Solution Studies of Cellulose Tricarbanilates Obtained in Homogeneous Phase

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SYNOPSIS

A number of cellulose samples was submitted to homogeneous phase carbanilation in dimethylacetamide/LiCl. The process is quantitative and leads to a completely substituted product, as verified by elemental analysis and UV spectroscopy. Tricarbanilated samples were characterized by viscometric and light-scattering measurements in tetrahydrofuran. Our results are in good agreement with those reported in the literature, concerning products obtained in the heterogeneous phase. Gel permeation chromatography was performed for evaluating the molecular weight distribution of the parent cellulose, using both universal and linear calibration. The chromatographic technique is not adequate for samples exhibiting a high degree of polymerization. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Determination of the molecular weight distribution (MWD) of cellulose samples is of great interest both for basic studies and for industrial applications. This characterization is difficult, due to the very limited number of solvents available for the polysaccharide.

A suitable method to obtain the MWD for a cellulose sample consists of chemical modifications of the macromolecule yielding derivatives with better solubility features. Such modifications must be quantitative and not depolymerizing, the product being then dissolved into an appropriate solvent and loaded onto a high-performance gel permeation chromatography (HPGPC) column.

Among possible compounds, cellulose tricarbanilates (CTC) are derivatives of choice, because of their stability in comparison with nitrates and their solubility in common organic solvents (acetone, tetrahydrofuran, dimethylacetamide, dimethylformamide, dimethylsulfoxide, pyridine). In addition, columns suitable for fractionating polymers at high

MW and treated with tetrahydrofuran (THF), a solvent for carbanilates, are commercially available.

As reported in the literature, carbanilation is usually carried out in the heterogeneous phase, using pyridine, dimethylsulfoxide (DMSO), or dimethylformamide (DMF) as solvents.[1–5] According to different authors, temperatures reached during the reaction range between 60 and 100°C, and reaction times last from 5 to 168 h. Some cellulose samples, e.g., regenerated celluloses, are poorly reactive to phenylisocianate in pyridine and must be activated (treatment with methylamine, water, or ammonia) prior to reaction.

We have now developed a method for cellulose carbanilation in the homogeneous phase using dimethylacetamide (DMAc)/LiCl as the solvent. Polysaccharide derivatization in the homogeneous phase allows a number of advantages, including high reaction rates and yields under relatively mild conditions, limited depolymerization, regularity in the substitution pattern, and possible selectivity.

It is worth recalling that a mixture of DMAc and LiCl at a salt concentration (c_s) ranging from 3 to 15% has been utilized as a solvent system for cellulose,[6] chitin,[7] and aromatic polyamides. Dissolution of cellulose requires a preliminary activation of the polysaccharide, with fiber swelling and pore

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opening, so as to allow solvent solvent inbibition. The solubilization process involves the interaction of one LiCl molecule per group containing labile protons, while the intramolecular hydrogen bond between OH-3 and the ring oxygen of the neighboring unit, which is responsible for the conformational rigidity, remains unaffected.

The solubilization process does not cause chemical modification or depolymerization. Cellulose was derivatized[8,9] in the DMAc/LiCl system to give esters, carbamates, sulfonates, and ethers.

EXPERIMENTAL

Materials

Several cellulose samples obtained from various sources (wood W, straw S, cotton linters L) were studied. The pretreatment and isolation of samples are reported in Table I. Polystyrene standards with molecular weights (M_p) in the range $5 \times 10^3 - 4 \times 10^6$ were obtained from Polymer Laboratories Ltd. (U.K.); the M_w/M_n values were ≤ 1.06.

