

Molecular Weight Distribution of Cellulose as Its Tricarbanilate by High Performance Size Exclusion Chromatography

ROBERT EVANS, ROSS H. WEARNE, and ADRIAN F. A. WALLIS, *Division of Forestry and Forest Products, CSIRO, Private Bag 10, Clayton, Victoria 3168, Australia*

Synopsis

Cellulose tricarbanilates (CTCs) were prepared from a range of cellulose samples (cotton linters, wood pulps, Avicel, amorphous cellulose, and cellulose II) for molecular weight distribution (MWD) studies by high performance size exclusion chromatography (HPSEC). The HPSEC columns were calibrated using CTC standards with the aid of a microcomputer. CTCs were prepared by reaction of cellulose samples with phenylisocyanate in pyridine at 80°C. For some samples, e.g., cellulose II, activation with liquid ammonia and pyridine was necessary prior to reaction in pyridine. All samples tested were also derivatised in dimethylsulfoxide at 70°C, although for high molecular weight (MW) cellulose samples some MW reduction occurred in this solvent. Conditions were determined for optimum precipitation of CTCs in aqueous methanol without coprecipitation of low MW impurities.

INTRODUCTION

High performance size exclusion chromatography (HPSEC) of the tricarbanilate derivative of cellulose has emerged as a useful technique for obtaining the molecular weight distribution (MWD) of cellulose samples.¹⁻⁷ The advantages of cellulose tricarbanilate (CTC) for this purpose are that it is a stable derivative, and the fully trisubstituted product may be readily obtained. Cellulose samples of technical interest vary widely in molecular weight (MW); e.g., cotton (high MW) and some regenerated celluloses (low MW). For maximum utility, the HPSEC system should be capable of handling the entire MW range.

In most of the HPSEC studies on CTC, the columns have been calibrated by applying the universal calibration procedure to polystyrene standards.^{1,2,4,5} However, there are difficulties in this approach,⁶ and more direct calibration methods give better results. Both Lauriol et al.⁷ and Cael et al.³ have used on-line low angle laser light scattering (LALLS) detection to obtain a direct estimation of tricarbanilate MW in the HPSEC eluate. This is particularly useful for the high MW end of the calibration curve. Another method is to obtain the weight average degree of polymerisation (\bar{P}_w) of a series of CTCs, and to use these as calibration standards.⁶ The advantage of the latter approach is that an on-line LALLS detector is not required.

To obtain accurate MWD data for cellulose samples, it is of paramount importance that the MWD of the derivative reflects that of the parent cellulose. Thus the derivatization should proceed without degradation of the

cellulose chains, and after reaction the mixture should be added to a medium from which all the CTC precipitates.⁵ Schroeder and Haigh² found that reaction of cellulose with phenylisocyanate in pyridine at 80°C gave CTCs without degradation of the cellulose chains, whereas at the higher temperatures favoured by earlier workers (e.g., Ref. 1), loss of MW took place. The reaction is affected by choice of solvent; the reaction rate increases in the order dimethylformamide (DMF) < pyridine < dimethylsulfoxide (DMSO) when these solvents are used as reaction media.⁸

Some cellulose samples, e.g., regenerated celluloses, are unreactive to phenylisocyanate in pyridine, and must be activated before derivatization proceeds. Activation procedures which have been used include treatment with methylamine⁸ or water⁹ and regeneration from DMSO-paraformaldehyde solution³ prior to reaction with phenylisocyanate. Recent studies have shown that if the derivatization is carried out in DMSO at 70°C, all the cellulose samples tested including regenerated celluloses were reactive without the need for prior activation.^{6,7}

We have undertaken a comparative evaluation of methods for preparation of CTCs for MWD studies, and propose a standard procedure for their preparation, including a simple cellulose activation process for use prior to reaction with phenylisocyanate in pyridine. We also present an alternative method for the calibration of an HPSEC column set using a series of CTC standards.

EXPERIMENTAL

Materials and Analytical Methods

Cellulose samples used were bleached cotton linters (99.3% α -cellulose), 10 hydrolyzed cotton linters, Avicel PH101, bleached *Pinus radiata* bisulfite pulp (86.3% α -cellulose), partially mercerized *P. radiata* bisulfite dissolving pulp (97.1% α -cellulose), amorphous cellulose (prepared by ball-milling bleached cotton linters for 112 h), and cellulose II (prepared by regeneration from a solution of Avicel in phosphoric acid after standing for 6 weeks¹⁰). The crystalline form of the cellulose samples was confirmed by X-ray diffraction.

Nitrogen contents were obtained by the Dumas method by the Australian Microanalytical Service, Melbourne.

