Carbanilation of Cellulose in the Paraformaldehyde–Dimethyl Sulfoxide Solvent System

YOSHIFUMI MIYAGI* and RAYMOND A. YOUNG,† *Department of Forestry, University of Wisconsin, Madison, Wisconsin 53706*

Synopsis

Methylol cellulose carbanilate (methylol cellulose phenylcarbamate) was prepared under homogeneous conditions with phenylisocyanate following the dissolution of cellulose into the paraformaldehyde–dimethyl sulfoxide system. Previously reported procedures were utilized to control the oligo-oxymethylene side chain length of the dissolved cellulose. Methylol cellulose carbanilates with different side chain lengths were characterized by infrared spectroscopy, proton nuclear magnetic resonance spectroscopy, and differential scanning calorimetry. The homogeneous carbanilation reaction was found to be completed with a degree of substitution of around 2.4 within 3 h at room temperature, which is substantially faster than heterogeneous carbanilation. Methylol cellulose carbanilates were found to have lower heats of decomposition (23.5–32.2 kcal/mol, depending upon the side chain length) and lower decomposition temperatures (236°C) under air compared with conventional cellulose carbanilate. This suggests that the decomposition mechanism of the methylol cellulose carbanilate is through decomposition of the oligo-oxymethylene side chains, while cellulose carbanilate decomposes by rupture of the cellulose carbamate linkage.

INTRODUCTION

Because of the tremendous commercial potential, chemical modification reactions of cellulose have received a considerable amount of attention for over 100 years. Recent emphasis on cellulose modification research is the result of a number of important factors including the shortages and increasing prices of petrochemical based polymers and the development of "new" solvent systems for the highly crystalline native cellulose polymer.

Recently, it has been found that cellulose can be dissolved without significant degradation in a nonaqueous medium containing, as the principal component, strongly polar aprotic solvents such as N,N-dimethylformamide (DMF) and acetamide (DMAc) and a sufficient amount of an additional chemical such as dinitrogen tetroxide (N_2O_4), sulfur dioxide (SO_2)–amine, nitrosyl chloride, or a lithium salt.[1-3]

More recently, Johnson and co-workers[4] reported that cellulose is also soluble in dimethyl sulfoxide (DMSO) containing less than 1% dissolved paraformaldehyde (PF). The mechanism by which cellulose dissolves in the PF/DMSO solution was shown to involve the formation of methylol cellulose, a hemiacetal, which is stabilized by hydrogen bonding with DMSO.[5] A number of cellulose

* Present affiliation Harima Chemicals, Inc., Kakogawa, Hyogo, Japan.
† To whom inquiries should be addressed.

CCC 0021-8995/82/020673-13$01.30

modification reactions have been investigated using this solvent system, including acetylation,[6–10] methylation,[11] carboxymethylation,[11,12] hydroxymethylation,[4] and trimethylsilylation.[13]

In this article, the homogeneous carbanilation of cellulose dissolved in the PF/DMSO solvent system is reported on and characteristics of several types of reaction products are discussed. Heterogeneous carbanilation of cellulose, which has been extensively studied by previous investigators,[14–25] was also performed, and the characteristics of the products from the one- and two-phase reactions are discussed.

EXPERIMENTAL

General Methods

Proton nuclear magnetic resonance spectroscopic analyses were carried out with a JOEL JNM-MH-100 NMR spectrometer (100 MHz). The purified sample (22 mg) was dissolved in DMSO-d_6 (0.5 mL) and chloroform-d, containing 1% TMS (0.2 mL) the latter of which was designed to reduce the high viscosity of the DMSO solution.

Infrared spectroscopic analyses were performed on KBr pellets with a Perkin–Elmer 467 grating infrared spectrophotometer.

The thermal properties of the products were assessed by differential scanning calorimetry using a Dupont 900 thermal analyzer. Each sample (2.5 mg) was placed in an aluminum pan with an aluminum cover followed by vacuum drying at room temperature overnight. The reference was a similar pan and cover without the sample. Calibration for calculation of heat of transition was made by fusion of indium metal under identical conditions; the heating rate was 20°/min under air.

Solvation of Cellulose in the PF–DMSO System: Three Types[7,13]

Type I. Dried cellulose (α-cellulose, Sigma) (1 g) and PF powder (paraformaldehyde, Fluka) (1 g) were well dispersed and swollen in DMSO (dimethyl sulfoxide), (methyl sulfoxide, spectrophotometric grade, Aldrich) (30 mL) for 30 min with stirring in a sealed 125-ml Erlenmeyer flask at room temperature. The flask was then fitted with an air-cooling condensor, heated in an oil bath of 120°C with stirring, and lightly degassed. Stirring and heating were terminated when viscous clear solution was obtained. The system should never be cooled immediately after the termination to avoid polymerization of formaldehyde gas, which should be removed from the system (degassed).

Type II. Dried cellulose was treated as for type I, except that the amount of PF powder was 2 g. The heating and stirring were stopped when a clear solution was obtained, but gas generation was still vigorous.

