

NMR Studies of Urea-Formaldehyde Resins

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Synopsis

A procedure used for analyzing urea-formaldehyde resins by NMR spectroscopy was developed. Using this procedure, the condensation of dimethylolurea under acidic and alkaline conditions was studied. It was confirmed that polymerization under acidic conditions proceeds via the formation of methylene linkages and under alkaline conditions, via the formation of dimethylene ether groups. The more highly condensed water-soluble urea resins were found to contain hemiformal groups, which could be quantitatively determined. Two butylated urea-formaldehyde resins with varying degrees of butylation were also studied and were found to differ in the number of methylene and dimethylene ether groups and degree of butoxylation. Both were found to contain hemiformal groups. The resin with lower degree of butylation was also found to contain dimethyl ether linkages. None of the resins studied showed any detectable amounts of fully substituted amide groups.

INTRODUCTION

The structure of urea-formaldehyde resins has been investigated by infrared spectroscopy,^{1,2,3} paper^{4,5,6} and thin-layer^{7,8} chromatography, and degradative techniques.⁹ They have been found to contain methylol (CH_2OH), butoxy (CH_2OBu), methylene (NCH_2N), dimethylene ether ($\text{NCH}_2\text{OCH}_2\text{N}$), and amide (CONH , CONH_2) groups. The quantitative determination of these groups has been attempted by volumetric¹⁰⁻¹³ and colorimetric¹⁴ techniques. The object of this work was to study the chemical structure of water-dispersed and butylated urea-formaldehyde resins. NMR spectroscopy was selected for this study because of simplicity and ease and also because this method requires minimum chemical treatment of samples under study. The analytical procedures developed and the results of examination of several urea resins are presented and discussed.

EXPERIMENTAL

Seven urea resins were prepared, as standards for analysis. Each of these were acetylated, ethoxylated or butylated and the NMR spectra of the resins and derivatives obtained. The procedure used for these are described below. The volumetric procedures used as necessary adjuncts are also given:

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Synthesis of Urea-Formaldehyde Resins

Synthesis of Dimethylolurea (UF-1). Aqueous formaldehyde (36%), 2.2 moles, was buffered with 5 g $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, and to it 1.0 mole urea was added. The reaction mixture was refluxed for 60 min and then neutralized with CO_2 . A precipitate was formed upon cooling, which was collected into a filter paper and washed with cold water and then dried.

Synthesis of Dimethylolurea Dimethyl Ether (UF-2). Into 100 g water containing 5% CH_2O , 10% K_2SO_3 was dissolved 60 g UF-1 at 60°-70°C. The reaction mixture was refluxed for 60 minutes and then condensed by distillation under atmospheric pressure until a heavy precipitate was formed. The precipitate was collected by filtration and dried.

Synthesis of Dimethylolmethylenurea (UF-3). Into 100 g neutralized solution of 5% CH_2O in water were added 60 g UF-1 and 10 g urea. The reaction mixture was acidified with HCOOH to pH 5.0 and refluxed for 60 min. At the end of this period, the reaction mixture was neutralized and distilled under vacuum until a paste remained in the vessel. This paste was freeze dried.

Synthesis of UF Resin, Formaldehyde-To-Urea Mole Ratio 1.7 (UF-4). Aqueous formaldehyde (44%), 1.7 moles, was buffered with triethanolamine to pH 7.5, and to it 1.0 mole urea was added. The reaction mixture was refluxed for 45 min and then acidified with HCOOH to pH 5.0. The reaction was allowed to proceed until the resin had a Brookfield viscosity of 100 cps. At this point, it was neutralized and condensed to a thick paste by vacuum distillation. This paste was then freeze dried.

Synthesis of UF Resin, Formaldehyde-To-Urea Mole Ratio 2.2 (UF-5). This resin was synthesized following the same procedure used for UF-4, except that the molar ratio of formaldehyde to urea was 2.2.

Synthesis of Butylated UF Resin (BUF-1). Formcell containing 40% CH_2O and 60% butanol was adjusted to pH 4.5 with phosphoric acid. To 150 g neutralized Formcell there were added 35 g butanol and 60 g urea. A decanter filled with water-saturated butanol was attached to the reaction vessel. The reaction mixture was heated so that the binary butanol-water distilled into the decanter. After 30 g water was collected, the reaction was stopped by cooling. The butylated UF resin had a Brookfield viscosity of 2100 cps and a xylene tolerance of 300% by weight.

Synthesis of Butylated Resin (BUF-2). This resin was synthesized following the same procedure used for BUF-1, except that no additional butanol was added and the reaction was stopped when 20 g H_2O was collected. The final viscosity of BUF-2 was 3000 cps, and its xylene tolerance was 80% by weight.

Preparation of Derivatives for NMR Analysis

One or more of the following derivatives of the above-listed urea-formaldehyde resins were prepared as follows:

Acetylation. The resin (2 to 3 g) was dissolved in acetic anhydride (5 g) and pyridine (10 g). The mixture was heated to 40°C for 90 min.

