ELSEVIER

Carbohydrate Polymers 50 (2002) 201–208

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Improved synthesis of cellulose carbamates without by-products

W. Mormann*, U. Michel

Fachbereich 8, Laboratorium für Makromolekulare Chemie, Universität Siegen, Adolf-Reichwein-Str. 2, D-57068, Siegen, Germany

Received 24 October 2001; revised 14 December 2001; accepted 17 January 2002

Abstract

The synthesis of cellulose carbamates in dimethylacetamide with dibutyltin dilaurate as a catalyst is reported. The new method gives cellulose carbamates without by-products. The reaction was carried out under mild conditions and low excess of isocyanate to prevent di- and trimerization of isocyanates and reaction of isocyanates with carbamates. Since the method takes place under anhydrous conditions it is also suited for silyl celluloses. The surface of cellulose crystallites was carbanilated using toluene as non-swelling reaction medium. For carbanilated silyl celluloses and cellulose crystallites carbanilated on the surface the degree of substitution (DS) could be determined from the weight loss in thermogravimetric analysis. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Cellulose; Silyl cellulose; Carbamoylation; Phenyl isocyanate; Butyl isocyanate; Dimethylacetamide

1. Introduction

Carbamates of cellulose are used for a number of purposes, mainly because they are soluble in organic solvents. Cellulose carbanilates do not form aggregates; hence, they are well suited to determine the molar mass of cellulose by viscometry (Burchard & Husemann, 1961) size exclusion chromatography (Saake, Patt, Puls, & Philipp, 1991) or light scattering (Schulz & Burchard, 1993). Cellulose carbanilates form lyotropic lc-solutions, which have been studied by Zugenmaier (Siekmeyer & Zugenmaier, 1990). Cellulose particles with carbamate groups on the surface have gained interest as sorbants for separation of enantiomers by chromatography (Okamoto, Aburatani, & Hatada, 1990).

Cellulose carbamates can be made under heterogeneous (Ellzey & Mack, 1959; Evans, Wearne, & Wallis, 1991; Hearon, Hiatt, & Fordyce, 1943; Wallis, 1991; Volozin, Koz'ma, & Danilov, 1963) or homogeneous conditions (Terbojevich, Cosani, Camilot, & Focher, 1995; Williamson & McCormick, 1998). Pyridine is used as solvent and catalyst together with a great excess of isocyanate and long reaction times or high temperatures are necessary. By-products like dimers and trimers of the isocyanate are likely to be formed from aromatic isocyanates in the presence of pyridine (Wallis and Wearne, 1990), ureas and urethanes in addition when alcohols or water are used as non-solvents for precipitation of the cellulose carbanilates (cf. Scheme 1).

These by-products can be separated if the cellulose carbamate is isolated by precipitation in methanol. Methanol, however, is not suited for isolation of carbanilates from cellulose with lower molar mass, e.g. hydrocellulose. Fractionation will be the result, because lower homologues are soluble (Saake et al., 1991; Terbojevich et al., 1995;). To truly mirror the cellulose starting material methanol/water mixtures have to be used as non-solvent. Under these conditions, the by-products mentioned earlier are also insoluble, which gives too high degrees of substitution from the nitrogen content (Evans et al., 1991; Wallis and Wearne, 1990) or wrong molar mass. Stoichiometric amounts of isocyanate and a catalysis, which prevents formation of by-products from the isocyanate, could solve this problem.

In this paper we describe a new method for the synthesis of cellulose carbamates without by-products. The method can also be applied to cellulose derivatives with moisture sensitive groups like silyl celluloses.

2. Experimental part

2.1. Methods of characterization

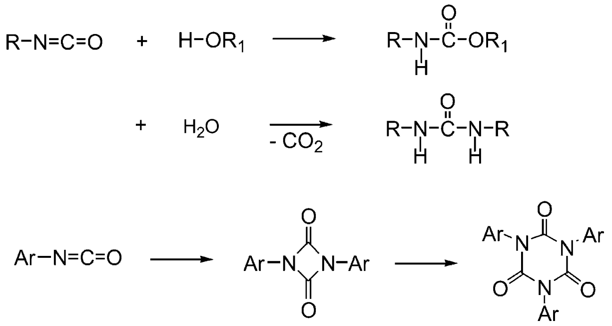
IR spectra were obtained from films using a Bruker Equinox 55 spectrometer. $^1H/^{13}C$-NMR spectra (Bruker WH-400) were obtained in DMSO-d_6, acetone-d_6 or $CDCl_3$. The

---

* Corresponding author. Tel.: +49-271-740-4713; fax: +49-271-740-2226.

E-mail address: mormann@chemie.uni-siegen.de (W. Mormann).