Type III. The clear solution of type II was additionally stirred at 128 ± 2° for 30 min, which resulted in reduced gas generation. Heating and stirring were then terminated.

Homogeneous Acetylation of Cellulose[7]

Cellulose solutions of the three types were submitted to acetylation by the procedure described by Shiraishi and co-workers.[7] Triethylamine (99%, Aldrich) (6 mL) and acetic anhydride (6 mL) were added dropwise through a pressure-equalizing funnel to the solution. The mixture was allowed to stand for 20 h with stirring at room temperature. The reaction mixture was poured into a cold mixture of water and methyl alcohol (1:1 by volume). The precipitate was centrifuged and dissolved in acetone. The acetone solution was centrifuged to remove the acetone-insoluble portion and poured into the water–methanol mixture, and the same procedure was repeated three times. The product was dried in vacuo at room temperature and stored in a desiccator over calcium chloride. The product had a dark-amber color.

Homogeneous Carbanilation of Cellulose

Cellulose solutions were also allowed to react with phenylisocyanate. Pyridine (analytical reagent, Mallinckrodt) (8 ml) and phenylisocyanate (98+%, Aldrich) (8 ml) were added dropwise through a pressure-equalizing funnel to the solution. The miture was allowed to stand for designed reaction times with stirring at room temperature. To stop the reaction, methanol (40 mL) was added to destroy excess phenylisocyanate. The solution was poured into a water–methanol mixture (6:1 by volume) with stirring. The resulting precipitate was dissolved in tetrahydrofuran (THF) (100 mL) and the THF solution was poured into water with stirring. This step was repeated twice to remove DMSO, pyridine, and noncellulosic materials. A very fine powderlike precipitate which was not considered to be a cellulosic material was decanted away each time. The THF solution was then centrifuged and the THF-insoluble portion was separated. The THF solution was finally poured into water and, the precipitate was dried in vacuo at room temperature and stored in the same manner as the acetylated products.

Heterogeneous Carbanilation of Cellulose[25]

In this article, the term heterogeneous carbanilation of cellulose means that the *initial* reaction was in the heterogeneous phase. This method eventually results in a homogeneous reaction at longer reaction times. Dried cellulose (1 g) was swollen in pyridine (20 mL) for 10 min at room temperature with stirring, and phenylisocyanate (8 mL) was added to the mixture. The 125-mL Erenmeyer flask containing the mixture was then equipped with a water-cooling condensor and immersed in an oil bath at $80 \pm 1°C$. The solution was continuously stirred for 48 h, after which a clear cellulose carbanilate solution was obtained. The solution was poured into a water–methanol mixture (6:1 by volume) with stirring. The resulting precipitate was dissolved in THF (100 mL) and the THF solution was poured into water with stirring. This step was repeated twice. The THF solution was then centrifuged and finally poured again into water. The precipitate was dried in vacuo at room temperature and stored as described for other products.

RESULTS AND DISCUSSION

Cellulose Dissolution in PF/DMSO

The mechanism of cellulose dissolution in the PF–DMSO system has been the subject of a number of investigations since the discovery by Johnson and co-workers in 1976.[4] It is now conceded that both C-2 and C-3 hydroxyl groups of the glucose moiety are subjected to the formaldehyde addition, although the C-6 hydroxyl group is the most reactive site.[9]

Additional investigations have been aimed at the determination of the extent of molar substitution (MS) of formaldehyde per glucose unit necessary to dissolve cellulose. In a study on isolated methylol cellulose,[4,5] the substitution of approximately 1 mol formaldehyde per glucose unit (1:1) was observed. Although monomethylol cellulose may form to some extent, it appears that the formation of oligo-oxymethylene chains on the cellulose polymer is a necessary step in the dissolution reaction (Fig. 1).[6,7,13]

Both Baker and co-workers[6] and Shiraishi and co-workers[7,13] have shown that the length of the pendent oligo-oxymethylene chain on the polymer is dependent on the conditions of the dissolution process. Thus the length of the pendent oligo-oxymethylene chain of the methylol cellulose is low if the reaction is stopped immediately after cellulose dissolution.[7,13] However, the cellulose solution may remain cloudy even after the initial dissolution due to remaining finely dispersed PF powder. As the excess PF is further dispersed and reacted, the oligo-oxymethylene chain increases in length and the solution eventually becomes transparent.[6,7,13] If this solution is further heated at higher temperatures for prolonged periods of time, demethylolation of the methylol cellulose becomes the predominant reaction and can result in precipitation of unsubstituted cellulose.[6,7,13]

A further analysis was performed on the conditions for cellulose dissolution in the PF–DMSO solvent system. Table I shows the different ratios of PF to cellulose and the corresponding molar ratio of formaldehyde per glucose unit. Clearly an excess of at least 5 mol formaldehyde per glucose unit is necessary for dissolution by the methods employed in this work.

