Effect of Amines on the Carbanilation of Cellulose with Phenylisocyanate

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

Various amines were added to carbanilation reactions of cellulose samples with phenylisocyanate in an effort to aid the preparation of cellulose tricabanilates (CTCs) for determining molecular weight distributions (MWDs). However, the amines catalyzed the conversion of phenylisocyanate to its trimer phenylisocyanurate, especially in dimethylsulfoxide (DMSO) and N,N-dimethylformamide (DMF) media. In some of the reactions to which amines were added, the CTC products had high-performance size exclusion chromatographic peaks that tailed badly. The tailing was not caused by incomplete carbanilation. The amines 1,4-diazabicyclo(2.2.2)octane (DABCO) and 4-N,N-dimethylaminopyridine (DMAP) accelerated the dissolution of cellulose during carbanilation, while others retarded the dissolution. DABCO in pyridine assisted the carbanilation of cellulose samples, which were otherwise unreactive in pyridine, although the reactions were slower than in uncatalyzed DMSO media. However, the reactions in DMSO with added amines gave CTCs with lower degree of polymerization (DP) values, and the DP reduction was particularly severe when N-methylimidazole was the added amine. The possible involvement of oxidation by DMSO in the depolymerization process is discussed. It was concluded that addition of amines to carbanilation reactions of cellulose has limited application for CTC preparation for MWDs.

INTRODUCTION

Cellulose tricarbanilate (CTC) has emerged as a preferred derivative for determining the molecular weight distribution (MWD) of cellulose with the aid of high-performance size exclusion chromatography (HPSEC).[1-10] Its attributes for this purpose are its stability, and its relative ease of preparation as the fully trisubstituted product.[2] The CTCs (II) for MWD studies are obtained by reacting the cellulose samples with phenylisocyanate (I) in pyridine at 80°C[2-5,10] or in dimethylsulfoxide (DMSO) at 70°C.[6,7,10] (Fig. 1). For high MW cellulose samples, the reaction times are long (ca. 48 h), and while the reactions proceed in pyridine without degradation of the cellulose, some degradation occurs during the reaction in DMSO.[10] Certain cellulose samples, e.g., regenerated celluloses, are unreactive to phenylisocyanate in pyridine and must be activated before derivatization proceeds.[3,10] We thus sought catalysts that would accelerate the reactions while maintaining the original degree of polymerization (DP) of the cellulose samples, and which would obviate the need for activation prior to the carbanilation reaction.

Tertiary amines are commonly used as catalysts in isocyanate reactions.[11] It was earlier suggested that their efficacies increase as the basicity of the amine (in aqueous solution) increases and the steric shielding of the amino nitrogen decreases. Chang and Chen[12] have recently proposed that the efficacies of catalysts in the reaction of phenylisocyanate with alcohols is dependent on the ability of the catalysts to form hydrogen-bonding complexes and on their electron donor numbers, rather than on their basicities. For the heterogeneous reaction of cellulose and phenylisocyanate, the extent of swelling of the cellulose by the reaction medium would also be a critical factor, as it is necessary for the reagents to penetrate

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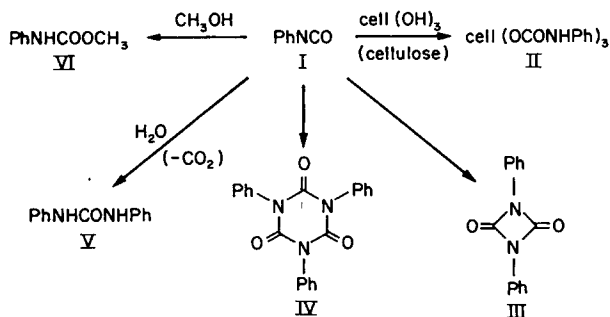* To whom correspondence should be addressed.

Figure 1   Reactions of phenylisocyanate.

the cellulose structure to gain access to the reaction sites.