Carbanilation

A weighed amount of DMAc (15-20 mL) was added to a weighed amount of cellulose ($\sim$ 200 mg). The

Table I Isolation and Pretreatment of Samples

Cellulose Sample	Isolation and Pretreatment
W_1	Prehydrolyzed sulfate pulp
W_2	Mixed poplar hard woods, steam exploded[10] (6 min, 230°C). Washed with water, ethanol, and acetone. Sodium chlorite pH 4.5 at room temperature for 1 week
W_3	Mixed poplar hard woods, steam exploded[10] (4 min, 230°C). Washed with water, ethanol, and acetone. Sodium chlorite pH 4.5 at room temperature for 1 week
W_4	Sulfate pulp
W_5	Regenerated cellulose II, viscose process
W_6	Sulfite pulp
S_1	Wheat straw, steam exploded (3 min, 220°C). Washed with water, ethanol, and acetone. Sodium chlorite pH 4.5 at room temperature for 48 h, KOH 2%
L_1	Microcrystalline cellulose (Avicel), obtained by hydrolysis of cotton linters
L_2	Cotton linters

mixture was heated to the reflux temperature for 20-30 min; after cooling to 100°C, a weighed amount of LiCl was added under stirring (c_s 5%).

For samples at a high degree of polymerization, we continued to stir the mixture at 70°C for 2 more h. A catalytic amount of pyridine (0.4-1 mL) and phenylisocianate (2 mL) were added and the derivatization reaction was carried out at 60-70°C for 2-3 h.

After cooling, dry methanol (2 mL) was added to eliminate excess phenylisocianate and the mixture was precipitated into methanol (MeOH) or into H_2O—MeOH (30 : 70). After washing with water, the cellulose carbanilates were dried under vacuum.

Preparation of Solutions

To prepare carbanilate solutions, stabilized THF (2,6-di-*tert*-butyl-*p*-cresol) was added to the material. After initial swelling, the suspension was stirred for several hours and filtered using PTFE 0.45 μm filters.

Intrinsic Viscosity [η]

Viscosities were determined using a multigradient suspended-level Ubbelohde viscometer at 25.0 $\pm$ 0.1°C with THF flow times of $\sim$ 60 s. Relative viscosities ranged between 1.1 and 1.6. Dilutions were made directly in the viscometer. Intrinsic viscosity data were calculated by the Huggins equation.[11]

Light Scattering (LS)

These measurements were performed in THF at 20°C using a Sofica Model 42000 photometer with cylindrical cells immersed in toluene. Nonpolarized laser light (633 nm) was used; scattering angles (ϑ) ranged between 30° and 150°. A Rayleigh ratio R_{90} = 8.96 $\times$ 10^{-6} cm^{-1} was used for calibration of the instrument with benzene.[12] Solutions and solvents were clarified by centrifugation at 25,000 g for 3 h. The data were treated as previously reported.[13] The value of dn/dc for all carbanilates in THF, determined using a Milton Roy KMX-16 refractometer at λ = 633 nm, was 0.166 $\pm$ 0.005, according to the literature.[4]

Liquid Chromatography

HPGPC measurements were carried out using a Knauer HPLC pump, Type 6400, a Rheodyne injector, and a differential refractometer, Erma CR

**Table II Carbanilation Reaction for Cellulose
S_1: Sample Amount 15 mL, mol C_6H_5NCO/mol
OH = 5, Polymer Concentration 1.3%**

Pyridine	Temperature	Time	N%	ε_{235nm}	$[\eta]_{THF}$ (dL/g)
0.4 mL	80°C	3 h	8.0	42,700	3.0
No	80°C	3 h	8.1	46,400	3.1
0.4 mL	60°C	2 h	8.1	43,000	3.2
No	60°C	2 h	8.1	42,500	3.1

Inc. Model ERC-7512 (Japan). Occasionally, a UV detector (1806 Bio-Rad) was used and results were consistent with those obtained by differential refractometry.

Automated data acquisition and processing systems were handled through an ASEM Personal Computer DS 386E/20 (microprocessor 80386SX) provided with PCLALLS™ Software Package, LDC Analytical Inc. Commercially available Phenogel columns (Phenomenex, USA) containing cross-linked polystyrene packings were used. The total volume V_m for the system with three columns (300 × 7.8 mm), PHOOH 0445KO, PHOOH 0446KO, and PHOOH 0447KO, having pore sizes 10^4, 10^5, and 10^6 Å, respectively, was 34 mL, as estimated by the external standard toluene, V_0, was about 16 mL.