PII: S0144-8617(02)00016-4



Scheme 1. Possible by-products during carbamoylation of cellulose.

degree of silylation (DS) was calculated from the content of silicon determined gravimetrically (SiO_2) according to McHard (McHard, Servais, & Clark, 1948). SEC was performed using Polymer Standards Service evaluating system 2000, a constaMetric 3200 pump (Thermo Separation Products) a RI-71 differential refractometer detector (Shodex) and a PSS SDV-Gel linear column or four PSS-SDV/5 columns (7.8 × 300 mm; 5 μm particle size; 10^2, 10^3, 10^5 and 10^6 Å pore size) with tetrahydrofuran as mobile phase (flow rate 1.0 ml/min, internal standard 2,6-di-tert-butyl-4-methylphenol). Thermal properties were investigated with a Mettler TC 11/15 system with DSC 30 and TG 50 under nitrogen. Heating rates for DSC measurements were 20 K/min, for TG measurements 5 K/min.

2.2. Materials

Cotton linters (Cuoxam-DP 565 from Buckeye) and microcrystalline cellulose (Avicel PH-101, DP 220 from Fluka) were dried to constant weight at 80 °C, 0.05 mbar. Hydrocelluloses were obtained by heterogeneous hydrolytic degradation of Avicel or LAT-Avicel with 6.5 m hydrochloric acid at 60 °C (Mormann & Michel, 2002). Trimethylsilyl celluloses were prepared as previously described (Mormann & Wagner, 2000). Phenyl isocyanate and butyl isocyanate were distilled before use. Dimethylacetamide was distilled over calcium hydride and MDI (diphenylmethane-4,4′-diisocyanate).

2.2.1. Cellulose carbamates and partially silylated cellulose carbamates

A 50 ml nitrogen flask equipped with a magnetic stirring bar was charged with cellulose or silyl cellulose according to Table 1, 20 ml dimethylacetamide, phenyl isocyanate or butyl isocyanate according to Table 1 0.23 g (0.37 mmol) dibutyltin dilaurate (0.03 ml for trimethylsilyl celluloses) were added and the mixture stirred at 60 °C. With linters half of the amount of the reactants but the same volume of solvent was used. The addition of isocyanate was repeated after periods given in Table 1. When a clear solution had formed the mixture was distilled to half of the volume to remove excess isocyanate and filled up with solvent to the original volume again. The product was precipitated in a methanol/water mixture (v/v = 5:1 for cellulose carbanilates and silylated cellulose carbamates, and in a 3:1 methanol/water mixture for cellulose butylcarbamates), filtered and dried at 80 °C, 0.05 mbar. Yields and DS are given in Table 1.

2.2.2. Cellulose tricarbanilate

IR (film): 3313 cm^{-1} (N–H), 1723 + 1537 cm^{-1} (amide), 1601, 1502 + 1445 (arom.); ^1H NMR (acetone-d_6): δ 8.1–9

Table 1
Reaction conditions and properties of cellulose carbamates and partially silylated cellulose carbamates

No.	Cellulose (DP_w)[a]	n NCO/n OH[b] (m NCO/m cell.)[c]	t (h)	Yield (%)	N (%)	DS			Weight loss, Δm/m (%)		
						DS_N	$DS_{N,TG}$	|Δ|	Calculated	Found	|Δ|
	carbanilate										
1	Linters (1222)	4:1 (8.8:1)	96	94	7.86	2.74	3.68	0.94	67	73	6
2	Avicel (249)	2:1 (4.4:1)	48	88	8.09	3.00	3.87	0.87	69	74	5
3	Hydrocellulose (144)	2:1 (4.4:1)	48	94	8.06	2.97	4.31	1.34	69	76	7
4	Hydrocellulose (45)	2:1 (4.4:1)	48	94	8.10	3.01	4.08	1.07	69	75	6
	Butyl carbamate										
5	Linters (1222)	4:1 (7.3:1)	96	94	8.45	2.43	3.03	0.60	60	65	5
6	Avicel (249)	2:1 (3.7:1)	48	95	8.91	2.79	2.45	0.34	63	60	3
7	Hydrocellulose (144)	2:1 (3.7:1)	48	90	8.61	2.55	1.70	0.85	61	51	10
8	Hydrocellulose (45)	2:1 (3.7:1)	48	65	8.87	2.76	1.70	1.06	63	51	12
						DS_{Si}	$DS_{Si,TG}$				
	Carbanilate										
9	Silylated hydrocellulose (45)	1.2:1 (1.00:0.63)	24	88	–	1.74	1.79	0.05	34	33	1
10		1.4:1 (0.50:0.56)	24	89	–	1.32	1.31	0.01	44	45	1
	Butyl carbamate										
11	Silylated hydrocellulose (45)	2.0:1 (0.75:0.65)	24	67	–	1.74	1.71	0.03	30	31	1
12		1.9:1 (0.75:0.48)	24	81	–	1.96	1.66	0.30	25	32	7

[a] Mass average of DP from SEC of carbanilates vs. PS-Standards.
[b] Mol ratio isocyanate to hydroxy groups.
[c] Mass of phenyl isocyanate or butyl isocyanate and cellulose or silylated cellulose in g.