Besides promoting the reactions of isocyanates with active hydrogen-containing compounds, e.g., alcohols, the amines catalyze self-condensation reactions to give isocyanate dimers, trimers, and polymers.[11] Trimerization in the presence of organometallic and amine catalysts is also promoted by strongly dipolar aprotic solvents such as DMSO and N,N-dimethylformamide (DMF).[13] The trimer phenylisocyanurate (IV) has already been isolated as a by-product of the reaction of cellulose with phenylisocyanate in DMSO.[10]

The amine catalyst 1,4-diazabicyclo(2.2.2)octane (DABCO) has been used to aid the carbanilation reaction of cellulose in DMF[14]; without the catalyst, the reaction is very slow in this solvent.[15] The efficacies of solvents for the reaction decrease in the order DMSO > pyridine ≫ DMF.[10] 4-N,N-Dimethylaminopyridine (DMAP) has also proved to be an excellent catalyst for reactions of isocyanates[16] and is believed to operate through a base-catalysis mechanism.[17] A third tertiary amine catalyst, N-methylimidazole (NMI), is a very effective catalyst for acetylations with acetic anhydride[18] and has been used as a catalyst for urethane formation.[19] These three amines and, for comparison, N,N-dimethylaniline (DMA), triethylamine (TEA), and tri-n-amylamine (TAA), were used in this study to test their effect on reactions of various cellulose samples with phenylisocyanate in pyridine and in DMSO. Some additional reactions were carried out with bleached cotton linters in DMF and N,N-dimethylacetamide (DMAc) media.

EXPERIMENTAL

Analytical Methods

Nitrogen contents of the CTC samples were obtained by the Dumas method and were performed

by the Australian Microanalytical Service, Melbourne. Fourier transform infrared (FT-IR) spectra were obtained for KBr discs (1% sample, 64 scans, 4 wave number resolution) on an Alpha Centauri FT-IR spectrometer (Mattson Instruments Inc). HPSEC of the CTC samples was carried out on columns containing crosslinked polystyrene, eluting with tetrahydrofuran, and MWDs were calculated according to a published method.[10]

Phenylisocyanate Reaction Products

The dimer III, mp 177–179°C (acetone), was prepared by DMAP-catalyzed reaction of phenylisocyanate at ambient temperature.[20] The trimer IV, mp 284–286°C (acetone), was the product of propylene-oxide-catalyzed condensation of phenylisocyanate in pyridine at 20°C.[21] 1,3-Diphenylurea (V) was obtained by careful addition of phenylisocyanate to water and had a mp of 236–237°C (ethanol). Methyl carbanilate (VI), mp 47–48°C (ether–hexane), was obtained by reaction of dry methanol with phenylisocyanate at 20°C.

Cellulose Samples

Four cellulose samples were used: bleached cotton linters (99.3% α-cellulose); partially mercerized Pinus 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 (FMC Aust Ltd, Melbourne) in phosphoric acid after standing for 6 weeks).[22]

Amine-Catalyzed Trimerization of Phenylisocyanate

Phenylisocyanate (200 mg, 1.7 mmol) and dry pyridine, DMSO, DMF, or DMAc (2.0 mL) were placed in a 5-mL reaction bottle capped with a PTFE-coated septum. Various amines (0.4 mmol) were optionally included in the mixtures, and the bottles were heated in an oven for 72 h at the appropriate temperatures (70 or 80°C) (Table I). After reaction, the bottles were cooled, and 0.5 mL dry methanol was added to the solutions. The mixtures were added to 40 mL water, and the aqueous solutions were extracted with ethyl acetate (4 × 20 mL). The combined extracts were placed in a 100-mL volumetric flask, and the solution was made up to 100 mL with fresh ethyl acetate. An aliquot of this solution (1.0 or 2.0 mL depending on the expected amount of methyl carbanilate) was added to a solution of

Table I   Amine-Catalyzed Trimerization of Phenylisocyanate[a]