Acetylation of Cellulose

Three different types of acetylated methylol celluloses have been prepared through methods previously described.[7] Acetylated methylol cellulose, dissolution type I (CAcOM-I), was prepared by acetylation of the methylol cellulose obtained immediately after dissolution of the cellulose in the PF–DMSO system (PF–cellulose 1:1 by weight). Acetylated methylol cellulose, dissolution type II (CAcOM-II), was prepared through acetylation of the clear methylol cellulose
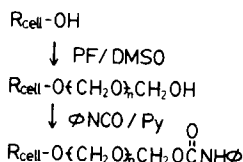
$R_{cell}-OH$

$\downarrow$ PF/ DMSO

$R_{cell}-O(CH_2O)_nCH_2OH$

$\downarrow$ ϕNCO / Py

$R_{cell}-O(CH_2O)_nCH_2OCNH\phi$

Fig. 1. Methylol cellulose formation (cellulose solvation in PF–DMSO) and consequent carbanilation with phenylisocyanate (n denotes length of oligo-oxymethylene chain).

TABLE I
Ratios of Paraformaldehyde to Cellulose for Dissolution

Sample no.	Paraformaldehyde, g	Cellulose, g	Molar ratio formaldehyde/glucose unit	Dissolution[a]
1	0.92	1.07	4.64	−
2	0.94	1.00	5.08	−
3	0.98	1.05	5.04	+
4	1.00	1.06	5.09	+
5	1.01	1.04	5.24	+
6	0.99	1.01	5.29	+
7	1.00	1.00	5.40	+
8	1.01	0.99	5.51	+

[a] A positive sign indicates cellulose dissolution, and a negative sign designates incomplete dissolution.

solution obtained by further heating of the dissolved cellulose in the presence of excess formaldehyde (PF–cellulose 2:1 by weight); and acetylated methylol cellulose, dissolution type III (CAcOM-III), was obtained from acetylation of the methylol cellulose solution which was submitted to prolonged heating at higher temperatures, a procedure known to result in a certain amount of demethylolation.[6,7,13]

PMR Interpretation[6,7]

Figure 2 shows the proton nuclear magnetic resonance (PMR) spectra of the three different types of acetylated methylol celluloses (CAcOM) prepared by the methods described above.[7] As discussed in previous reports,[6,7] the methyl protons of the acetyl group resonate around 2.1 ppm, and the cellulose ring protons are observed as a broad band occurring between about 3.2 and 5.6 ppm. Two types of methylenedioxy (—OCH$_2$O—) protons were observed and assigned.[6,7] The carbonyl group of the acetyl function deshields the neighboring protons such that the methylene protons at the end of the oligo-oxymethylene chain give a signal near 5.3 ppm. If two or more formaldehyde molecules form the chain, the methylene protons within the oligo-oxymethylene chain (length denoted n in Fig. 1) resonate at about 4.8 ppm. Because the intensity of the peak at 4.8 ppm is directly related to the number of protons in the segment, the length of the oligo-oxymethylene chain can be ascertained by interpretation and integration of this peak.

The PMR spectrum of CAcOM-I indicates that this derivative has shorter oligo-oxymethylene chains or a lower MS of the formaldehyde than CAcOM-II because the peak at 4.8 ppm for CAcOM-I is smaller than that of CAcOM-II. Likewise, CAcOM-III has shorter oligo-oxymethylene chains than CAcOM-II.[6,7] However, the broader signals of the methylenedioxy protons for CAcOM-III demonstrate a greater variety of magnetic environments, indicating that these protons are more randomly distributed along the backbone compared to CAcOM-I.
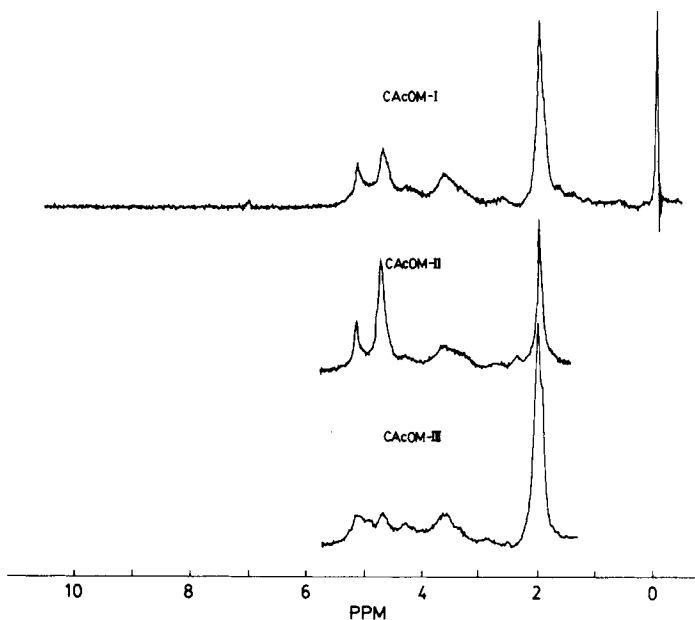
Fig. 2. Proton magnetic resonance spectra of three types of methylol cellulose acetates.