Table 2
Reaction conditions for cellulose crystallites carbanilated on the surface (NCO: Phenyl isocyanate)

No.	Cellulose	T (°C)	t (h)	Solvent	m NCO:m cell (g)	n NCO/n OH	DS
1	Avicel	60	1.5	Toluene	1.1:1	0.5	0.13
2	Hydrocellulose	25	168	Toluene	4.4:1	2.0	0.10
3	Avicel	60	48	Toluene	4.4:1	2.0	0.03
4	Avicel	25	168	THF	4.4:1	2.0	0.00

(NH); 6.5–7.7 (H-arom.), 3.3–5.3 (H-1–H-6); ^{13}C NMR (DMSO-d$_6$): δ 152.0, 152.4, 153.5 (C=O), 119, 123, 128, 138 (C-arom.), 62.5, 72.3, 72.7, 73.5, 76.2, 100 (C-1–C-6).

2.2.3. Cellulose butylcarbamate

IR (film): 3338 cm^{-1} (N–H + O–H), 1722 + 1538 cm^{-1} (amide); ^{1}H NMR (CDCl$_3$): δ 2.5–6.2 (H-1–H-6 + N–CH$_2$ + N–H), 1.1–1.8 (CH$_2$), 0.6–1.1 (CH$_3$).

2.2.4. Carbanilated trimethylsilyl cellulose

IR (film): 3310 cm^{-1} (N–H), 1744 + 1534 cm^{-1} (amide), 1602, 1503, 1444 cm^{-1} (arom.), 1251 + 843 (Si–CH$_3$); ^{1}H-NMR (acetone-d$_6$): δ 8.0–8.8 (NH), 6.3–7.7 (H-arom.), 3.0–5.3 (H-1–H-6), −0.6–0.4 (Si–CH$_3$).

2.2.5. Butylcarbamoylated trimethylsilyl cellulose

IR (film): 3357 cm^{-1} (N–H), 1738 + 1512 (amide), 1250, 842 + 750 cm^{-1} (Si–CH$_3$); ^{1}H-NMR (acetone-d$_6$): δ 2.4–6.0 (H-1–H-6 + N–CH$_2$ + N–H), 1.1–1.6 (CH$_2$), 0.6–1.0 (CH$_3$), −0.6–0.3 (Si–CH$_3$).

2.2.6. Carbanilation in pyridine

In a 100 ml nitrogen flask with a magnetic bar 50 mg (0.31 mmol) hydrocellulose was suspended in 50 ml pyridine for 4 h at 80 °C and 0.3 ml (2.8 mmol) phenyl isocyanate was added. The addition of phenyl isocyanate was repeated three times in intervals of 24 h. The solution was precipitated in methanol/water, filtered and dried at 80 °C, 0.05 mbar.

2.2.7. Carbanilation of cellulose crystallites

In a 50 ml nitrogen flask equipped with a magnetic stirring bar 1 g (6.17 mmol) cellulose was suspended in 25 ml of the solvent given in Table 2. To this suspension phenyl isocyanate (see Table 2) and 0.23 g (3.64×10^{-4} mol) dibutyltin dilaurate was added. The suspension was stirred under the conditions given in Table 2. The insoluble parts were filtered off under argon and washed three times with the corresponding solvent. The product was dried at 80 °C, 0.05 mbar.

3. Results and discussion

Reactions of isocyanates with alcohols require catalysis and a solvent which is free of catalytic impurities. Aromatic isocyanates if stored in dimethylacetamide (DMAc) or dimethylformamide (DMF) are not stable. Distillation of the amides from a high boiling diisocyanate like diphenylmethane-4,4′-diisocyanate removes catalytic impurities and stable solutions can be made. Dibutyltin dilaurate is an efficient catalyst for isocyanate–alcohol reactions. If these reactions are made below 60–70 °C no further reaction of carbamates (urethanes) with isocyanate takes place.