Solvent	Amine	Temp. (°C)	% Yield Trimer (IV)	% Yield Diphenylurea (V)
Pyridine	—	80	—	7.8
Pyridine	DABCO[b]	80	10.5	6.7
Pyridine	DMAP[c]	80	2.7	5.4
Pyridine	DMA[d]	80	0.8	7.5
Pyridine	NMI[e]	80	0.5	4.9
Pyridine	TEA[f]	80	6.9	8.3
Pyridine	TAA[g]	80	5.6	2.4
DMSO	—	70	2.0	10.4
DMSO	DABCO	70	82.3	13.0
DMSO	DMAP	70	86.2	12.1
DMSO	DMA	70	30.1	16.7
DMSO	NMI	70	24.3	11.2
DMSO	TEA	70	44.1	15.6
DMSO	TAA	70	50.5	24.3
DMF	—	80	21.1	11.9
DMF	DABCO	80	83.3	14.2
DMAc	—	80	1.6	13.8
DMAc	DABCO	80	12.9	17.3

[a] 1.7 mmol phenylisocyanate, 0.4 mmol amine, 2.0 mL solvent, 72 h.
[b] 1,4-Diazabicyclo(2.2.2)octane.
[c] 4-N,N-dimethylaminopyridine.
[d] N,N-dimethylaniline.
[e] N-methylimidazole.
[f] Triethylamine.
[g] Tri-n-amylamine.

methyl 3,4-dimethoxybenzoate (internal standard) in methanol (0.1%, 1.0 mL), and the combined solution was evaporated to dryness. The residue was dissolved in 25 mL methanol and was analyzed by high-performance liquid chromatography (HPLC). Column: Waters RESOLVE C-18 5μ Radial-PAK cartridge (8 mm $\times$ 10 cm). Solvent: 1.0 mL/min; 50% aqueous methanol for 10 min, then gradient elution during 10 min to 70% aqueous methanol and elution with this solvent for a further 15 min. Detector: UV at 225 nm. Sample volume: 20 μL. Retention times: VI, 11.6 min; IV, 15.3 min; int. stand., 20.4 min; V, 24.5 min; III, 32.1 min. A calibration curve was made for each component against the internal standard, and the amounts of reaction products were calculated from these curves. Beer's law was followed within the range of concentrations used.

Reaction of Cellulose Samples with Phenylisocyanate in the Presence of Amines

Dry cellulose (50 mg) was treated with phenylisocyanate (1.0 mL) in dry solvent (pyridine, DMSO, DMF, or DMAc) (10 mL) at 60–100°C in a 15-mL reaction bottle capped with a PTFE-coated septum. An amine (2.0 mmol) was also included in some of the reaction mixtures. The contents of the bottle were periodically gently swirled to aid the reaction. After dissolution of the cellulose, dry methanol (1 mL) was added, and the CTC was recovered by precipitation from the reaction solution in 100 mL aqueous methanol, prepared by mixing seven volumes of water with three volumes of methanol. In some cases, a drop of saturated aqueous sodium sulfate was added and the mixture was swirled vigorously to break the colloidal dispersion that formed. The derivative was collected by centrifugation, washed successively with aqueous methanol, twice with water, and dried. The values obtained for nitrogen contents of CTC samples were 8.1 ± 0.2% (calcd. for CTC: 8.09%).

RESULTS AND DISCUSSION

Amine-Catalyzed Trimerization of Phenylisocyanate

Carbanilation of cellulose is typically carried out in pyridine or DMSO with an excess of phenyliso-

Table II   Effect of Amines on the Carbanilation of Cellulose Samples with Phenylisocyanate[a]