Stabilized THF was used as the eluent at a flow rate of 1 mL/min at room temperature. Polymer concentration (c_p) was 0.1% and the injected volume 100–150 μL. Average MW and MWD were determined by using both universal calibration and linear calibration methods, with a carbanilate sample having a broad MWD.[14]

RESULTS AND DISCUSSION

A number of cellulose samples were treated with DMAc/LiCl c_s 5%; all materials, except cotton lint-

ers, gave a clear solution at c_p 1.3%. No experiment has been carried out at higher concentration.

These solutions were submitted to viscometric and LS measurements before the derivatization process. As reported in the literature,[14] the determination of molecular parameters in underivatized samples is not always possible, as aggregated polymer species, and not only molecularly dispersed entities, may occur in dilute solutions. This is the case for Avicel sample (L_1), where association is present in the concentration range investigated and stable aggregates appear to persist at $c_p \to 0$.

Preparation of CTC was carried out by treatment of cellulose in DMAc/LiCl with phenylisocianate under milder conditions than those reported in the literature,[1-5] so as to avoid depolymerization of the polysaccharide chains. Further examination of the reaction conditions was carried out using cellulose from steam-exploded wheat straw S_1. The results (Table II) indicate that the chemical parameters of the products and the $[\eta]$ value do not vary with temperature and time of reaction. Moreover, the presence of pyridine is not essential.

Cotton linters cellulose (L_2) was modified at the same conditions used for cellulose materials fully soluble in DMAc/LiCl. By the time phenylisocianate was added, the whole material was solubilized. After precipitation and recovery, the product was soluble in THF and elemental analysis was consistent with a degree of substitution (DS) equal to 3.

The quantitative precipitation of the modified chains is very important to safely determine the MWD of cellulose from carbanilate samples. Wood et al.[3] suggested removing all solvents before HPGPC analysis. On the contrary, Evans et al.[4] recommended a H_2O—MeOH (30 : 70) mixture as a precipitant, to ensure recovery of the low MW fraction of CTC and to eliminate low molecular weight compounds formed in the derivatization reaction.

Table III Characteristics of CTC Obtained from Cellulose W_2 and L_2 at Different Experimental Conditions

Cellulose Sample	mol C_6H_5NCO/mol OH	Precipitant	Yield %	N%[a]	ε_{235nm}	$[\eta]_{THF}$ (dL/g)
W_2	5	MeOH	80	7.9	43,800	1.57
		H_2O—MeOH 30 : 70	85	8.0	41,500	0.91
L_2	15	MeOH	95	8.2	47,300	6.50
		H_2O—MeOH 30 : 70	>100	9.2	26,700	4.05

[a] Theoretical N% for DS 3 is 8.09.

Table IV   Analytical Data of CTC

Sample	N%	ε_{235nm}	Precipitant
W_1TC	8.1	46,600	MeOH
W_2TC	7.9	43,800	MeOH
W_3TC	8.0	44,050	MeOH
W_4TC	8.1	44,300	MeOH
W_5TC	8.1	43,500	H_2O—MeOH
W_6TC	8.1	43,000	H_2O—MeOH
S_1TC	8.1	46,400	H_2O—MeOH
L_1TC	8.3	45,600	H_2O—MeOH
L_2TC	8.4	46,000	H_2O—MeOH

As the recovery of CTC depends on the solvent power of the reaction mixture, we carried out the precipitation of carbanilates obtained in DMAc/LiCl both into MeOH and H_2O—MeOH (30 : 70). The products were characterized by elemental analysis, UV spectroscopy, and viscometric measurements in THF.

Since the byproducts formed in the reaction, N,N'-diphenylurea and phenylcarbamate[4] contain a larger percent amount of N, the results reported in Table III show that these products are almost absent in the W_2TC sample obtained using both precipitating media. The only difference is a higher value of $[\eta]$ for the sample precipitated into MeOH, probably due to a loss of a small fraction of low MW.

Consistent with this result, further treatment of the sample isolated with the H_2O—MeOH mixture, including solubilization in acetone and precipitation into water, yields a product having the same chemical and hydrodynamic features. This conclusion is not true in the presence of a large excess of phen-

ylisocianate used for carbanilation of the L_2 sample: Yield and chemical characteristics of the material obtained after H_2O—MeOH precipitation showed the presence of byproducts.