Celluloses with different degrees of polymerization were

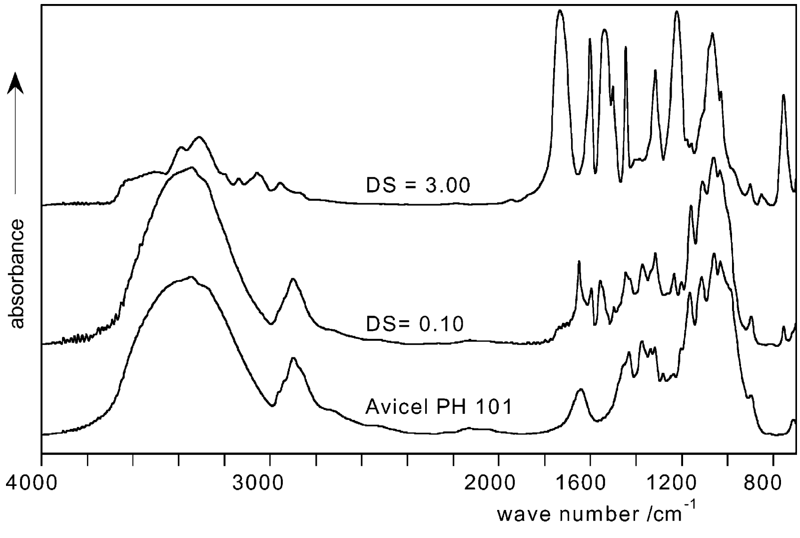


Fig. 1. IR-spectra of cellulose tricarbanilate (DS = 3.0), cellulose crystallites carbanilated on the surface (DS = 0.10) and Avicel PH 101.

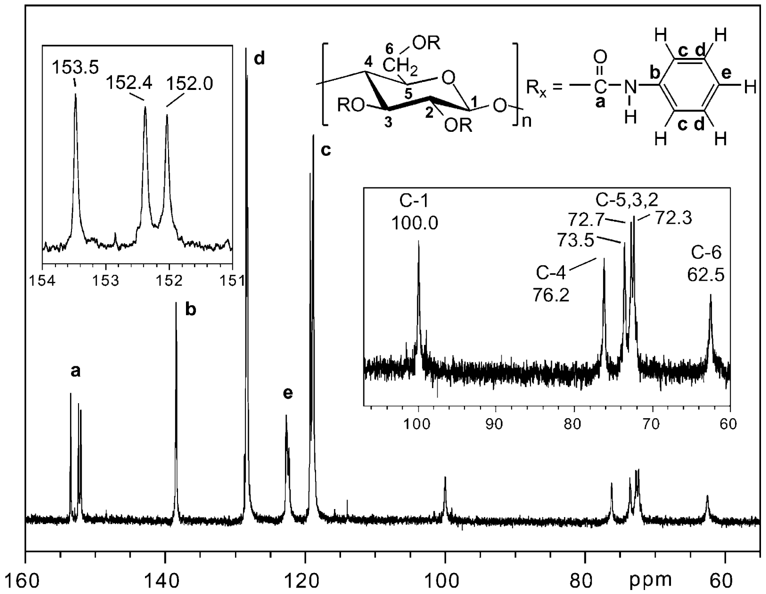
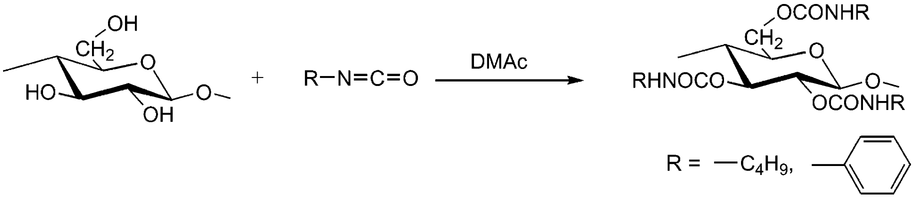


Fig. 2. ^{13}C-NMR spectrum of cellulose tricarbanilate in DMSO-d$_6$, 60 °C.

chosen for the experiments: Cotton linters, microcrystalline Avicel, and hydrocelluloses obtained from hydrolytic degradation of the former.



(1)

The carbamoylation of cellulose with isocyanates is shown in Eq. (1). Reactions were started using stoichiometric amounts of isocyanate with respect to hydroxy groups, after 24 h the same amount of isocyanate was added to the mixture in case no clear solution had been obtained, with linters this procedure was repeated three times. The initially heterogeneous mixtures became clear as the reaction proceeded. As phenyl isocyanate has a slightly lower boiling point (162–163 °C) than DMAc (165–166 °C) approximately half of the solvents was distilled off at reduced pressure to remove excess isocyanate which was controlled by IR-spectroscopy (absence of the isocyanate absorption at 2267 cm^{-1}).

Since carbamoylation of cellulose proceeds under mild and anhydrous conditions it is also suited for partially substituted celluloses like esters, ethers or trimethylsilylated cellulose. As the latter seem to be most critical partly silylated celluloses were carbamoylated. Due to the enhanced solubility of the starting material the reaction time could be reduced to 24 h and the ratio of isocyanate to hydroxy groups to 1.4.