Preparation of CTCs

With Pyridine as Solvent. Some samples, e.g., regenerated celluloses, were activated before derivatization. Dry cellulose (50 mg) was placed in a 15 mL reaction bottle with liquid ammonia (5 mL) and pyridine (0.5 mL) under a blanket of dry nitrogen. The ammonia was allowed to evaporate and, after ca. 2 h, the residual ammonia was driven off by gentle heating.

Dry cellulose (50 mg), or cellulose activated as above, was treated with phenylisocyanate (1 mL) in dry pyridine (10 mL) at 80°C in a 15 mL reaction bottle capped with a PTFE-coated septum. The contents of the bottle were periodically gently swirled, to aid the reaction. After dissolution of the cellulose (usually less than 48 h was required), dry methanol (1 mL) was added to remove excess phenylisocyanate, and the CTC was recovered by precipita-

tion from the pyridine solution in 100 mL aqueous methanol, prepared by mixing 7 volumes water with 3 volumes methanol. In some cases, a drop of saturated aqueous sodium sulfate was added and the mixture was swirled vigorously to break the colloidal dispersion which formed. The derivative was collected by centrifugation, washed successively with aqueous methanol, twice with water, and dried.

The 12 CTC standards, derived from bleached cotton linters, 10 hydrolyzed linters samples, and Avicel PH101 were prepared by scaling up the above procedure, and the reaction mixtures were precipitated with methanol and purified by reprecipitation from acetone solution into water. Nitrogen contents for the standards were measured as $8.10 \pm 0.19\%$ (calcd for CTC: 8.09%). For other CTC samples, purification was by reprecipitation of acetone solutions into methanol prior to elemental analysis.

With DMSO and DMF as Solvents. The reaction was carried out as above, except that dry DMSO or DMF was substituted for the pyridine, and the reaction temperatures were 50–70°C for the DMSO and 100°C for the DMF reactions.

After precipitation of some of the reaction mixtures containing DMSO, needlelike crystals appeared, which after collection and drying were identified as phenylisocyanurate (3), mp 275–284°C (lit.¹¹ mp 285°C), mass spectrum [M^+] 357, with identical IR and UV spectra to authentic material.¹¹

HPSEC of CTC Solutions

HPSEC was carried out on a system made up of a Spectra-Physics SP8700 pump, a Waters WISP 710B autosampler, and a Waters 481 variable wavelength UV detector. The detector output was connected to a Data Translation DT2801A data acquisition board in an Olivetti M24SP computer, and numerical analysis was carried out with programs written in DAOS/PC, a data acquisition and analysis operating system from Laboratory Software Associates, Melbourne. Two column sets containing crosslinked polystyrene packings were used: (a) a series of 3 × 30 cm Shodex columns KF-806, -805, and -804 with polystyrene exclusion limits of 4×10^7 , 4×10^6 , and 4×10^5 daltons respectively, and a KF-800P guard column; (b) a series of 3 × 30 cm Polymer Laboratories columns (PL gel 10 μm) having pore sizes 10^6 , 10^6 , 10^3 Å, and a guard column. Stabilized HPSEC-grade tetrahydrofuran (THF) was delivered to the columns at a rate of 1.0 mL/min. The injection volume was 40 μL of a 0.02% solution of CTC in THF containing 0.05% toluene as a reference marker. Detection was by UV at 236 nm. Solutions of CTC samples in THF were kept under nitrogen in the dark to avoid degradation. The solutions were analyzed as soon as possible after preparation, particularly those from the high MW samples.

Photometry

CTC samples chosen for use as calibration standards in HPSEC were characterized by low angle laser light scattering (LALLS) photometry using a Chromatix KMX6 photometer in conjunction with a Chromatix KMX16 differential refractometer. The solvent was stabilized THF. The 4.5–5.5° annulus and 0.2 mm field stop were used. dn/dc was determined from three

samples to be $0.165 \pm 0.002 \text{ cm}^3 \text{ g}^{-1}$. The second virial coefficient A_2 was ca. $4.6 \times 10^{-4} \text{ cm}^3 \text{ mol g}^{-2}$ and appeared to decrease with increasing \bar{P}_w .

RESULTS AND DISCUSSION

Calibration of HPSEC Columns

Samples covering a range of MW were chosen as calibration standards for the HPSEC columns. These comprised samples of bleached cotton linters, 10 hydrolyzed linters, and Avicel PH101. The CTC standards prepared from these samples had nitrogen contents that were consistent with a trisubstituted product. The \bar{P}_w range covered was approximately 350–5000 as determined by light scattering photometry. The 12 standards had very similar UV spectra in THF, with an absorption maximum at 236 nm and a molar extinction coefficient $(4.5 \pm 0.1) \times 10^4$, which confirms the suitability of UV detection for this system. Beer's law was obeyed by all CTC solutions under the conditions of the HPSEC experiments.