Sample	Solvent	Amine Additive	Temp. (°C)	Time (h)	MWD of CTCs		
					$\bar{P}_w$	$\bar{P}_n$	$\bar{P}_w/\bar{P}_n$
Amorphous	Pyridine	—	80	96	[b]		
cellulose	Pyridine	DABCO	80	72	38	23	1.7
	Pyridine	DMAP	80	91	36	22	1.6
	Pyridine	NMI	80	24	37	24	1.5
	DMSO	—	70	5	39	24	1.6
Cellulose II	Pyridine	—	80	96	[b]		
	Pyridine	DABCO	80	77	20	14	1.4
	Pyridine	DMAP	80	96	[b]		
	Pyridine	NMI	80	96	[b]		
	DMSO	—	70	5	21	15	1.4
Partially mercerized	Pyridine	—	80	96	[b]		
pine bisulfite	Pyridine	DABCO	80	77	[c]		
dissolving pulp	Pyridine	DMAP	80	96	[b]		
	Pyridine	NMI	80	96	[b]		
	DMSO	—	70	5	2550	456	5.6
Bleached cotton	Pyridine	—	80	32	4450	1420	3.1
linters	Pyridine	DABCO	80	20	[c]		
	Pyridine	DMAP	80	19	4400	1450	3.0
	Pyridine	DMA	80	46	4260	1360	3.1
	Pyridine	NMI	80	72	4350	1460	3.0
	Pyridine	TEA	80	30	4400	1420	3.1
	Pyridine	TAA	80	91	4330	1350	3.2
	DMF	—	100	96	[b]		
	DMF	DABCO	80	19	[c]		
	DMF	DMAP	80	96	[b]		
	DMF	NMI	80	96	[b]		
	DMAc	—	100	96	[b]		
	DMAc	DABCO	80	32	[c]		
	DMAc	DMAP	80	96	[b]		
	DMAc	NMI	80	96	[b]		
	DMSO	—	60	46	3970	1420	2.8
	DMSO	DABCO	60	9	3510	1070	3.3
	DMSO	DMAP	60	19	3620	1250	2.9
	DMSO	DMA	60	49	[c]		
	DMSO	NMI	60	50	533	179	3.0
	DMSO	TEA	60	96	[b]		
	DMSO	TAA	60	45	3430	1220	2.8

[a] 50 mg cellulose, 1.0 mL phenylisocyanate, 2.0 mmol amine, 10 mL solvent.
[b] Incomplete reaction.
[c] Tailing peak in HPSEC trace.

cyanate, and the soluble tricarbanilate (II) is the product.[1-10] After completion of the reaction, the excess phenylisocyanate is removed by treatment with methanol to give methyl carbanilate (VI). Unless the reactants and solvents are completely dry, phenylisocyanate reacts with the water to form carbon dioxide and 1,3-diphenylurea (V). The phenyl-

isocyanate dimer III and trimer IV are formed from phenylisocyanate under certain catalytic conditions[11] (Table I).

The CTCs are isolated by precipitation into aqueous methanol.[10] Since the solubilities of the by-products of the carbanilation reaction in aqueous methanol decrease in the order VI $\gg$ V > IV > III,

the formation of compounds III–V should be suppressed, as they may coprecipitate with the CTCs. In addition, phenylisocyanate would be consumed in the formation of compounds III–V.

To estimate the amount of compounds III–V that would be expected to form during carbanilation of cellulose in the presence of amines, a series of blank runs was carried out without cellulose. After reaction for 72 h, the remaining starting material was decomposed with methanol, and the products were analyzed by HPLC[23] (Table I). In every case, the chromatograms showed no more than three product peaks, which were assigned to compounds IV–VI; the dimer III was not a component of any of the reaction mixtures.

When phenylisocyanate was simply heated in solvents for 72 h, the yields of trimer in the pyridine, DMSO, and DMAc reactions were < 3%, although the trimer yield in the DMF reaction was 21% (Table I). When amines were included in the reactions, the yields of trimer were higher, particularly for the amines DABCO and 4-N,N-dimethylaminopyridine (DMAP) and for the solvents DMSO and DMF. The catalytic effect of amines such as DABCO on the trimerization of phenylisocyanate in DMSO and DMF has already been noted.[13] The yields of the diphenylurea V from reactions in DMSO, DMF, and DMAc were higher than for reactions in pyridine, which may be indicative of the difficulty of completely removing water from the former solvents. Thus the products IV and V are less likely to form as by-products from reactions of phenylisocyanate in pyridine and in DMAc than from reactions in DMSO and in DMF, and formation of the trimer is promoted by amines.