The cellulose carbamates were characterized by IR- and NMR-spectroscopy. In the IR spectrum (Fig. 1) the typical absorptions of cellulose tricarbanilate are at 3313 cm^{-1}(N–H), 1723 + 1537 cm^{-1} (amide) and 1601, 1502 + 1445 cm^{-1} (C–H aromatic). For cellulose butylcarbamate (DS = 2.55) the absorptions are at 3338 (N–H + O–H) and 1722 + 1538 cm^{-1} (amide).

Figs. 2 and 3 show the ^{13}C-NMR spectra of cellulose tricarbanilate and cellulose butylcarbamate (DS = 2.55) from hydrocellulose. Cellulose tricarbanilate shows six signals for the carbons of the glucose monomer unit (100.0, 76.2, 73.5, 72.7, 72.3, 62.5 ppm), four signals for the aromatic carbons (119, 123, 128, 138 ppm) and three signals for the carbonyl groups (153.5, 152.4, 152.0 ppm). The high resolution of the spectrum is due to complete conversion of hydroxy-groups, which leads to a high uniformity of the sample and the low molecular weight, which decreases the viscosity of the solution. The ^{13}C-NMR spectrum of cellulose butylcarbamate (DS = 2.55) shows five signals in the region of the absorption of the glucose monomer unit (102.3, 78.4, 73.3, 72.1, 63.0 ppm), four signals for the butyl residue (41, 32, 20, 14 ppm) and three signals for the carbonyl groups (155.9, 155.4, 155.0 ppm).

In the ^{1}H-NMR spectra carbanilated silyl celluloses (Fig. 4) show resonances from 6.3 to 7.7 ppm (aromatic protons), 8.0 to 8.8 ppm (N–H protons), 3 to 5.3 ppm (protons of

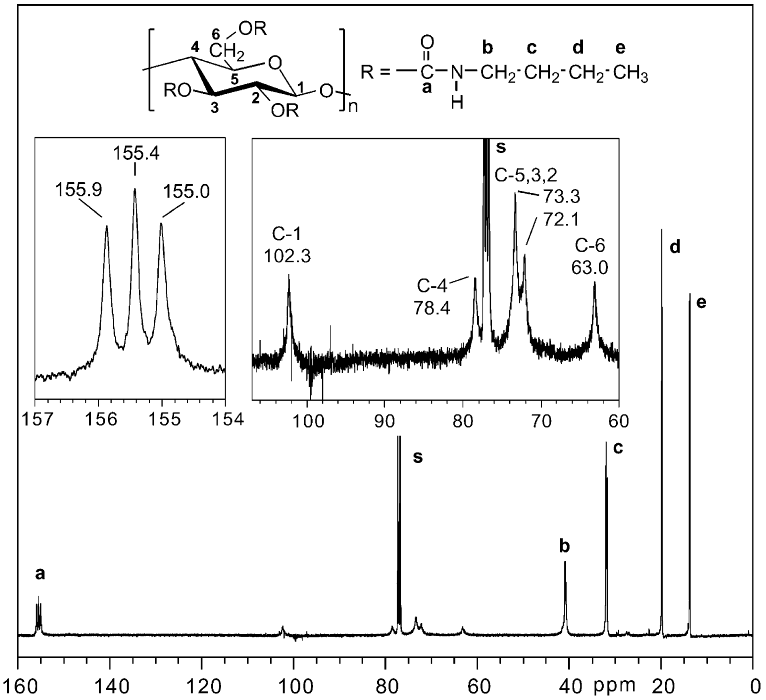


Fig. 3. ^{13}C-NMR spectrum of cellulose butylcarbamate in $CDCl_3$ (DS = 2.55).

glucose monomer unit) and −0.6 to 0.4 ppm (silyl protons). The DS of carbamoylated silyl celluloses can be calculated from the ratio of the integral resonances of the aromatic (aliphatic in case of butylcarbamates) or of the silyl protons to the protons of the glucose monomer unit.

The DS of the parent trimethylsilyl celluloses was determined gravimetrically by the method of McHard (McHard et al., 1948). The DS of cellulose carbamates was calculated from the nitrogen content as obtained by elemental analysis.

Table 1 shows that with Avicel and hydrocellulose complete conversion of the hydroxy groups could be achieved with phenyl isocyanate. The DS of linters was slightly lower (2.74) which may be due to the higher viscosity of the solution or to aggregates of cellulose, which are not broken in the course of reaction. With butyl isocyanate the degrees of substitution are lower because aliphatic isoyanates are less reactive than aromatic ones.

With carbamoylated silyl celluloses a comparison of the gravimetrically determined DS_{Si} values with those obtained from ^{1}H-NMR spectra showed that within experimental error no desilylation occured. Complete conversion of hydroxy groups was achieved with a 1.4-fold excess of phenyl isocyanate (2-fold in case of butyl isocyanate).