Two general criteria were used to generate the calibration curve. First, the \bar{P}_w values obtained using the calibration had to agree with those determined by LALLS photometry and, second, the number distribution (obtained by division of the mass distribution by the calibration function) and the weighted mass (z) distribution (obtained by multiplication by the calibration function) had to be of reasonable and consistent form. The low MW end of the calibration curve was additionally checked using the retention time of cellobiose carbanilate. The above calibration criteria were satisfied simultaneously by computer-assisted iteration. The second criterion was found to be necessary because of the lack of MW information outside the range of our standards. Although this procedure may seem to be subjective, we found that small changes in the final curve result in obvious inconsistencies in the shapes of the weighted differential distribution functions. Although an on-line LALLS detector should make this calibration procedure unnecessary at high MWs, we recommend that the number and z distributions always be inspected for anomalous behavior at the extremes. Errors and noise levels are relatively large in these areas and are greatly amplified by the choice of baseline and by application of the calibration function. We have not included corrections for axial dispersion because the symmetric spreading factor^{12,13} was found to be less than 1.005 for both column sets (polystyrene standards). Three of the CTC standards were included in each series of runs to check and adjust the calibration curve.

The calibration curves for column sets a and b, shown in Figure 1, are adequately represented by fifth order polynomials; third order gave insufficient accuracy. Column set b gave a more linear calibration curve than column set a, and both column sets gave similar results for CTC samples. Universal calibration using published Mark–Houwink–Sakurada parameters for polystyrene and CTC was found to be unsatisfactory, particularly at the high MW end of the calibration curve; shear degradation of the highest MW polystyrene standards apparently occurred where CTC continued to be efficiently fractionated.

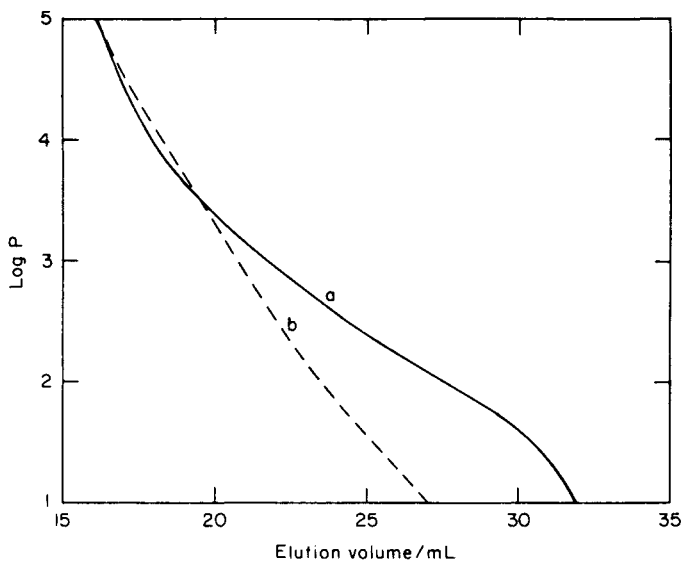


Fig. 1. Calibration curves for column sets a (—) and b (---).

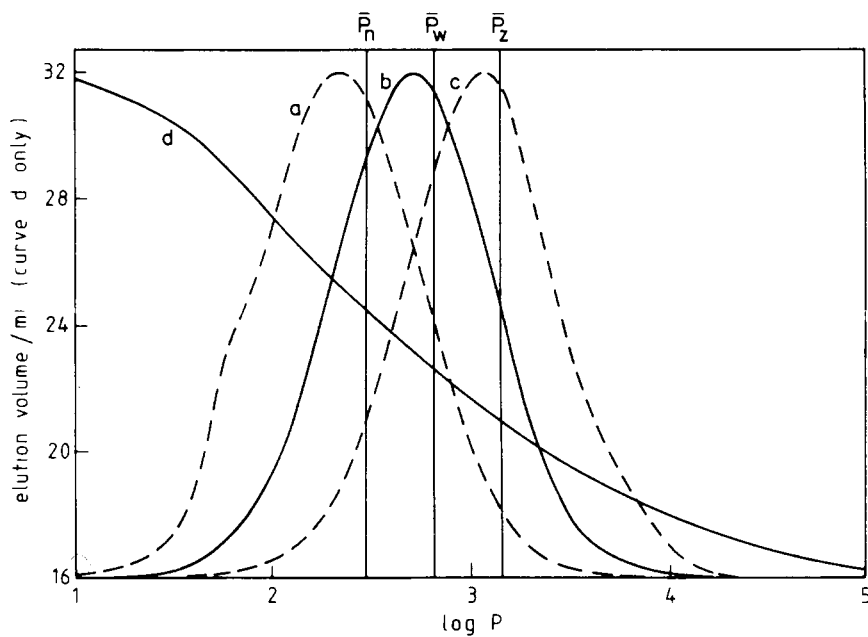


Fig. 2. Typical HPSEC analytical result (column set a) for a CTC from hydrolyzed cotton linters. Normalized (height) differential number (a), mass (b), and z (c) distributions are shown. Curve (d) represents the calibration function and the positions of \bar{P}_n , \bar{P}_w , and \bar{P}_z are indicated.