We are led to conclude that precipitation in the H_2O—MeOH mixture using a ratio (mol reagent/ mol OH) equal to $\sim$ 5 does not cause a change in the MWD of the parent cellulose with no presence of byproducts, while precipitation in MeOH gives much more homogeneous samples having lower polydispersity indexes M_w/M_n.

Nitrogen percent values and absorbance measurements at 235 nm for all carbanilates are reported in Table IV. These values are unaffected by the possible presence of pentosan dicarbanilates, the amount of which is not higher than 10%.

The LS and viscometric data of these compounds are summarized in Table V. Increasing $[\eta]$ follows up with an increasing weight-average MW (M_w) and the gyration radius (R_G), while the second virial coefficient (A_2) is decreasing.

Figure 1 shows a quantitative comparison with the literature data.[2,15] M_w values obtained by LS measurements are in good agreement with average viscometric values evaluated by viscometric measurements.

Elution patterns of S_1TC samples (Fig. 2), prepared at different conditions (see Table II), are very similar. DP_w and DP_n values, calculated by means of universal calibration, are reported in the same figure: They are in good agreement with DP_w values obtained via LS.

The different $[\eta]$ values for W_2TC samples isolated from the reaction mixture by precipitation with MeOH or with H_2O—MeOH (see Table III) are in agreement with the different elution patterns (Fig.

Table V   Intrinsic Viscosity and Light-scattering Data of CTC in THF

Sample	$A_2 \times 10^4$ (mol mL/g^2)	R_G (Å)	$[\eta]_{THF}$ (dL/g)	M_W (DP$_w$)^a
W_1TC	6	—	0.79	110,000 (212)
W_2TC	5	450	1.57	288,000 (555)
W_3TC	3	480	1.75	394,000 (759)
W_4TC	4	890	4.10	808,000 (1557)
W_5TC	5	480	1.20	210,000 (405)
W_6TC	4	810	3.67	764,000 (1427)
S_1TC	5	750	3.10	560,000 (1079)
L_1TC	8	—	0.62	90,000 (173)
L_2TC	3	980	6.65	1,300,000 (2505)

