethylformamide and pyridine medium and pre-treated, at 60°C for 60 min, with triphenylclorosilane. Then, the temperature was raised up 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 minutes at 115-120°C. All operations were done under inert nitrogen atmosphere. The reaction medium was cooled to 60°C, while the TPSC was separated by precipitation with isopropanol p.a., washed with isopropanol and finally washed-up with acetone. The samples were purified by successive precipitations with isopropanol from benzene and chloroform solutions. The synthesis conditions and the characteristics of these samples have been discussed elsewhere [16].

The TPSC samples were characterized both in terms of degree of substitution and of polydispersity.

The substitution degree is determined by the method of acid decomposition, as evidenced by the IR spectra plotted with a SPECORD M 90 device, Carl Zeiss Jena, with KBr pellets.

A PL-EMD 950-type Gel Permeation Chromatograph (GPC) was used for polydispersity measurements. All measurements were carried out at 25°C, with o-xylene as eluent, at a flow rate of 0.5 mL/min. The apparatus was calibrated according to narrow distribution polystyrene standards.

Viscosity of the TPSC solutions was measured on an Ubbelohde-type Dilution Viscometer introduced into a

---

* email: gisandu@yahoo.com; Tel.: 0040742.505160; 0040232.227627

thermostating bath with controlled temperature (0.02°C variation).

Viscosity was measured with solutions of 1,1,1-trichloroethan and o-xylene, in chloroform.

Variation of viscosity as a function of temperature was performed in o-xylene, at a temperature range between 30-70°C.

The dynamic viscosities were calculated with relation:

$$\eta = \eta_0 \frac{\tau \cdot \rho}{\tau_0 \rho_0} \qquad (1)$$

where:

η_0 is the dynamic viscosity of o-xylene;

τ_0 and t - flow times for pure solvent and solution;

ρ_0 and ρ - densities of pure solvent and solution at the same temperature and concentration values.

The density of both solvent and solution was determined gravimetrically, at 30-70°C temperature interval.

The molecular weight of triphenylsilylcellulose was determined with a H–P Automatic Osmometer, Model 502, with CR-type regenerated cellulose membranes.

Results and discussions

Determination of the intrinsic viscosity index $[\eta]$ for silylcellulosic derivatives was performed in three solvents of various polarity (1,1,1-trichloroethane > chloroform > o-xylene), for studying the influence of solvent nature on the viscosity of the silylcellulosic derivative.

For each sample, osmotic pressure was measured for five different concentrations, ranging between 0.2 and 1.0 g/dL, obtained by diluting a 1.0 g/dL concentrated solution. Within the concentration range applied, the (η_{sp}/c) *versus* **c** plots is linear (fig.1) for all the TPSC samples used. The average molecular weights (M_n) and the second virial coefficients (A_2) were evaluated with the straight line coefficients, using the least squares method.

The characteristics of the five triphenylsilylcellulose samples under analysis are listed in table 1.

Application of the Huggins equations, frequently employed for flexible polymers, did not permit linear representations in the corresponding coordinates $(h_{sp}/c = f(c))$.

Figure 1 plots the ς_{sp}/c curves according to *Huggins equation*, for triphenylsilylcellulose solutions with TPSC-1, as a function of the temperature.

The Fedors equation, specific for semiflexible or rigid polymers, was applied, leading to linear extrapolation in $f(h_{sp}/c)$ coordinates for silylcellulosic derivatives, in three solvents, at 30°C, and also in o-xylene, at various temperatures, ranging between 30 and 70°C. The Fedors equation takes the form:

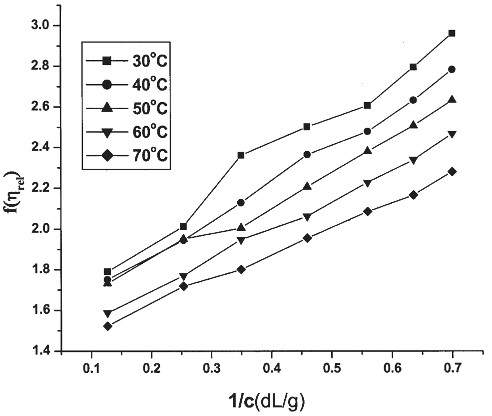

Fig. 1. Huggins equation for TPSC in o-xylene, at various temperatures. ■ 30°C, • 40°C, ▲ 50°C, ▼ 60°C, ♦70°C