Carbanilation of Cellulose

Three different types of carbanilated methylol celluloses were also prepared by reaction of the dissolved methylol cellulose with phenylisocyanate in the presence of pyridine. As with the acetylated methylol celluloses, carbanilated methylol cellulose (methylol cellulose phenyl carbamate, CPCOM) dissolution type I (CPCOM-I), type II (CPCOM-II), and type III (CPCOM-III) were obtained (Fig. 1). A directly carbanilated cellulose was prepared by heterogeneous reaction by standard methods[25] (initial phase heterogeneous but eventually a homogeneous reaction). The latter cellulose carbanilates (cellulose phenyl-carbamates, CPC) were prepared both at 80°C (CPC-1) and at room temperature (CPC-2).

The formation of the carbanilated derivatives was confirmed by infrared spectroscopy (IR). IR spectra of pure cellulose and cellulose carbanilates prepared both heterogeneously (CPC-1 and CPC-2) and homogeneously (CPCOM-I) are shown in Figure 3. The spectrum of CPCOM-I shows a high degree of carbanilation evidenced by strong peaks at 1595, 1495, and 1440 cm^{-1} associated with the phenyl group; at 1715 (amide I), 1540 (amide II), and 1310 cm^{-1} (amide III) associated with the amide group; and at 690 cm^{-1} indicative of a monosubstituted phenyl group.[26] The intensities of these peaks are similar to those for CPC-1, the carbanilate prepared under conditions reported to yield the fully substituted cellulose derivative (tricarbanilate, DS = 3).[25]

Figure 4 shows a typical PMR spectrum of CPCOM samples prepared by homogeneous reaction in PF–DMSO solution. The pertinent sections of the PMR spectra for the three different types of CPCOM samples (dissolution types I through III) and for the cellulose phenylcarbamate (cellulose carbanilate) prepared in a heterogeneous reaction (CPC-1) are shown in Figure 5. Two different types of methylenedioxy protons are observed near 5 ppm for the CPCOM
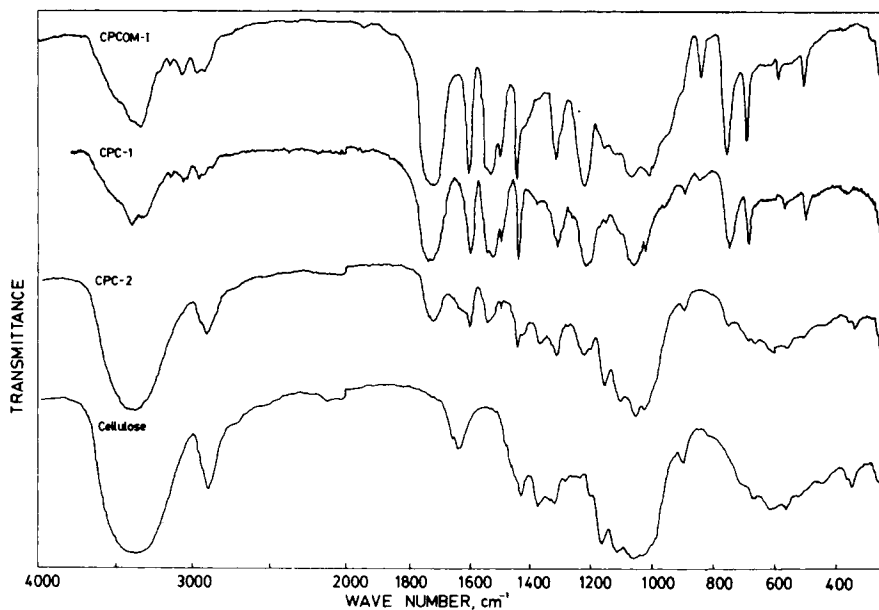
Fig. 3. Infrared spectra of methylol cellulose carbanilate (CPCOM-I), cellulose carbanilates with high DS (CPC-1) and low DS (CPC-2), and cellulose.

samples, as shown for CAcOM samples in Figure 2. However, each of the CPCOM samples exhibits quite different shapes for the PMR signals near 5 ppm compared with the signals for the CAcOM samples. The differences in the shapes and intensities of the peaks suggest that in the carbanilation reaction there is some decrease in the length of the oligo-oxymethylene chains and/or a redistribution of the —OCH$_2$— units on the glucose moiety of the cellulose polymer during the reaction.