^{a} DP_w is equal to $M_w/519$, where 519 is the weight of the repeating unit of CTC.
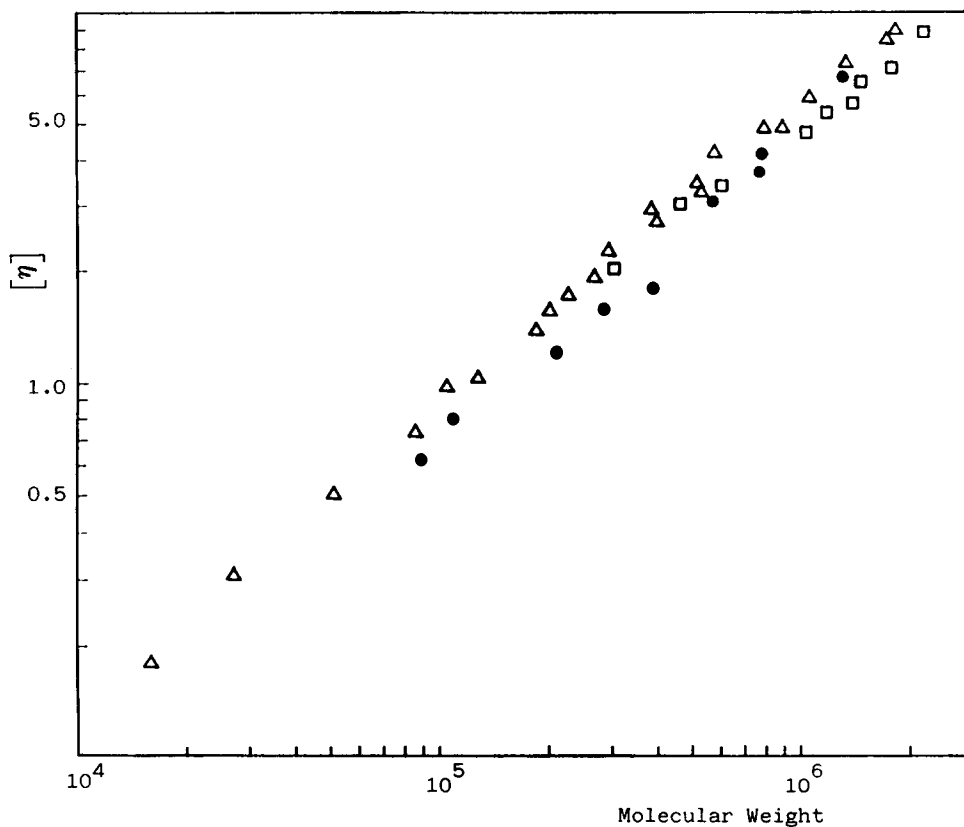
Figure 1 Logarithmic plot of $[\eta]$ vs. $(M_w)_{LS}$ for CTC of Table V (●) in comparison with some literature data [(△) Danhelka et al.[15]; (□) Cael et al.[2]].
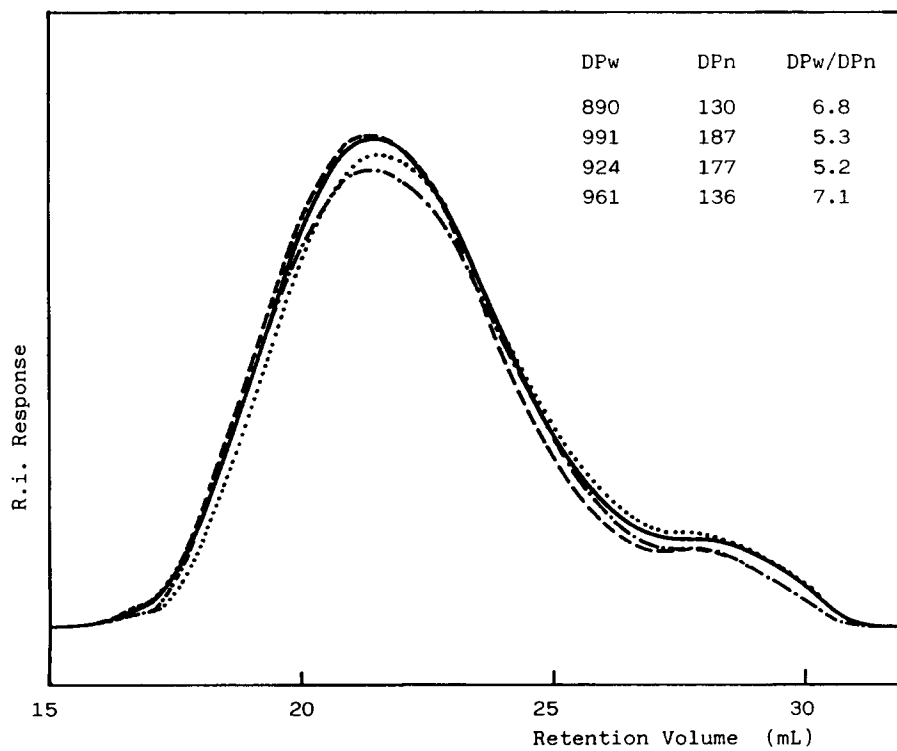