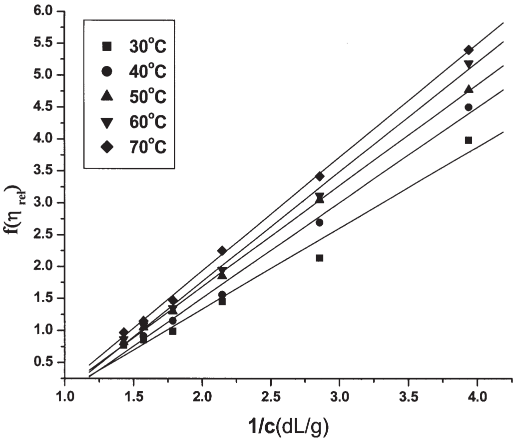

Fig. 2. Fedors curves for the TPSC sample in o-xylene, at various temperatures. ■ 30°C, • 40°C, ▲ 50°C, ▼ 60°C, ♦70°C

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

where:

η_r - relative viscosity;

c - solution concentration;

c_m - concentration of maximum packing;

$[\eta]$ - index of intrinsic viscosity.

The curves plotted according to Fedors equation for the index of intrinsic viscosity of the solutions of silylcellulosic derivatives are presented versus the results obtained with Huggins equation.

Figures 2 and 3 show the curves corresponding to Fedors equation for triphenylsilylcellulose, in o-xylene, at 30°C, and also the Fedors curves for the TPSC samples in o-xylene, at various temperatures.

Table 1

CHARACTERISTICS OF THE TRIPHENYLSILYLCELLULOSE SAMPLES IN O-XYLENE, 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
DS(CH)	2.85	2.84	2.82	2.85	2.85
DS(IR)	2.56	2.75	2.60	2.70	2.58
$[\eta]$, dL/g	0.911	1.344	1.616	2.106	2.509
$I_P(M_W/M_n)$	2.21	2.14	2.18	2.65	3.11

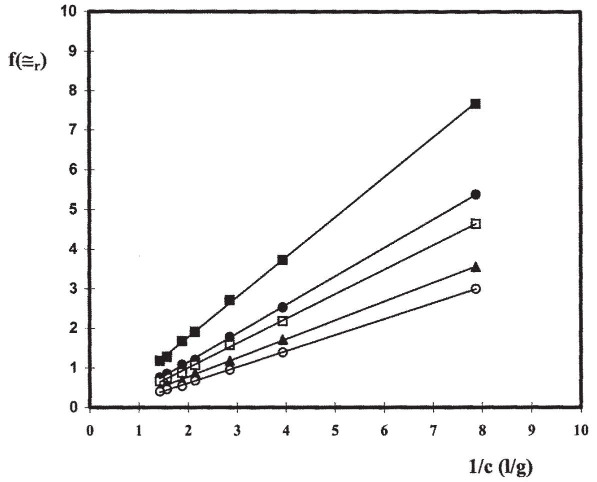

Fig. 3. Fedors type curves for the TPSC samples in o-xylene at 30°C. ■– TPSC-1 (Mn = 128200 g/mol); • – TPSC-2 (Mn = 152400 g/mol); □– TPSC-3 (Mn = 167900 g/mol); ▲ – TPSC-4 (Mn = 188000 g/mol); o – TPSC-5 (Mn = 207400 g/mol)

Table 2

INTRINSIC VISCOSITY INDEX [η] FOR TRIPHENYLSILYLCELLULOSE IN VARIOUS SOLVENTS, AT 30°C

Sample / Solvent	**TPSC$_1$**	**TPSC$_2$**	**TPSC$_3$**	**TPSC$_4$**	**TPSC$_5$**
chloroform	0.886	1.301	1.611	1.986	2.518
1,1,1-trichloroethane	0.839	1.255	1.553	1.941	2.401
o-xylene	0.911	1.344	1.616	2.106	2.509