TABLE I
 Characteristics of CTC Standards

Standard no. ^a	% N	LALLS		HPSEC ^d		
		\bar{P}_w ^b	\bar{P}_w ^c	\bar{P}_w	\bar{P}_n	\bar{P}_w/\bar{P}_n
1	8.1	4830		4900	1700	2.9
2	7.9	4150		4010	1740	2.3
3	8.1	3590		3280	1420	2.3
4	8.0	2709		2710	1250	2.2
5	8.3	2360		2380	1110	2.1
6	8.0	2020		1980	947	2.1
7	8.3	1915		1580	726	2.2
8	8.1	1530		1500	724	2.1
9	8.2	1180		1170	591	2.0
10	8.2	1070		1090	565	1.9
11	8.1	780		909	488	1.9
12	8.0	364		376	211	1.8
13			4700	4550	1710	2.7
14			3950	3950	1540	2.6
15			2370	2190	842	2.6
16			1630	1770	725	2.4
17			1410	1510	599	2.5
18			645	613	291	2.1
19			511	514	246	2.1
20			434	422	213	2.0

^aStandards 1–12: this work; 13–20: donated by Dr. F. Pla, Grenoble.

^bThis work.

^cData from Ref. 7.

^dColumn set a used.

A typical analytical result for a CTC obtained from hydrolyzed cotton linters is given in Figure 2. Differential number, mass, and z distributions are shown, together with the corresponding average degrees of polymerization and the calibration curve. Note that the number and z distributions return smoothly to the baseline.

Table I shows the results of HPSEC analysis of the standards, together with the LALLS photometry results. Also included in the table are the data for eight CTC samples obtained from an independent source.⁷ The correlation between the \bar{P}_w from LALLS photometry and that from HPSEC is shown in Figure 3, where the diagonal line represents perfect correspondence (slope = 1, intercept = 0). The least squares line of best fit was not significantly different from this line.

Precipitation of the CTCs

To ensure that the MWDs of the CTC preparations are the same as those of the parent cellulose samples, the CTCs must be precipitated quantitatively from the reaction solutions. Wood et al.⁵ found that only 80% of the CTC from Avicel was recovered by precipitation into methanol, and they recommended removal of all solvent before HPSEC analysis. However, low MW compounds are formed in the derivatization reactions, and these would inter-

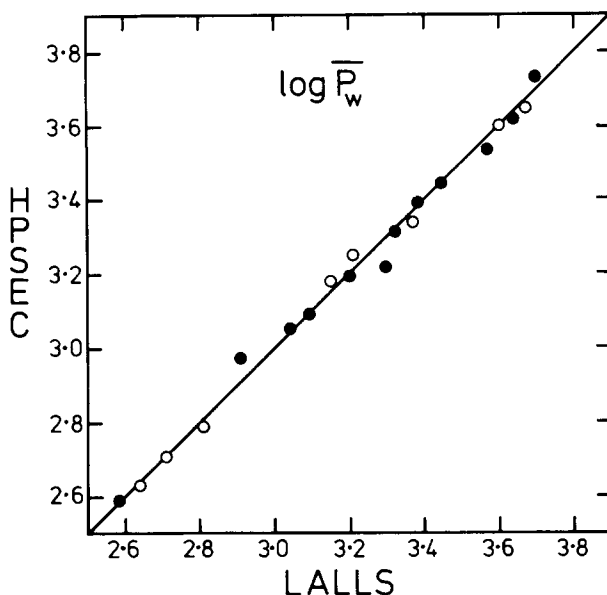


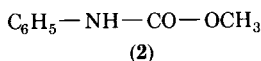
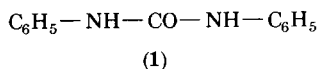
Fig. 3. Comparison of HPSEC and LALLS results for the broad CTC standards (●) and a series of samples characterized by LALLS independently⁷ (○). HPSEC results all obtained from column set a.

ferre with other methods for characterization of the CTCs, e.g., elemental analysis. We therefore sought conditions under which the CTC precipitates quantitatively and at the same time the dissolution of the low MW impurities is maximized.

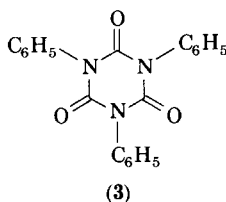
The precipitation method was optimized by determining the methanol/water ratio required to maximize recovery of CTC from the reaction mixture and minimize the coprecipitation of the low MW byproducts. Avicel, which exhibits a broad MWD covering the range of interest, was chosen for this optimization procedure. The carbanilation reaction was carried out both with DMSO and pyridine as the solvent. In each case a single large-scale preparation gave sufficient reaction mixture to test the precipitation efficiency of 12 aqueous methanol solutions covering the range 0–55% water (in 5% increments) based on volumes before mixing. The volume ratio of reaction medium to precipitating medium was 1:10 for all tests. In some cases, part of the precipitate was in a stable colloidal form. A drop of saturated sodium sulfate solution destabilized such dispersions without significantly affecting the composition of the medium.