DPw	DPn	DPw/DPn
890	130	6.8
991	187	5.3
924	177	5.2
961	136	7.1

Figure 2 Elution patterns of tricarbanilates obtained from S_1 cellulose at different reaction conditions (see Table II).
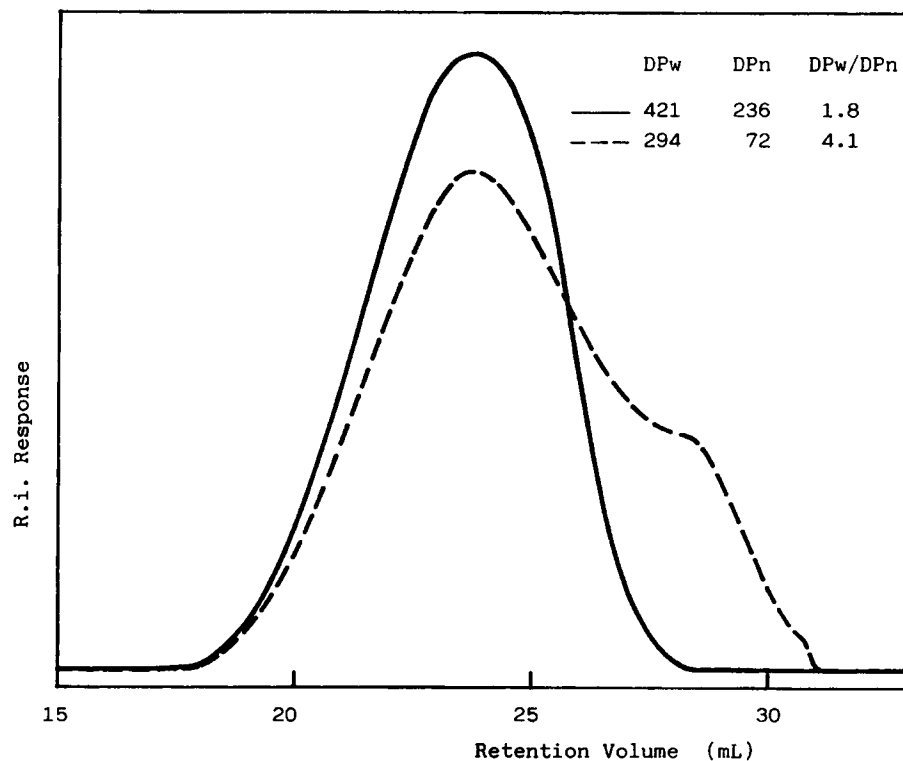
Figure 3   Elution patterns of W₂TC samples obtained by precipitation into (- - -) water–methanol mixture and into (——) methanol. DP$_w$ and DP$_n$ are calculated using universal calibration.
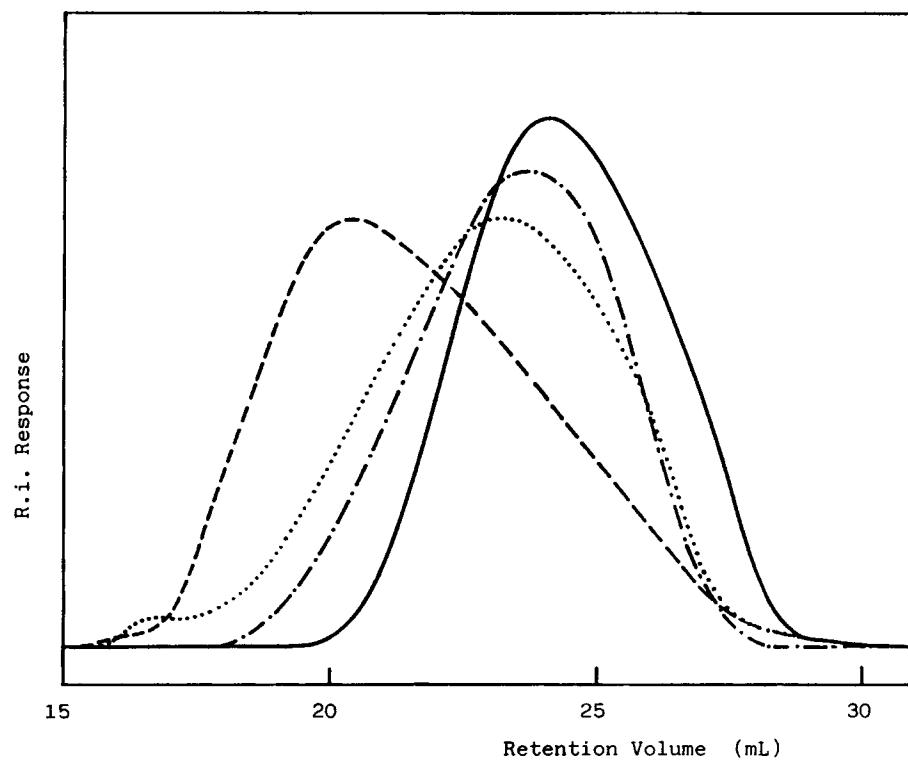

Figure 4   Elution patterns of samples precipitated with methanol: (——) W₁TC; (- · -) W₂TC; (· · · ·) W₃TC; (- - -) W₄TC.