Precipitation of the carbanilate from Avicel in methanol reduces the polydispersity of the sample as compared to

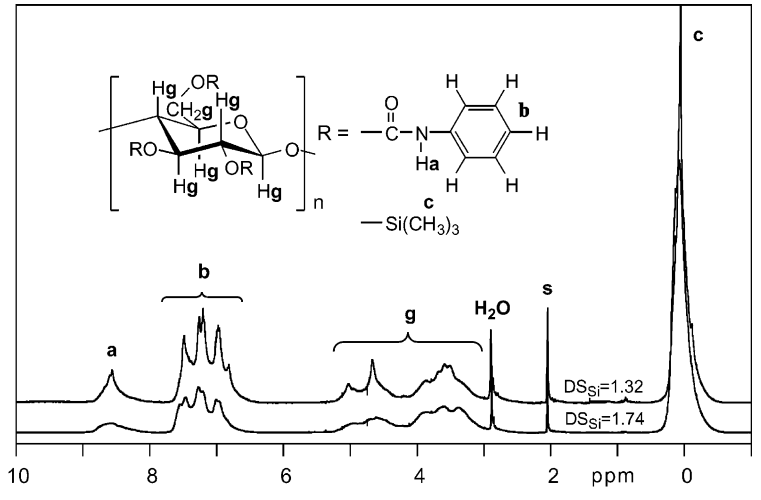


Fig. 4. ^{1}H-NMR spectra of carbanilated silyl celluloses in acetone-d_6, DS_{Si} = 1.32 and 1.74.

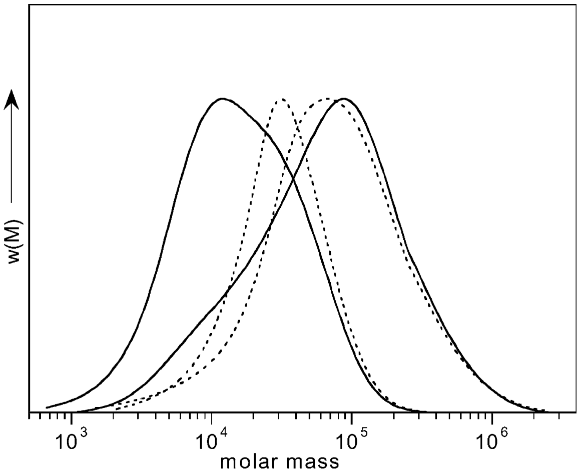


Fig. 5. Molar mass distribution of tricarbanilates from Avicel (right) and hydrocellulose (left) precipitated in methanol/water (full line) and methanol (dashed line).

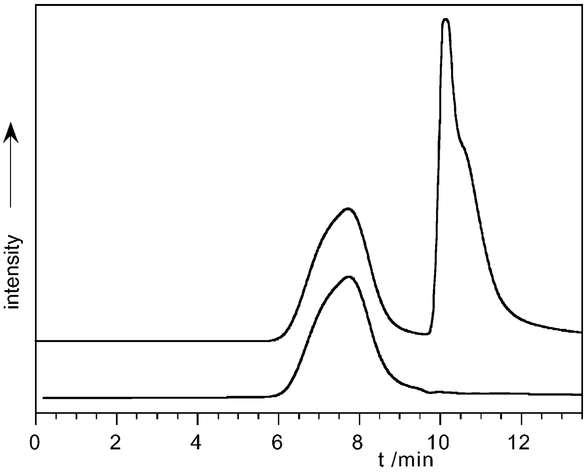


Fig. 6. SEC elution curves of cellulose tricarbanilates obtained in pyridine (upper curve) and dimethylacetamide (lower curve) precipitated in methanol/water.

precipitation in methanol/water (v/v = 5:1) because lower homologues are soluble (Fig. 5, Table 3). This leads to an increase of the average molar mass and to decrease in polydispersity. The fractionation is more pronounced with hydrocellulose. Therefore, methanol/water mixture were used as non-solvent to mirror the molar mass distribution of the cellulose used.

In methanol/water mixtures by-products formed during reaction or precipitation are not soluble. In Fig. 6 elution curves obtained from SEC of carbanilated hydrocellulose prepared in pyridine and by the new method described in this work are compared. With pyridine an additional peak appears due to by-products with low molecular weight. In case of the carbanilate prepared by the new method in DMAc no impurities were found.

The thermal properties of cellulose carbamates and partially silylated cellulose carbamates were investigated with differential scanning calorimetry (DSC) and thermogravimetry (TGA). The DSC trace of cellulose tricarbanilate shows two endotherms (Fig. 7). The endotherm at lower temperature (284 °C) is due to thermal cleavage of the urethane bond under elimination of phenyl isocyanate. At the second endotherm (322 °C) cellulose decomposes. The DSC trace of cellulose butylcarbamate shows an endotherm at 306 °C with a shoulder at lower temperatures.