The broad signal near 9.5 ppm in the PMR spectrum is assigned to N—H protons, and the signal near 7.3 ppm is assigned to aromatic protons (Fig. 5).
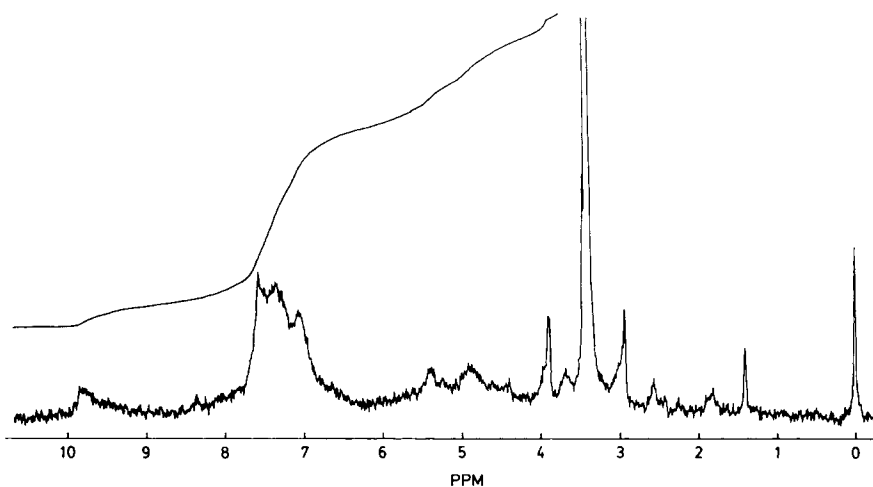

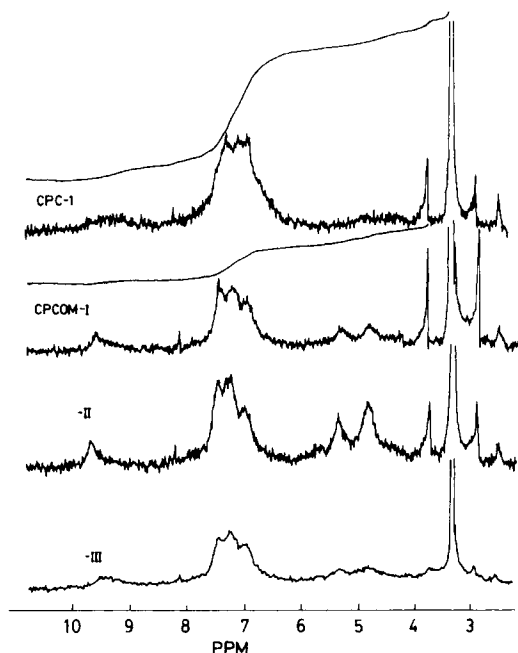Fig. 4. Proton magnetic spectrum of methylol cellulose carbanilate (dissolved in PF–DMSO as type I).

Fig. 5. Proton magnetic resonance spectra of cellulose carbanilate (CPC-1) and three types of methylol cellulose carbanilates (CPCOM-I through CPCOM-III).

Some of the cellulose ring protons are masked by the solvent (DMSO-d_6) signal and the spinning side bands (around 3.4 ppm). The number of cellulose ring protons in the 3.9–6.2 ppm region of the PMR spectrum of CPC-1 was assumed to be 3 (c' in Fig. 6), which gives 13–14 aromatic protons. If it is assumed that 4 or more protons are present in this region, DS values greater than 3 are derived, which obviously cannot be the case.
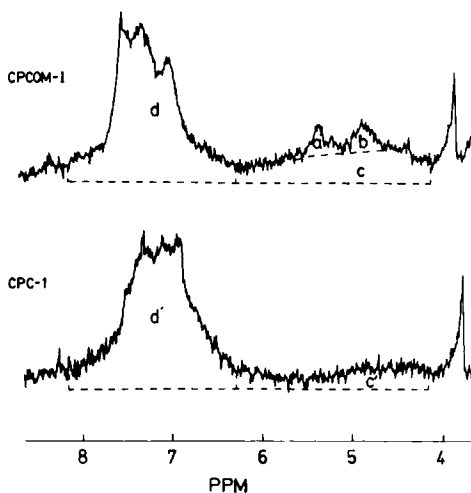

Fig. 6. Division of PMR spectra for methylol cellulose carbanilate (CPCOM-I) and cellulose carbanilate (CPC-1): a and b denote methylenedioxy protons, c denotes cellulose ring protons and part of the methylenedioxy protons, c' denotes cellulose ring protons, and d and d' denote aromatic protons.

TABLE II

Quantitative Estimation of Methylenedioxy Protons Originating from Formaldehyde per Glucose Unit

Sample	d/c^a	$d/(a + b)^a$	Protons			Protons due to formal-dehyde	Formal-dehyde moieties
			a	$a + b$	$a + b + c$		
			$d = 15$ protons, DS = 3				
CPCOM-I	2.04	6.88	7.35	2.18	9.53	6.53	3.27
CPCOM-II	1.53	3.78	9.80	3.97	13.77	10.77	5.39
CPCOM-III	2.05	10.52	7.32	1.43	8.75	5.76	2.88
			$d = 10$ Protons, DS = 2				
CPCOM-I	2.04	6.88	4.90	1.45	6.35	3.35	1.68
CPCOM-II	1.53	3.78	6.54	2.65	9.19	6.19	3.10
CPCOM-III	2.05	10.52	4.88	0.95	5.83	2.83	1.42

[a] See Figure 6 for designated areas.