**Table VI DP$_w$ Values from LS and
HPGPC Measurements**

Sample	Light Scattering DP$_w$	Universal Calibration		Linear Calibration	
		DP$_w$	DP$_n$	DP$_w$	DP$_n$
W$_1$TC	212	267	151	279	130
W$_2$TC	555	429	238	531	206
W$_3$TC	759	772	225	812	205
W$_4$TC	1557	1314	342	1603	436
W$_5$TC	405	369	140	412	129
W$_6$TC	1427	791	82	900	91
S$_1$TC	1079	991	187	1128	184
L$_1$TC	173	174	44	176	46
L$_2$TC	2505	997	156	1160	146

3). The sample with lower [η] value shows a higher polydispersity index, because the low MW fraction, eluted at high retention volume, is not soluble in H$_2$O—MeOH.

Elution patterns for samples obtained by precipitation into MeOH, i.e., with narrow distributions, are shown in Figure 4. The polymeric material was

eluted within the separation range of the chromatographic system and the resolution was good both at high and low retention volumes.

A shift of the maximum peak toward lower retention volumes is observed on increasing [η]. None of the elution patterns shows shoulders that could indicate the presence of low MW fractions.

The calibration curve (lg M_p vs. V_r) for CTC can be obtained from the calibration curve of standards having narrow MWD by applying the universal calibration technique, once the a and K viscometric parameters are known. In this work, the a and K values in THF were 0.72 and 1.12×10^{-4} for the polystyrene standards[3] and 0.84 and 4.3×10^{-5} for CTC,[2] respectively. DP$_w$ values for the samples of Figure 4 were calculated and compared to DP$_w$ values obtained by LS measurements (Table VI). The agreement is good and therefore it is reliable to evaluate DP$_n$ values and the corresponding distribution curves from HPGPC measurements.

Figure 5 shows elution patterns for CTC obtained by precipitation in MeOH—H$_2$O. As already shown, in this case, the low MW fractions are not lost and the MWD curve should correspond to the one of the parent cellulose. For L$_1$TC, L$_2$TC, and S$_1$TC sam-
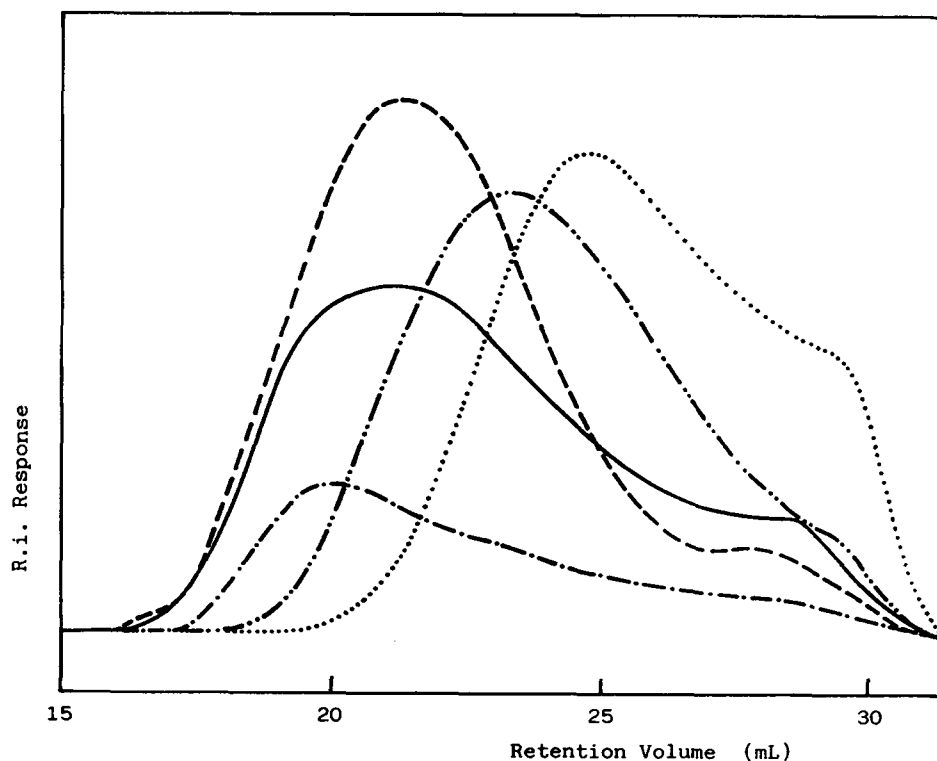