## Effect of Amines on the Carbanilation of Cellulose with Phenylisocyanate

Four cellulose samples were used in this study; three were unreactive to phenylisocyanate in pyridine, i.e., they did not completely dissolve in the reaction medium after 96 h at 80°C[10] and could thus not be used for MWD studies, and a bleached cotton linters sample. The celluloses were treated with phenylisocyanate in the presence of amines, and the MWDs of the resulting CTCs were determined by HPSEC. The weight and number average DPs ($\bar{P}_w$ and $\bar{P}_n$, respectively) and the polydispersities ($\bar{P}_w/\bar{P}_n$) are given in Table II.

The three cellulose samples that were unreactive to phenylisocyanate in pyridine were treated under the same conditions in the presence of the amines

DABCO, DMAP, and NMI. Although in the absence of amines the cellulose was not completely dissolved after 96 h at 80°C, with added DABCO the samples dissolved after 72–77 h and gave CTC products (Table II). For the amorphous cellulose sample, DMAP and NMI were also effective catalysts for the reaction. In DMSO solution without added amines, the three cellulose samples were completely converted to CTCs after 5 h at 70°C, and these CTC products had the same MWD characteristics as those prepared by the amine-catalyzed reactions in pyridine (Table II), with the exception of the DABCO-catalyzed reaction of the partially mercerized pine dissolving pulp. In this case, the HPSEC trace had a CTC peak that tailed, and it was not possible to obtain sensible MWD data from the abnormal trace (see below). Thus DMSO is a better reaction medium than pyridine/amines for carbanilation of these samples.

Addition of amines to the carbanilation reaction of bleached cotton linters in pyridine gave differing effects; the dissolution time was shorter in the presence of DABCO or DMAP, unchanged with TEA, but longer with the three remaining amines, requiring 91 h with TAA (Table II). With the exception of the CTC prepared in the presence of DABCO, all the products had similar MWD characteristics, although the DPs of the product from the TAA reaction were somewhat lower than the reaction without an amine additive. The CTC prepared with the aid of DABCO had an HPSEC peak that tailed, and the trace did not return to the baseline until well past the MW range covered by the column system, shown in Figure 2 together with the trace from the reaction without an amine additive.

Carbanilation of bleached cotton linters in DMF or DMAc at 100°C was incomplete after 96 h, although in the presence of DABCO, the reactions
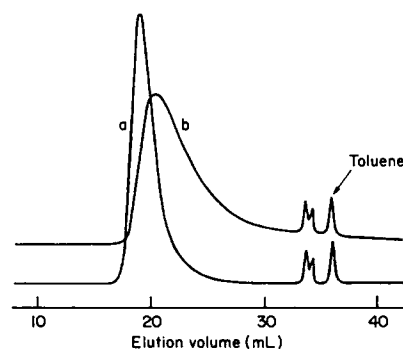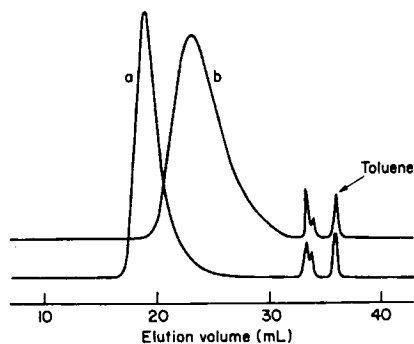

Figure 2   HPSEC elution curves for cotton linter CTCs prepared in pyridine at 80°C (lower curve a) and in 0.2 M DABCO in pyridine at 80°C (upper curve b).

were complete after 19 and 32 h, respectively. The CTC products had HPSEC curves similar to that of the CTC from the pyridine–DABCO reaction, which had a sloping tail. Hall and Horne[14] reported that CTCs were prepared from various cellulose samples without degradation of the cellulose by reaction with DMF catalyzed by DABCO, although they did not conduct HPSEC experiments. The amines DMAP and NMI added to the reactions in DMF and DMAc at 80°C did not effect dissolution of the cellulose after 96 h.

The carbanilation of bleached cotton linters in DMSO was carried out at 60°C. Both DABCO and DMAP accelerated the dissolution, the former amine allowing dissolution after 9 h rather than the 46 h required for the reaction without added amine (Table II). With TEA as an additive, the dissolution was incomplete after 96 h. The three remaining amines tested had little effect on the dissolution time. The HPSEC trace of the CTC prepared from reaction in DMSO in the presence of DMA had a tailing peak similar to those already discussed.