To determine the extent of the reaction, an attempt was made to quantify the number of phenyl groups per glucose unit. The MS of formaldehyde was kept constant by control of the cellulose dissolution reaction and was estimated as follows: The broad band for the cellulose ring and methylenedioxy protons (3.9–6.2 ppm) of CPCOM-I was divided as shown in Figure 6. The area c for CPCOM-I was assumed to contain 3 cellulose ring protons similar to c' of CPC-1. Ratios of the designated areas, d/c and $d/(a + b)$, were then determined and are shown in Table II. From these ratios, the number of protons in c and $(a + b)$ for each type of CPCOM sample was calculated based on a DS of both 3 and 2, accounting for 15 and 10 aromatic protons, respectively. Subsequently, the number of formaldehyde moieties possible per glucose unit for each type of methylol cellulose derivative was calculated. Based on both the IR and PMR analyses, it was concluded that CPCOM-I has about 3 formaldehyde moieties per glucose unit and CPCOM-II about 5 under the conditions utilized in this work.

The number of phenyl groups per glucose unit was then plotted against the carbanilation time of the CPCOM-I samples and is shown in Figure 7. Three
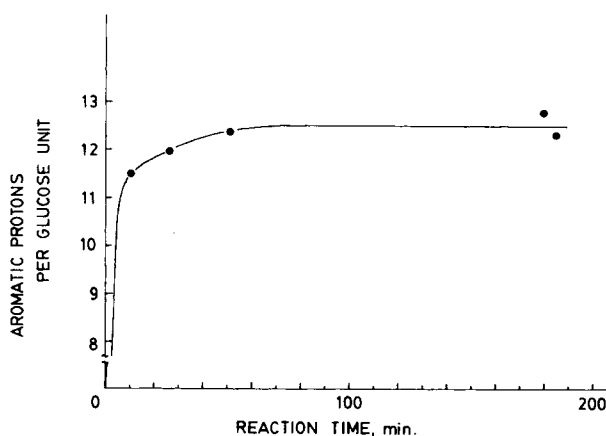

Fig. 7. Number of aromatic ring protons per glucose unit vs. carbanilation reaction time of methylol cellulose (CPCOM-I).

formaldehyde moieties were assumed to be present per glucose unit in the carbanilation reaction. The results indicate that within 60 min a DS of 2 is obtained and the DS goes up as high as 2.4 within 180 min. However, if the reaction system is allowed to stand overnight, an insoluble gel-like material is obtained which is very likely a crosslinked product. This gelling phenomenon has also been observed by Fu.[27] Further complexity of the carbanilation reaction was evidenced by an exothermic effect and gas evolution in the early stages of the reaction.

Thermal Properties of Carbanilates

DSC curves for the homogeneously prepared cellulose carbanilates with short (CPCOM-I) and long (CPCOM-II) side chains and for the heterogeneously prepared cellulose carbanilate (CPC-1) are shown in Figure 8. A calibration curve of indium metal (heat of fusion 6.80 cal/g, mp 156.6°C) is also shown in the figure.

Glass transition temperatures appear as baseline changes in DSC curves. A very slight transition is noted near 75°C for sample CPCOM-I, which is not observed for sample CPC-1. The glass transition temperature of cellulose carbanilate has been reported to be around 220°.[20]

Melting and decomposition of polymeric materials can both cause endothermic transitions. In 1966, Mack and Hobert[17] reported that an endothermic peak around 320°C for the reaction products of phenylisocyanate and cotton cellulose yarn was due to the decomposition of the cellulose carbanilate with the release of phenylisocyanate and cellulose.

Decomposition of a sample is usually recognized by evolution of noxious gases, and this occurred over 210°C for methylol cellulose carbanilate (CPCOM samples) and over 300°C for cellulose carbanilate (CPC samples), following softening of the sample and accompanied color changes. The endothermic peaks for CPCOM-I and -II, shown in Figure 8, have been assigned to decomposition of the polymers based on these observations. The CPCOM and CPC samples did not melt.
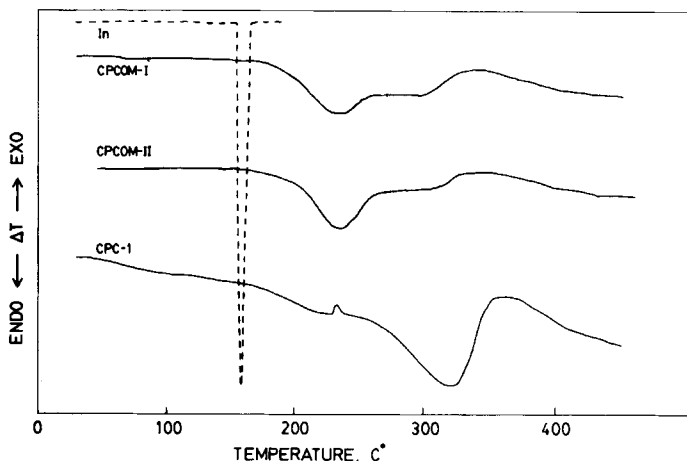

Fig. 8. Differential scanning calorimetry curves for methylol cellulose carbanilates (CPCOM-I and -II) and cellulose carbanilate (CPC-1). (indium (In) metal 17.1 mg, CPCOM-I 1.6 mg, CPCOM-II 1.9 mg, CPC-1 1.7 mg). Heating rate 20°/min with empty reference pan in air.