Figure 5 Elution patterns of samples precipitated with water–methanol mixture:
(– · · –) W$_5$TC; (——) W$_6$TC; (- - -) S$_1$TC; (· · · · · ·) L$_1$TC; (– · –) L$_2$TC.

ples, the material eluted at retention volumes exceeding 28 mL should represent low MW tricarbanilated cellulose, while for W_5TC and W_6TC, in the same range of the retention volume, pentosan dicarbanilates should be eluted along with the low MW cellulose tricarbanilated fraction.

All elution patterns of Figures 4 and 5 have been obtained at the same conditions of polymer concentration and injected volume. The equivalence of the elution pattern areas should reflect the equality of the injected polymer mass. This has been found for all samples in Figure 4 and for samples W_5TC, S_1TC, and L_1TC of Figure 5. The W_6TC elution pattern area is just 80% of what it is expected to be, while the L_2TC elution pattern area barely reaches 30% of the total. To prevent this apparent loss of material, the polymer concentration and injected volume were modified in a wide range, the pore size of filters was increased, the THF stabilizer was changed, and carbanilation was carried out under more drastic conditions. In no case could we modulate the anomalous elution pattern.

Table VI reports DP_w values calculated by means of universal calibration for elution patterns of Figure 5, compared with DP_w values obtained by LS measurements. For samples quantitatively eluted, the agreement is good: On the contrary for W_6TC and L_2TC, DP_w values obtained by universal calibration represent 40–50% of the values obtained by LS measurements.

Since the universal calibration procedure was found to be unsatisfactory,[4] especially at the high molecular weight end of the calibration curve, we tried to evaluate DP_w values by the linear calibration method, using as the standard the W_4TC sample, whose DP_n was calculated via LS.[16]

The results are reported in Table VI. Although all DP_w values are increased, again, a good agreement is found only for samples quantitatively eluted. Thus, on decreasing the chromatographic peak area, a dramatic drop in DP occurs. We have experimentally checked that this result is not due to depolymerization of the chains by shear or by oxidation processes.[4]

CONCLUSIONS

We submitted a number of cellulose samples from different sources and having different degrees of polymerization to homogeneous phase carbanilation. The method is performed in a 100 mg scale and requires an overall time of about 8 h for dissolution,

reaction, and isolation. Even in the presence of cellulose aggregates in DMAc/LiCl, the derivatization leads to molecularly dispersed species, as demonstrated by LS measurements on the carbanilated products. Swollen cellulose samples give trisubstituted derivatives at the same experimental conditions.

The H_2O—MeOH mixture precipitating medium does not cause a change in the MWD of the starting cellulose, without giving rise to the byproducts, while precipitation with MeOH gives much more homogeneous samples, with lower polydispersity. Viscometric and LS measurements allow an evaluation of the macromolecule persistence length as well as of the carbanilate–THF χ interaction parameter. They are found to be similar to those reported in the literature.[15] For most text samples, molecular weights determined by LS are in excellent agreement with those obtained by HPGPC, using both universal and linear calibration. For the two samples, characterized by high DP, the chromatographic data indicate lower molecular weights and exhibit dramatic decreases in the peak area. These effects cannot be eliminated by changing experimental conditions and cannot be due to depolymerization phenomena occurring during the chromatographic process.

At present, this result cannot be easily explained. Being responsible for the loss of material could be a preferential adsorption of high MW fractions by column packing matrix.

Chromatographic analysis of cellulose solutions in DMAc/LiCl[17] appears to be the only choice when using samples giving a nonquantitative chromatographic response. Of course, new problems may arise from partial solubility and/or possible aggregation of highly crystalline and high-DP celluloses like cotton linters.

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