Reduction of DP of high molecular weight cellulose samples during carbanilation in DMSO was reported in our earlier paper,[10] and this DP reduction is exacerbated by the presence of amines in the reaction mixtures (Table I). The $\bar{P}_w$ and $\bar{P}_n$ values obtained for the CTC from the carbanilation reaction in the presence of NMI were remarkably low; the difference in the HPSEC traces for this product and for the product of reaction in DMSO without added amine are illustrated in Figure 3.

The reasons for the reduction in DP of bleached cotton linters cellulose during carbanilation reactions in DMSO are not clear. DMSO is a known oxidant,[24] and could possibly be oxidizing some cellulose hydroxyl groups, rendering the glucosidic

Figure 3   HPSEC elution curves for cotton linter CTCs prepared in DMSO at 60°C (lower curve a) and in 0.2 M NMI in DMSO at 60°C (upper curve b).

Table III   Properties of Carbanilation Solvents

Solvent	Dieletric Constant[a]	Electron Donor Number[b]
DMSO	46.6	29.8
Pyridine	12.3	33.1
DMF	36.7	26.6
DMAc	37.8	27.8

[a] Data from Ref. 26.
[b] Data from Ref. 27.

linkages more susceptible to cleavage. However, the FT-IR spectra of the depolymerized CTC samples were not different from those of authentic CTC samples. In particular, there were no additional carbonyl absorptions in the spectra, which would be expected in an oxidized product. The nitrogen contents of the depolymerized CTC samples were those expected for a CTC. The scope of the depolymerization of cellulose during carbanilation in DMSO with amines has been examined further[25] and has not revealed details of the reaction mechanism.

The factors responsible for the chromatographic behavior of the four CTC samples from bleached cotton linters that had tailing HPSEC peaks could not be ascertained. The FT-IR spectra and nitrogen contents were those of an authentic CTC, and the reactions when replicated gave products with identical chromatographic characteristics, as did the CTC prepared from cotton linters in pyridine–DABCO resubjected to the carbanilation reaction. In general terms, tailing chromatography peaks occur when there is heterogeneous adsorption between the solute and the chromatographic medium; in this case the medium is a nonpolar crosslinked polystyrene, and the column could be exhibiting reverse-phase behavior. This would require the four CTC samples to have different solution properties than the normal CTC samples.

From these results and those obtained earlier,[10] the efficacy of the solvents for the carbanilation reaction of cellulose decreases in the order DMSO $\gg$ pyridine $>$ DMF $\approx$ DMAc. It has been proposed[11] that solvents with high dielectric constants are particularly effective for promoting urethane formation. Later, Chang and Chen[12] concluded that the efficacy of solvents in the reactions is related to their electron donor number. Both of these characteristics for the carbanilation solvents tested are given in Table III, and they show no relationship to the ability of the solvents to assist the reaction of phenylisocyanate

Table IV   Ionization Constants K_a of Protonated Amine Ions in DMSO at 25°C

Amine	pK_a
DABCO	8.9[a]
TEA	8.4[b]
NMI	6.2[c]
DMA	2.5[a]

[a] Ref. 28.
[b] Ref. 29.
[c] Ref. 30.

with cellulose. Instead, the rate of dissolution of cellulose during the carbanilation reaction is probably governed by the rate or extent of swelling of the cellulose by the medium.

The efficacies of the amine additives in the carbanilation reactions have earlier been correlated with their basicities in water.[11] A series of pK_a measurements of amines in DMSO have been made[28-30] and are given for the amines tested in this study in Table IV. There is no correlation between these values and the ability of the amines in DMSO to assist the carbanilation reaction of cellulose; thus although TEA has a relatively high pK_a value, it has a negative effect on the dissolution of cellulose in carbanilation, whereas DMA did not retard the dissolution, even though it had a low pK_a value. However, it should be pointed out that the pK_a values relate to the *basicities* of the amines and not necessarily their *nucleophilicities*,[31] and the reactivities of the amines could be a consequence of their nucleophilicities.