Table 3

INTRINSIC VISCOSITY INDEX [η] FOR TRIPHENYLSILYLCELLULOSE IN O-XYLENE, AS A FUNCTION OF TEMPERATURE

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

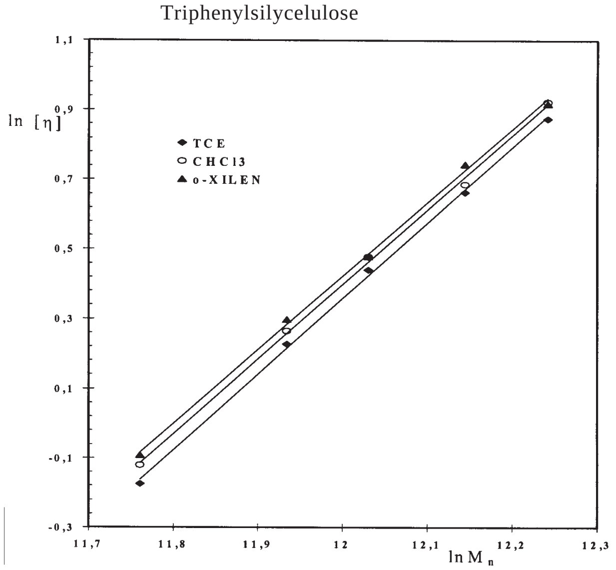

Fig. 4. Dependence [η] of molar weight (M_n) for TPSC solutions in various solvents, at 30°C. • 1,1,1-trichloroethane,■ chloroform, ▲ o-xylene

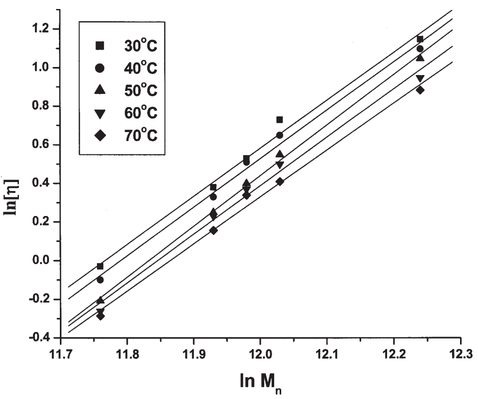

Fig. 5. Dependence of intrinsic viscosity index, [η], on molar weight (M_n), at various temperatures, for TPSC. ■ 30°C, • 40°C, ▲ 50°C, ▼ 60°C, ♦ 70°C.

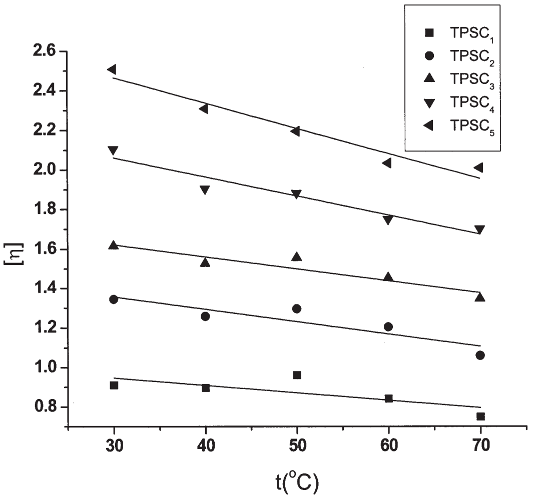

Fig. 6. Dependence of intrinsic viscosity index, [η], on temperature for triphenylsilylcellulose samples. ■ $TPSC_1$, ● $TPSC_2$, ▲$TPSC_3$, ▼ $TPSC_4$, ♦$TPSC_5$.

The values obtained for the index of intrinsic viscosity of the triphenylsilylcellulose solutions in various solvents and at different temperatures are listed in tables 2 and 3.

The graphical representation of the dependence of intrinsic viscosity [η] on the average molar number (M_n) for TMSC in various solvents is plotted in figure 4.

The index of intrinsic viscosity of the TPSC samples in trichloroethane is the highest, comparatively with the viscosity values recorded in chloroform and o-xylene (the two curves get intersected), as a result of the different polarity of the solvents employed (1,1,1-trichloroethane > chloroform > o-xylene).

The dependence of intrinsic viscosity, η, on the average molar number weight (M_n) at different temperatures up to 70°C is plotted graphically in the figure 5, while the intrinsic viscosity, η, in the case of the five samples of triphenylsilylcellulose in o-xylene, depending of temperature, is plotted graphically in the figure 6.

The dinamic viscosity number [η] of TPSC in o-xylene evidences an intense linear decrease with temperature, respectively decrease the limit number of viscosity.

Conclusions

Coupling of the triphenylsilyl groups to the cellulosic chains can be realized, with a 95% degree of substitution, by the reaction between activated celluloses and triphenylchlorosilane in DMF and o-xylene/pyridine medium, at 120°C, under inert atmosphere. The stability of the obtained samples can be improved by successive solving/precipitating operations until complete elimination of the hydrochloric acid.