Mass distributions are shown in Figures 4 and 5 for the two series of products. Number distributions, which are much more sensitive indicators of change at low MW, are shown in Figures 6 and 7. All distributions are normalized with respect to peak height. These results indicate that the recovery of CTC increases with increasing water:methanol ratio and approaches a limit near 30:70. At lower ratios, the difference in solvent power between DMSO and pyridine is reflected in the MWDs.

Low MW byproducts which are formed in the reaction include *N,N'*-diphenylurea (1) and methyl phenylcarbamate (2)¹⁴:



The former derives from reaction of phenylisocyanate with water, and its generation is minimized by careful drying of both cellulose and solvents; the latter is formed after decomposition of the excess phenylisocyanate with methanol. In some of the DMSO reactions, the phenylisocyanate trimer (3) was produced:



Formation of a dimer on reaction of stoichiometric amounts of phenylisocyanate and DMSO has already been noted.¹⁵ When larger amounts of methanol relative to water are used in the precipitating medium, less of these low MW compounds coprecipitate with the CTCs. The trimer, however, is much less soluble in aqueous methanol than are the other contaminants and cannot be removed by this method. In those cases where significant amounts of trimer are present in the precipitate, we found toluene extraction at 20°C to be useful. Sutter and Burchard¹⁴ have previously found that CTC oligomers are soluble in toluene.

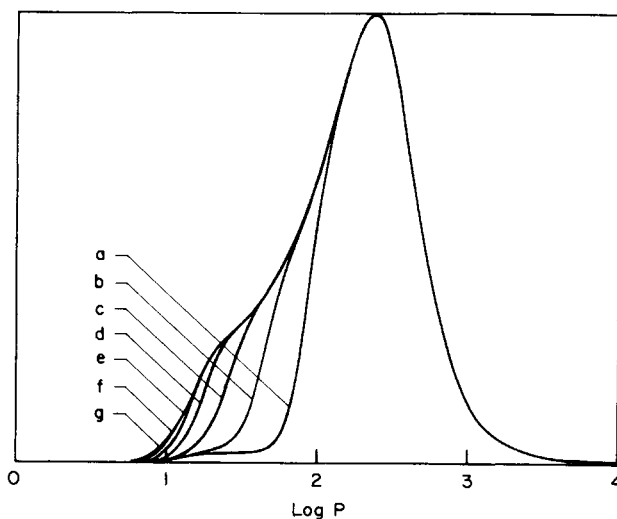


Fig. 4. Differential mass distributions for Avicel CTC precipitated from DMSO (10 mL) using a series of aqueous methanol solutions (100 mL) prepared by mixing water and methanol in the volume ratios: (a) 0:100; (b) 5:95; (c) 10:90; (d) 15:85; (e) 20:80; (f) 25:75; (g) 30:70-55:45.

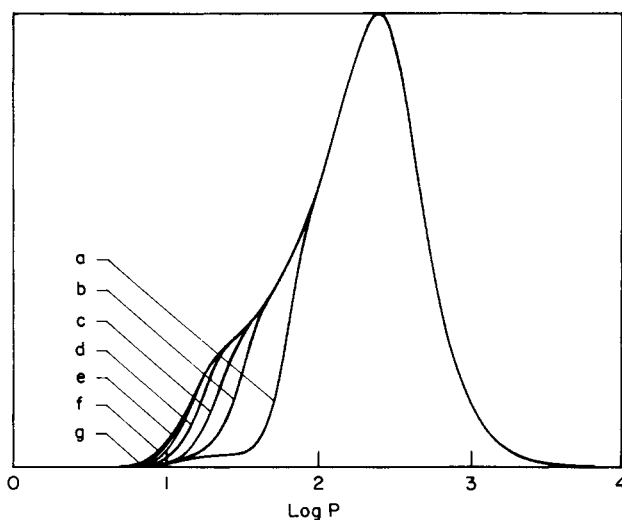


Fig. 5. Differential mass distributions for Avicel CTC precipitated from pyridine (10 mL) using a series of aqueous methanol solutions (100 mL) prepared by mixing water and methanol in the volume ratios: (a) 0 : 100; (b) 5 : 95; (c) 10 : 90; (d) 15 : 85; (e) 20 : 80; (f) 25 : 75; (g) 30 : 70-55 : 45.