CONCLUSIONS

The amines DABCO and DMAP accelerated the dissolution of cellulose during carbanilation, and DABCO in pyridine assisted the carbanilation of cellulose samples, which were otherwise unreactive in pyridine. However, there were several disadvantages of amine addition to the carbanilation mixtures:

1. The phenylisocyanate was consumed in amine-catalyzed conversion to its trimer phenylisocyanurate, especially in DMSO and DMF media.
2. Some of the amines tested retarded the carbanilation reactions.

3. Carbanilation in DMSO for the amorphous cellulose and mercerized cellulose samples was faster in DMSO than in pyridine/DABCO.
4. CTCs from amine-catalyzed reactions of cotton linters in DMSO had lower DP values, especially with N-methylimidazole as the added amine.
5. Some CTCs from amine-catalyzed reactions had HPSEC peaks that tailed. This effect was not due to incomplete carbanilation.

On the basis of these elements, it was concluded that amines have only limited value as additives to carbanilation reactions of cellulose.

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. 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. L. Lloyd, C. A. White, A. P. Brookes, J. F. Kennedy, and F. P. Warner, *Brit. Polym. J.*, **19**, 313 (1987).
9. T. Rantanen and J. Sundquist, *Tappi*, **70**(9), 109 (1987).
10. R. Evans, R. H. Wearne, and A. F. A. Wallis, *J. Appl. Polym. Sci.*, **37**, 3291 (1989).
11. K. C. Frisch and L. P. Rumao, *J. Macromol. Sci. Revs. Macromol. Chem.*, **C5**(1), 103 (1970).
12. M.-C. Chang and S.-A. Chen, *J. Polym. Sci., Polym. Chem. Ed.*, **25**, 2543 (1987).
13. S. Dabi and A. Zilka, *Eur. Polym. J.*, **16**, 95 (1980).
14. D. M. Hall and J. R. Horne, *J. Appl. Polym. Sci.*, **17**, 3727 (1973).
15. L. I. Kutsenko, V. V. Gromova, and N. I. Klenkova, *Zh. Prikl. Khim.*, **47**, 1838 (1974).
16. G. Höfle, W. Steglich, and H. Vorbrüggen, *Angew. Chem. Int. Ed.*, **17**, 569 (1978).

17. E. F. V. Scriven, *Chem. Soc. Rev.,* **12,** 129 (1983).

18. K. A. Connors and N. K. Pandit, *Analyt. Chem.,* **50,** 1542 (1978).

19. T. Ito, M. Wada, and S. Suzuki, Japan. Kokai 78 40,097, (1978).

20. J. H. Wild and F. E. G. Tate, U.S. Patent 3,144,452 (1964).

21. J. I. Jones and N. G. Savill, *J. Chem. Soc.,* 4392 (1957).

22. R. H. Atalla, J. D. Ellis, and L. R. Schroeder, *J. Wood Chem. Technol.,* **4,** 465 (1984).

23. D. K. Hoffman, *J. Cell. Plast.,* **20,** 129 (1984).

24. L. F. Fieser and M. Fieser, *Reagents for Organic Synthesis,* Wiley, New York, 1967, p. 296.

25. R. Evans, R. H. Wearne, and A. F. A. Wallis, *J. Appl. Polym. Sci.,* **42,** 821–827 (1991).

26. J. A. Dean, *Lange's Handbook of Chemistry,* 13th ed., McGraw-Hill, New York, 1985, Chap. 10, p. 103.

27. V. Gutmann, *Angew. Chem. Int. Ed.,* **9,** 843 (1970).

28. R. L. Benoit, D. Lefebvre, and M. Fréchette, *Can. J. Chem.,* **65,** 996 (1987).

29. A. Mucci, R. Domain, and R. L. Benoit, *Can. J. Chem.,* **58,** 953 (1980).

30. R. L. Benoit, D. Boulet, L. Séguin, and M. Fréchette, *Can. J. Chem.,* **63,** 1228 (1985).

31. C. Reichart, *Solvents and Solvent Effects in Organic Chemistry,* 2nd ed., Verlag-Chemie, New York, 1988, p. 213.