The viscosity of triphenylsilylcellulose solutions markedly decreased with the increase of temperature, which permits obtaining of concentrated solutions for high triphenylsilylcellulose molar weights, to be further employed in the production of highly resistant fibers and yarns of regenerated cellulose.

Obtaining of yarns, fibers and leaves of regenerated cellulose from triphenylsilylcellulose derivatives avoids formation of reaction subproducts, once the hexaphenyldisilyloxane formed through precipitation in an acid bath may be transformed into hexaphenyldisilazane and triphenylchlorosilan, to be further reintroduced into the process

Obtaining of triphenylsilylcellulose derivatives with partial substitution degrees (DS about 2.8) permits substitution of the free hydroxyl groups with various reaction agents, possessing special properties.

References

1.KLEBE, J.F., FINKBEINER, H.L., J. Polym.Sci. A1, **7**, 1969, p.1947.

2.NAGY, J., BORBÉLY, A., BECKER,K., Die Makromolekulare Chemie, **165**, 1973, p. 335.

3.STEIN, A., KLEMM, D., Makcromol.Chem., Rapid Commun., **9,** (8), 1988, p. 569.

4.SCHULDT, U., Philipp, B., Klemm, D., Stein, A., Jannke, H., Nehls, I., Papier (Darmstadt), **48**, (1), 1994, p. 3.

5.GREBER, G., PASCHINGER, O., Papier (Darmstadt), **35** , (12), 1981, p. 547.

6.COOPER, G.K., SANDBERG, K.R., HINCK, J.F., J.Appl.Polym.Sci., **26**, (11), 1981, p. 3827.

7.WEIGEL, P., GENSRICH, J., WAGENKNECHT, W., Papier (Darmstadt), **50**, (9), 1996, p. 483.

8.TOFOLEANU, F., BALAU-MÎNDRU, T., BRÎNZA, F., SULIŢANU, N., SANDU, I.G., RAILEANU, D., FLORIŞTEAN,V., HAGIU, B.A., IONESCU, C., SANDU, I., TURA, V., Silver Nanoparticles: Properties, Characterization and Applications, Series: Nanotechnology Science and Technology (Editors: Audrey E. Welles), (ISBN 978-1-61728-062-7), Nova Science Publishers, 2010.

9.TURA, V., TOFOLEANU, F., MANGALAGM, I., MINDRU, T. BALAU, BRINZA, F., SULITANU, N., SANDU, I., RAILEANU, I.D., IONESCU, C., Journal of Optoelectronics and Advanced Materials, Bucharest, **10,** (12), 2008, p.3505.

10.TOFOLEANU, F., MINDRU, T. BALAU, BRINZA, F., SULITANU, N., SANDU, I.G., RAILEANU, D., FLORISTEAN, V., HAGIU, B.A., IONESCU, C., SANDU, I.,TURA, V., Journal of Optoelectronics and Advanced Materials, Bucharest, **10**, (12), 2008, p. 3512.

11.SANDU, I., VRÎNCEANU, N., COMAN, D., Rev. Chim., Bucharest, **60**, no. 9, 2009, p. 944.

12.KLEMM, D., STEIN, A., J.M.S.-Pure Appl.Chem., A32, **4,** 1995, p. 899.

13.KIM, S.K., HONG, S.I., KANG, T.J., Cellulose, **6**, 1990, p. 361.

14.KLEMM, D., SCHNABELRAUCH, M., STEIN, A., NIEMANN, M., RITTER, H., Makromol. Chem., **191** (12), (1990), 2985-2991.

15.KLEMM, D., STEIN, A., ERLER, U., WAGENKNECHT, W., NEHLS, I., PHILIPP, B., New Precedures for regioselective synthesis and modification of trialkylsilylcelluloses**,** in: Cellulosics: Materials for Selective Separation and Other Technologies (Kennedy, J.F., Phillips, G.O., Williams P.A. Eds.); E. Horwood Ltd., New York, London, Toronto, Sydney, Tokyo, Singapore, 1993, p. 221.

16.BONTEA, D., CARUNTU, G., AELENEI, N., J. Macromol. Sci.- Pure Appl. Chem. A37, **4**, 2000, p. 395.

17.BONTEA, D., IORDACHE, C., BONTEA, A.-M., SANDU, I., LUCA, A., SANDU, I.G., Rev. Chim. (Bucharest), **62**, no. 12, 2011, p. 1161

Manuscript received: 24.05.2011