The cellulose carabanilates prepared in this investigation by homogeneous reactions are known to contain oligo-oxymethylene chains (CPCOM-I, -II), and these samples exhibit lower decomposition peak temperatures (235 and 238°C) compared with both the samples prepared heterogeneously (without oligo-oxymethylene side chains), (CPC-1) and the carbanilated cotton yarn of Mack and Hobert[17] (Table III). Thus, the introduced oligo-oxymethylene side chains lower the glass transition temperatures of the carbanilates and result in a more thermally unstable cellulose carbanilate. The length of the oligo-oxymethylene chains does not appear to alter the decomposition temperature significantly since both the short side-chain (CPCOM-I) and the long side-chain (CPCOM-II) samples have approximately the same decomposition temperature, 238 and 235°C, respectively.

The heat of decomposition of the polymers under air was estimated by a widely used standard method.[28,29] If the heating rate for the measurement is kept constant, the following equation is valid for the calculation of H, the heat of decomposition:

$$K'A = m\Delta H$$

where A is the peak area and m is the sample mass. The constant K', which relates peak area to the absorbed heat, was determined by calibration with the indium metal standard. At a heating rate of 20°/min, K was calculated to be 4.78 cal/g. The estimates for heats of decomposition (ΔH) for the methylol cellulose carbanilates (CPCOM-I, -II) are shown in Table III based on the proposed repeating unit compositions.

The differences in decomposition temperatures and heats of decomposition between methylol cellulose carbanilates (CPCOM) and cellulose carbanilates (CPC) can be explained by the type of the chemical bonds responsible for the decomposition. In contrast to the cellulose carbanilate, thermal decomposition of the oligo-oxymethylene chain is assumed to be the mechanism of decomposition of methylol cellulose carbanilate upon heating under air.

Mack and Hobert[17] claimed that there is a linear correlation between degree of substitution and decomposition energy of cellulose carbanilates. This may explain the greater value of heat of decomposition for sample CPC-1 (Table III), which was prepared under conditions that generally yield the tricarbanilate.

The difference in the heat of decomposition (per mol repeating unit) between the two types of methylol cellulose carbanilates, CPCOM-I and -II, can also be

TABLE III

Sample	Exotherm peak temperature, °C	Heat of decomposition ΔH, cal/g	Heat of decomposition ΔH, kcal/mol[a]
CPCOM-I[d]	238	48.1	23.5[b]
CPCOM-II[d]	235	58.7	32.3[c]
CPC-1	324	141.0	73.2
Carbanilated cotton yarn[e]	320	—	31.2

[a] Per mol repeating units.
[b] Based on the estimate of 3(OCH$_2$) units and 2 phenylcarbamoyls per glucose unit.
[c] Based on the estimate of 5(OCH$_2$) units and 2 phenylcarbamoyls per glucose unit.
[d] Average of three measurements of two different samples of each type.
[e] Reported by Mack and Hobert.[17] DS was extrapolated to 1.

explained on the basis of differences in degree of substitution. If it is assumed that the number of formaldehyde moieties in the side chain, which are responsible for the decomposition, is reflected in the value of heat of decomposition, then a calculation of heat of decomposition per mol —OCH_2 units can be made. This gives about 7 kcal, or 48 kJ, after dividing the heat of decomposition (per mole of repeating unit) by 3, the number of —OCH_2 units per glucose unit. This value, 48 kJ/mol for CPCOM-I, is close to the reported value of the heat of polymerization of formaldehyde, 51.1 kJ/mol.[30,31]

It should be noted, however, that the ether bond strength of the units in oligo-oxymethylene chains may be variable depending upon the distances from the cellulose ring or the phenylcarbamoyl groups, both of which may cause steric or dipole interaction. Therefore, the calculated heat of the decomposition per mol —OCH_2 units should only be considered a rough estimate.

SUMMARY AND CONCLUSIONS

Cellulose was successfully carbanilated under homogeneous conditions. The cellulose was dissolved in the PF–DMSO solvent system which introduces oligo-oxymethylene side chains onto the cellulose backbone to give a methylol cellulose. The methylol cellulose was then reacted with phenylisocyanate in the presence of pyridine to yield methylol celluose carbanilate. A high degree of substitution (up to 2.4) was obtained within 3 h without additional heating. Integration of PMR spectrum curves and area measurements of the peaks made quantitative analyses of each type proton possible. By control of the dissolution reaction, methylol cellulose carbanilate with about 3 formaldehyde moieties per glucose unit and another with about 5 formaldehyde moieties were obtained. DSC studies have demonstrated that the methylol cellulose carbanilates decompose exothermally upon heating under air at about 235°C, with a heat of decomposition of about 23.5–32.3 kcal/mol repeating units, depending on the length of the oligo-oxymethylene side chain. It appears that the thermal decomposition of the methylol cellulose carbanilate initiates along the oligo-oxymethylene side chains, while cellulose carbanilate, without the side chains, decomposes through the rupture of the cellulose carbamate linkage at a higher temperature (about 320°C) and with a greater heat of decomposition. Understanding the factors which affect the final properties of cellulose derivatives prepared homogeneously in the PF–DMSO system is important for future appliations of this system in industry.