Elimination of isocyanate causes a step in the TGA curve (Fig. 8). Carbanilated silyl celluloses show a better-developed plateau because of the increased thermal stability of the silyl cellulose, which does not decompose after elimination of phenyl isocyanate. The thermal stability of silyl celluloses increases with increasing DS. Butylcarbamoylated silyl celluloses show two steps probably because urethanes from secondary alcohols are less stable than urethanes from primary alcohols.

In Table 1 the DS values calculated from the TGA weight loss ($DS_{N,TG}$) are compared to those determined by nitrogen (DS_N) or silicon (DS_{Si}) content. The $DS_{N,TG}$ was calculated from the weight loss at the inflection point as determined from the maximum of the first derivative of the curve.

Both values are in good agreement for carbanilated silyl cellulose. Therefore, TGA can be used to determine the DS. The curves of cellulose carbamates and butylcarbamoylated silyl celluloses are not suitable for quantitative evaluation because the step has no developed plateau.

Using a non-swelling solvent like toluene instead of dimethylacetamide results in carbanilation of the surface of cellulose crystallites. The carbanilation was carried out under the conditions given in Table 2. The DS was calculated from the TGA curves. As for carbanilated silyl cellulose, the step of the curve is strongly developed due to the increased thermal stability of the crystallites remaining after elimination of phenyl isocyanate.

The largest DS of 0.13 was achieved with a 0.5 fold excess of phenyl isocyanate related to the hydroxy groups

Table 3
Influence of non-solvent on molar mass distribution of cellulose carbanilates

No.	Cellulose tricarbanilate	Non-solvent	SEC		
			DP_n	DP_w	DP_w/DP_n
1	Avicel	$MeOH/H_2O$ (v/v = 5 : 1)	53	249	4.7
2		MeOH	66	264	4.0
3	Hydrocellulose	$MeOH/H_2O$ (v/v = 5 : 1)	17	45	2.6
4		MeOH	42	77	1.8

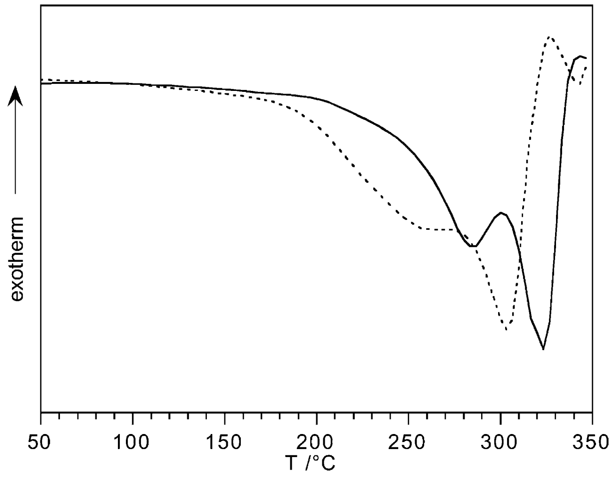


Fig. 7. DSC curves of cellulose tricarbanilate (full line) and cellulose butylcarbamate ($DS_N = 2.79$, dashed line).

after 1.5 h at 60 °C using microcrystalline Avicel as starting material. An increased reaction time gave a lower DS. With hydrocellulose a DS of 0.1 was obtained at room temperature (25 °C) after 168 h. With THF instead of toluene the TGA curve of the product showed no weight loss due to elimination of phenyl isocyanate probably because the carbanilated cellulose is soluble.

The IR spectrum of cellulose crystallites carbanilated on the surface (Fig. 1) shows a shoulder in the region of the absorption of the carbonyl group at $1734\ \mathrm{cm}^{-1}$. The broad absorption of unsubstituted cellulose at $1648\ \mathrm{cm}^{1}$ is caused by a O–H deformation vibration. In the spectrum of cellulose crystallites carbanilated on the surface this absorption is sharper. Since it is known that hydrogen bonding shifts the absorption to lower wave numbers the band could also be attributed to the second harmonic of a carbonyl vibration.

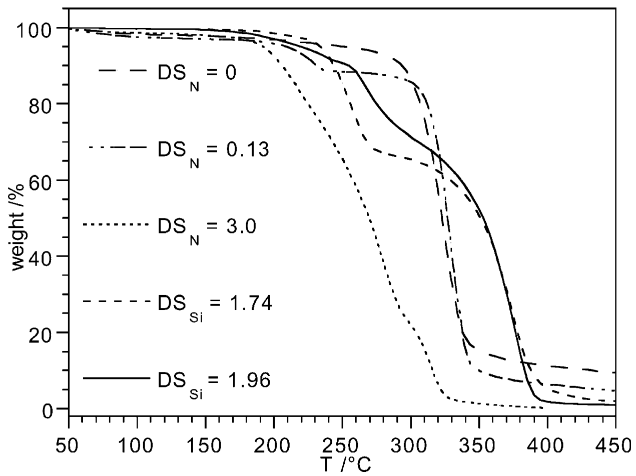


Fig. 8. TGA curves of cellulose carbamate ($DS_N = 3.0$), carbanilated silyl cellulose ($DS_{Si} = 1.74$), butylcarbamoylated silyl cellulose ($DS_{Si} = 1.96$) and cellulose crystallites carbanilated on the surface ($DS_N = 0.13$).