As a final test of the suitability of the 30 : 70 water : methanol solution for precipitating the CTCs, a very low MW CTC ($\bar{P}_w \sim 20$), previously precipitated into 0.02M sodium sulfate solution, was redissolved in DMSO (150 mg/10 mL) and precipitated into 100 mL 30 : 70 water : methanol. The combined liquor and washings were evaporated to remove methanol, diluted with water, and extracted with ethyl acetate. Comparison of the HPSEC elution curve for the material precipitated according to our method with that of the

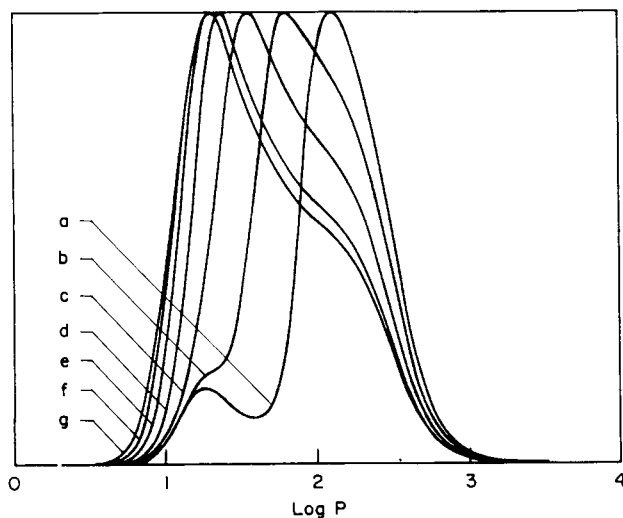


Fig. 6. Differential number distributions for Avicel CTC precipitated from DMSO (10 mL) using a series of aqueous methanol solutions (100 mL) prepared by mixing water and methanol in the volume ratios: (a) 0 : 100; (b) 5 : 95; (c) 10 : 90; (d) 15 : 85; (e) 20 : 80; (f) 25 : 75; (g) 30 : 70-55 : 45.

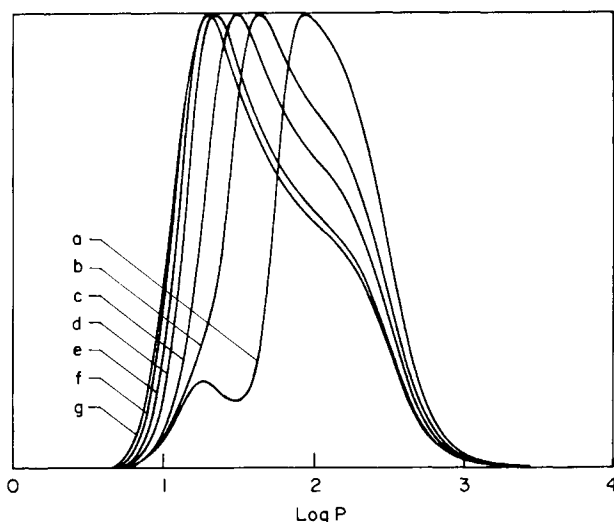


Fig. 7. Differential number distributions for Avicel CTC precipitated from pyridine (10 mL) using a series of aqueous methanol solutions (100 mL) prepared by mixing water and methanol in the volume ratios: (a) 0:100; (b) 5:95; (c) 10:90; (d) 15:85; (e) 20:80; (f) 25:75; (g) 30:70-55:45.

ethyl acetate extract (Fig. 8) shows that the selectivity of the precipitation is excellent. At least 92% of the low \bar{P}_w CTC was recovered with very little residual impurities. Further examination of the data showed that the CTC extracted from the supernatant had a very similar MWD to that which precipitated, except at very low MW ($P < 10$). Much of the extracted CTC may therefore have been in the above-mentioned colloidal particles and

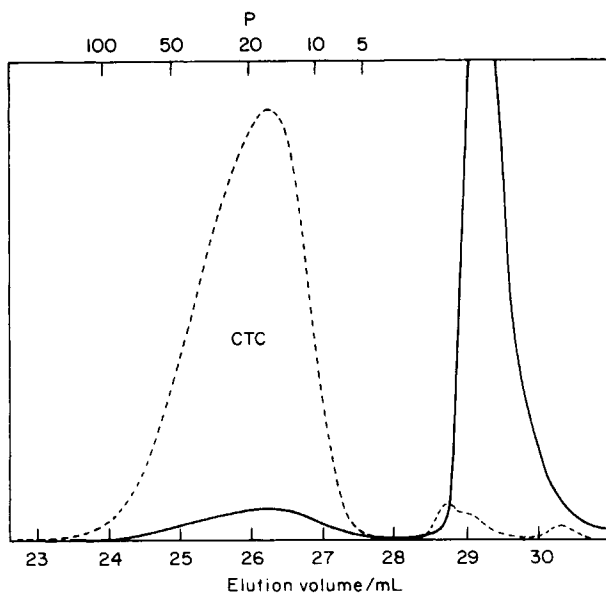


Fig. 8. HPSEC elution curves (column set b) indicating the partitioning of low MW CTC and impurities between the precipitate (---) and the supernatant medium (—). The solvent was DMSO (5 mL) and the precipitant 30:70 water:methanol (50 mL).