References

1. A. F. Turbak, R. B. Hammer, R. E. Davis, and H. L. Hergert, *Chemtech*, 51 (1980).

2. B. Phillip, H. Schleicher, and W. Wagenknecht, *Cellulose Chem. Technol.*, **9**, 265 (1975); *Chemtech*, 702 (1977).

3. C. L. McCormick and D. L. Lichatowich, *J. Polym. Sci., Polym. Lett.*, **17**, 479 (1979).

4. D. C. Johnson, M. D. Nicholson, and F. C. Haigh, *Appl. Polym. Symp.*, **28**, 931 (1976).

5. R. B. Seymour and E. L. Johnson, *J. Appl. Polym. Sci.*, **20**, 3425 (1976).

6. T. J. Baker, L. R. Schroeder, and D. C. Johnson, *Carbohydr. Res.*, **67**, C4 (1978).

7. N. Shiraishi, Y. Miyagi, Y. Hayashi, and T. Yokota, Effects of reaction conditions on methy-

lolation of cellulose in paraformaldehyde/dimethylsulfoxide system. Paper Presented at the 29th National Meeting, Japan Wood Research Soc., Sapporo, July 1978.

8. R. B. Seymour and E. L. Johnson, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 1 (1978).

9. N. Shiraishi, T., Katayama, and T. Yokota, *Cellulose Chem. Technol.*, **12**, 429 (1978).

10. K. Arai, Y. Ogiwara, and E. Mameuda, *Sen'i Gakkaishi*, **34**, T557 (1978).

11. M. D. Nicholson and D. C. Johnson, *Cellulose Chem. Technol.*, **11**, 349 (1977).

12. R. B. Seymour, *J. Coatings Technol.*, **49**(626), 36 (1977).

13. N. Shiraishi, Y. Miyagi, S. Yamashita, T. Yokota, and Y. Hayashi, *Sen'i Gakkaishi*, **35**, T466 (1979).

14. W. M. Hearon, G. D. Hiatt, and C. R. Fordyce, *J. Am. Chem. Soc.*, **65**, 829 (1943).

15. E. Husemann and R. Werner, *Makromol. Chem.*, **59**, 143 (1963).

16. R. J. Brewer, L. J. Janghe, S. Baiby, and J. T. Burr, *J. Polym. Sci., Part A-1*, **6**, 1697 (1968).

17. C. H. Mack and S. R. Hobert, *Appl. Polym. Symp.*, **2**, 133 (1969).

18. R. S. Colborne, *Makromol. Chem.*, **122**, 261 (1969).

19. D. M. Hall and J. R. Horne, *J. Appl. Polym. Sci.*, **17**, 3727 (1973).

20. J. M. Cowie and S. A. E. Henshall, *Eur. Polym. J.*, **12**, 215 (1976).

21. J. Danhelka, I. Kossler, and V. Bohackova, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 287 (1976).

22. Y. Ohno and I. Uchimoto, *Nippon Kagakukaishi*, **(3)**, 508 (1976).

23. B. Pfannemuller and A. Berg, *Makromol. Chem.*, **180**, 1183 (1979).

24. B. Pfannemuller and A. Berg, *Makromol. Chem.*, **180**, 1201 (1979).

25. L. R. Schroeder and F. C. Haigh, *Tappi*, **62**(10), 103 (1979).

26. K. Nakanishi and P. H. Solomon, *Infrared Absorption Spectroscopy*, 2nd ed., Holden–Day, San Francisco, 1977.

27. Y. L. Fu, Modification of the dimethyl sulfoxide/paraformaldehyde solvent system for cellulose and new reaction products of cellulose hemiformals. Paper Presented in the Division of Cellulose, Paper, and Textiles, American Chemical Society, Second Chemical Congress of the North American Continent, Las Vegas, August 1980.

28. T. Daniels, *Thermal Analysis*, A Halsted Press Book, Wiley, New York, 1973.

29. W. Wm. Wandlandt, *Thermal Methods of Analysis*, 2nd ed., *Chemical Analysis*, Vol. 19, Wiley, New York, 1974.

30. J. D. Dauba, *Plast. Mod. Elastom.*, **17**, 133 (1965).

31. G. H. Stempel, in *Polymer Handbook*, 2nd ed., J. Brandrup and E. H. Immergut. Eds., Wiley, New York, 1975.