4. Conclusions

The synthesis of cellulose carbamates and partially silylated cellulose carbamates in dimethylacetamide with dibutyltin dilaurate as catalyst has been investigated. The procedure allows the synthesis of pure cellulose carbamates. Compared to previous methods in pyridine the reaction was carried out at low temperature and with low excess of isocyanate. With phenyl isocyanate low molecular weight celluloses (Avicel, hydrocellulose) were completely carbanilated. With butyl isocyanate, the degrees of substitution were slightly lower. The hydroxy groups of partially silylated celluloses were completely carbamoylated with butyl and phenyl isocyanate without desilylation. Cellulose crystallites were carbanilated at the surface using toluene as non-swelling solvent. A maximum degree of substitution of 0.13 was reached with Avicel. At elevated temperature urethanes were cleaved with elimination of isocyanate. For carbanilated trimethylsilyl cellulose and cellulose crystallites carbanilated on the surface the degree of substitution was calculated from the weight loss of phenyl isocyanate determined by TGA. The new method allows to exactly mirror the molar mass and its distribution of the cellulose used.

Acknowledgement

We are indebted to the Deutsche Forschungsgemeinschaft for financial support.

References

Burchard, W., & Husemann, E. (1961). Eine vergleichende strukturanalyse von cellulose- und amylose-tricarbanilaten in Lösung. *Makromolekulare Chemie*, *44/46*, 358–379.

Ellzey, S. E., & Mack, C. H. (1959). Reaction of aryl isocyanates with cotton cellulose. *Textile Research Journal*, *32*, 1023–1033.

Evans, R., Wearne, R. H., & Wallis, A. F. A. (1991). Pyridine-catalyzed depolymerization of cellulose during carbanilation with phenylisocyanate in dimethylsulfoxide. *Journal of Applied Polymer Science*, *42*, 813–820.

Hearon, W. M., Hiatt, G. D., & Fordyce, C. R. (1943). Carbamates of cellulose and cellulose acetate. I. Preparation. *Journal of the American Chemical Society*, *65*, 829–836.

McHard, J. A., Servais, P. C., & Clark, H. A. (1948). Determination of silicon in organosilicon compounds. *Analytical Chemistry*, *20*, 325–328.

Mormann, W., & Michel, U. (2002). Hydrocelluloses with low degree of polymerisation from liquid ammonia treated (LAT) cellulose. *Carbohydrate Polymers*, in press.

Mormann, W., & Wagner, T. (2000). Silylation of cellulose with hexamethyldisilazane in liquid ammonia. *Carbohydrate Polymers*, *43* (3), 257–262.

Okamoto, Y., Aburatani, R., & Hatada, K. (1990). Chromatographic optical resolution on 3,5-disubstituted phenylcarbamates of cellulose and amylose. *Bulletin of the Chemical Society of Japan*, *63* (3), 955–957.

Saake, B., Patt, R., Puls, J., & Philipp, B. (1991). Molmassenverteilung an cellulosen. *Das Papier*, *45*, 727–735.

Schulz, L., & Burchard, W. (1993). Lösungsstruktur verschiedener cellulose-derivate. *Das Papier*, *47*, 1–10.

Siekmeyer, M., & Zugenmaier, P. (1990). Solvent dependence of lyotropic liquid-crystalline phases of cellulose tricarbanilate. *Makromolekulare Chemie*, *191*, 1177–1196.

Terbojevich, M., Cosani, A., Camilot, M., & Focher, B. (1995). Solution studies of cellulose tricarbanilates obtained in homogeneous phase. *Journal of Applied Polymer Science*, *55*, 1663–1671.

Volozhin, A. I., Koz'ma, O. P., & Danilov, S. N. (1963). Synthesis and properties of N-substituted carbamic esters of cellulose. *Zhurnal Prikladnoi Khimii*, *37*, 1578–1583.

Wallis, A. F. A., & Wearne, R. H. (1990). Side reactions of phenyl isocyanate during amine-catalyzed carbanilation of cellulose. *European Polymer Journal*, *26* (11), 1217–1720.

Williamson, S. L., & McCormick, C. L. (1998). Solution studies of cellulose tricarbanilates obtained in homogeneous phase. *Journal of Macromolecular Science, Pure and Applied Chemistry.*, *A35*, 1915–1927.