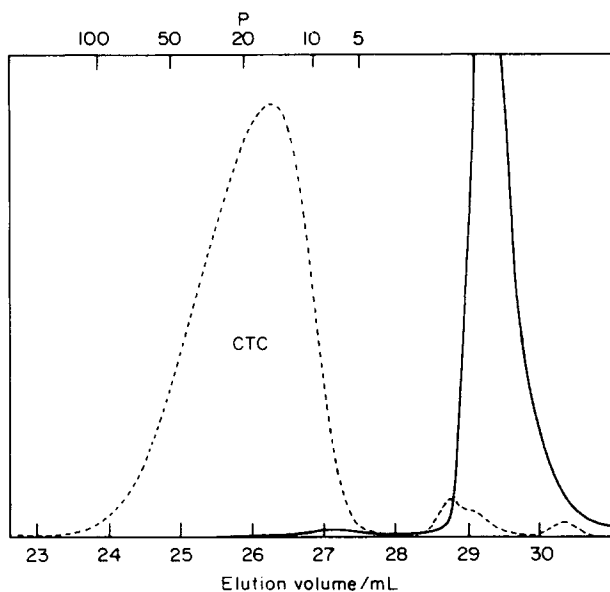


Fig. 9. Same as for Figure 8, corrected for incomplete coagulation of colloidal CTC.

potentially recoverable with the precipitate. Adjustment of the elution curve of the supernatant extract, to allow for this effect, gave the result shown in Figure 9. We conclude that this technique allows essentially quantitative recovery of CTC from the reaction medium, for $P > 10$.

Scope of the Carbanilation Reaction

The carbanilation reaction on bleached cotton linters was first carried out by reaction with phenylisocyanate in DMF. Even after 1 week at 100°C, the linters were not completely solubilized (Table II). The reaction was successfully carried out in pyridine at 80°C,^{2,5} or DMSO at 70°C,⁷ giving tricarbaniates after 32 h in both cases. When the reaction times were extended, the MWs of the CTCs prepared in pyridine were largely maintained, whereas those of the CTCs prepared in DMSO were reduced, especially after reaction for 96 h. However, a cotton linters CTC did not suffer appreciable MW loss after treatment with phenylisocyanate in DMSO at 70°C for 72 h. Evidently, some additional factor is operative in the former case to effect the degradation. The problem of degradation of the CTCs in DMSO was not alleviated by reaction at lower temperatures. At 50 and 60°C, reaction times to achieve solubilization were longer and there was considerable MW reduction. The nitrogen contents of the CTCs were sometimes lower than the theoretical (8.1%), indicating incomplete reaction.

A bleached pine bisulfite pulp reacted in either pyridine or DMSO for various times gave similar MW values (Table II). The reaction was faster in DMSO than in pyridine. Although reaction in DMSO did not give rise to lower MW values, there was a considerable amount of the trimer **3** formed. The trimerization reaction is catalyzed by low MW compounds such as propylene oxide¹¹ and residual low MW substances in the pulp may fulfill a

TABLE II
 Preparation and Properties of CTCs

Sample	Solvent	Temp (°C)	Reaction time (h)	%N	HPSEC ^a		
					\bar{P}_w	\bar{P}_n	\bar{P}_w/\bar{P}_n
Bleached cotton linters	DMF	100	168		Incomplete reaction		
	Pyridine	80	32	7.9	4446	1417	3.1
	Pyridine	80	56	n.d. ^b	4204	1445	2.9
	Pyridine	80	96	8.0	4161	1423	2.9
	DMSO	70	32	8.0	4126	1378	3.0
	DMSO	70	56	n.d.	3760	1270	3.0
	DMSO	70	96	8.0	3134	1101	2.9
	DMSO	60	46	7.8	3972	1424	2.8
	DMSO	60	94	8.0	3386	1276	2.7
	DMSO	50	75	7.8	4053	1397	2.9
	DMSO	50	168	8.0	3800	1167	3.3
Bleached pine bisulfite pulp	Pyridine	80	29	7.8	2082	184	11.3
	Pyridine	80	53	7.9	2104	197	10.7
	DMSO	70	9	7.8	2034	185	11.0
	DMSO	70	33	7.9	2103	188	11.2
Avicel PH-101	Pyridine	80	24	8.1	242	56	4.3
	Pyridine	80	48	n.d.	242	59	4.1
	DMSO	70	31	8.2	238	57	4.2
Partially mercerised pine bisulfite dissolving pulp	Pyridine	80	96		Incomplete reaction		
	Pyridine ^c	80	4	7.9	2556	447	5.7
	DMSO	70	5	7.8	2550	456	5.6
Amorphous cellulose ^d	Pyridine	80	96		Incomplete reaction		
	Pyridine ^c	80	2	n.d.	41	24	1.7
	DMSO	70	5	n.d.	39	24	1.6
	DMSO	70	24	n.d.	38	24	1.6
Cellulose II ^e	Pyridine	80	96		Incomplete reaction		
	Pyridine ^c	80	2	n.d.	21	16	1.3
	DMSO	70	5	n.d.	21	15	1.4
	DMSO	70	24	n.d.	20	15	1.3

^a Column set b used.

^b n.d. = not determined.

^c Pretreatment with liquid ammonia/pyridine.

^d Cotton linters ball-milled for 112 h.

^e Prepared by regeneration of Avicel from phosphoric acid solution after 6 weeks.¹⁰

similar role. For Avicel, reactions in pyridine or DMSO gave similar MWDs, and were faster in DMSO.

Several cellulose samples (a partially mercerized dissolving pulp, an amorphous cellulose, and a low MW cellulose II sample) did not completely react with phenylisocyanate in pyridine at 80°C (Table II). However, if the cellulose samples were first treated with liquid ammonia containing a small amount of pyridine, they became activated towards carbanilation in pyridine, and gave CTCs after 2–4 h at 80°C. With the above samples, carbanilation in DMSO at 70°C gave CTCs after 5 h without the need for prior activation. DMSO is a good swelling agent for cellulose, and thus acts as a medium for both activation and reaction of these samples. Rantanen et al.⁶ have made similar observations for reactions in DMSO. They state that it is not necessary to use

completely dry DMSO and cellulose for the reaction with phenylisocyanate. When water is present, however, the diphenylurea **1** is formed, and if present in large amounts it would coprecipitate with the CTCs.

CONCLUSIONS

When DMSO is used as a solvent for carbanilation of cellulose, activation is unnecessary and the reaction rates are faster than those in pyridine. However, DMSO has the disadvantage of leading to partial degradation of high MW cellulose samples during derivatization and occasionally giving trimer **3** as a byproduct. We thus recommend pyridine as the reaction medium for the samples that do not require activation, and DMSO for the remaining samples. Activation with liquid ammonia prior to carbanilation in pyridine is an alternative to reaction in DMSO for some cellulose samples. Optimum precipitation of the CTCs from reaction media containing either pyridine or DMSO is achieved with 30 : 70 water : methanol at a solvent : precipitant volume ratio of 1 : 10.

The authors wish to thank Dr. F. Pla, University of Grenoble, France, for the gift of eight CTC samples, and Dr. D. G. Hawthorne, CSIRO Division of Chemicals and Polymers, Melbourne, for providing the facilities for and assisting with the LALLS photometry experiments.

References

1. L. Valtasaari and K. Saarela, *Pap. Puu*, **57**, 5 (1975).
2. L. R. Schroeder and F. C. Haigh, *Tappi*, **62**(10), 103 (1979).
3. J. J. Cael, D. J. Cietek, and F. J. Kolpak, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **37**, 509 (1983).
4. H. U. Körner, D. Gottschalk, and J. Puls, *Papier (Darmstadt)*, **38**, 255 (1984).
5. B. F. Wood, A. H. Conner, and C. G. Hill, *J. Appl. Polym. Sci.*, **31**, 3703 (1986).
6. T. Rantanen, P. Färm, and J. Sundquist, *Pap. Puu*, **68**, 634 (1986).
7. J.-M. Lauriol, P. Froment, F. Pla, and A. Robert, *Holzforschung*, **41**, 109 (1987).
8. L. I. Kutsenko, V. V. Gromova, and N. I. Klenkova, *Zh. Prikl. Khim.*, **47**, 1838 (1974).
9. J. Sundquist and T. Rantanen, *Pap. Puu*, **65**, 733 (1983).
10. R. H. Atalla, J. D. Ellis, and L. R. Schroeder, *J. Wood Chem. Technol.*, **4**, 465 (1984).
11. J. I. Jones and N. G. Savill, *J. Chem. Soc.*, 4392 (1957).
12. ASTM Standard D3593-80, Standard Test Method for Molecular Weight Distribution of Certain Polymers by Liquid Size-Exclusion Chromatography (Gel Permeation Chromatography—GPC) using Universal Calibration.
13. W. W. Yau, J. J. Kirkland, and D. D. Bly, *Modern Size-Exclusion Liquid Chromatography*, Wiley-Interscience, New York, 1979, Chap. 10.
14. W. Sutter and W. Burchard, *Makromol. Chem.*, **179**, 1961 (1978).
15. Y. I. Dergunov, N. N. Bochkareva, and E. P. Trub, *Zh. Prikl. Khim.*, **53**, 2405 (1983).

Received November 4, 1987

Accepted February 24, 1988