Ethoxylation or Butoxylation, with Ether Splitting. The resin (2 to 3 g) was dissolved in excess alcohol (ethanol or butanol) containing 5% phosphoric acid. The mixture was heated at 40°C for 40 min, neutralized with alcoholic KOH, and excess alcohol was removed by flash evaporation.

Volumetric Analysis

All of the UF resins were analyzed for free formaldehyde using the sodium bisulfite method¹⁰ and for total formaldehyde using a degradation method.¹¹ The nonbutylated water-soluble UF resins were analyzed for methylol groups by iodometric titration.¹⁰

NMR Spectra

The spectra were obtained using a Varian A-60 spectrograph. Samples were dissolved in deuterated dimethyl sulfoxide (DMSO), using nondeuterated DMSO as an internal standard. No solvent addition was found necessary for the acetylated samples, as the samples were already in noninterfering solvents, namely, pyridine and acetic acid.

RESULTS

Typical NMR spectra of water-dispersable UF resins and their acetylated and ethoxylated (with ether splitting) derivatives are given in Figure 1. The NMR spectra of butylated UF resins and their acetylated and butoxylated (with ether splitting) derivatives are given in Figure 2.

The NMR chemical shifts (PPM) and the corresponding functional groups assigned to them are given in Table I. The water-dispersable UF resin gave an NMR spectrum with three distinct peaks. The first two peaks, with chemical shifts 6.6 and 5.7, were assigned to substituted (—NH) and nonsubstituted (—NH₂) amide groups, respectively. The concentrations of unsubstituted (NH₂), of monosubstituted (—NH), and of disubstituted amide groups (N) can then be calculated from the following equations:

$$(\text{NH}_2) = 3 \frac{(\text{DMSO})}{A_{2.5}} A_{6.4}$$

$$(\text{NH}) = 6 \frac{(\text{DMSO})}{A_{2.5}} A_{5.6}$$

$$(\text{N}) = 2 (\text{urea}) - (\text{NH}) - (\text{NH}_2)$$

where (urea) represents the original concentration of urea. The third peak, with a chemical shift 4.7, must contain the remaining groups that is, ethers, methylols, and hemiformals.

The butylated UF resin gave three peaks, in addition to the three mentioned above. These were assigned to the three nonequivalent proton groups of the butyl function.

In the NMR spectra of the acetylated samples, the peak area at 4.7 decreases by an amount corresponding to the OH protons in the methylol groups. Additional peaks, attributed to pyridine (6.6–7.5 and 7.8–8.5) and CH_3COO (1.9), appear; the absorption due to $\text{C}_3\text{H}_7\text{CH}_2\text{O}$ — gives two

TABLE I
Chemical Shifts of Functional Groups in UF Resins*

Functional group	Chemical shift ppm, δ	Peak area	Peak shape
— $\text{CH}_2\text{NHCONHCH}_2$ —	6.4–6.8	$A_{6.4}$	broad
— $\text{CH}_2\text{NHCONH}_2$	5.6–5.9	$A_{5.6}$	broad
— $\text{CH}_2\text{NHCONHCH}_2\text{OH}$	4.4–5.0	$A_{4.6}$	unresolved
— $\text{CH}_2\text{NHCONHCH}_2\text{O}(\text{CH}_2\text{O})_3\text{CH}_2\text{OH}$	4.4–5.0	$A_{4.7}$	unresolved
— $\text{CH}_2\text{NHCONHCH}_2\text{NHCONHCH}_2$ —	4.4–5.0	$A_{4.7}$	unresolved
— $\text{CH}_2\text{NHCONHCH}_2\text{OCH}_2\text{NHCONHCH}_2$ —	4.4–5.0	$A_{4.7}$	unresolved
— $\text{CH}_2\text{NHCONHCH}_2\text{OC}_4\text{H}_9$	4.4–5.0	$A_{4.7}$	unresolved
— $\text{CH}_2\text{NHCONHCH}_2\text{OC}_2\text{H}_5$	4.4–5.0	$A_{4.7}$	unresolved
$\text{C}_4\text{H}_9\text{OH}$	4.4–5.0	$A_{4.7}$	unresolved
— $\text{CH}_2\text{NHCONHCH}_2\text{OCH}_2\text{CH}_3$	3.0–3.2	$A'_{3.0} A''_{3.0}$	quartet
— $\text{CH}_2\text{NHCONHCH}_2\text{OCH}_2\text{CH}_3$	1.6–1.8	—	triplet
— $\text{CH}_2\text{NHCONHCH}_2\text{C}_2\text{H}_4\text{CH}_3$	3.0–3.2	$A'_{3.0} A''_{3.0}$	triplet
— $\text{CH}_2\text{NHCONHCH}_2\text{OCH}_2\text{C}_2\text{H}_4\text{CH}_3$	1.0–1.5	—	broad multiplet
— $\text{CH}_2\text{NHCONHCH}_2\text{OCH}_2\text{C}_2\text{H}_4\text{CH}_3$	0.7–1.0	—	broad triplet
$\text{C}_3\text{H}_7\text{CH}_2\text{OH}$	3.0–3.2	$A'_{3.0} A''_{3.0}$	triplet
$\text{C}_3\text{H}_7\text{CH}_2\text{OOCCH}_3$	3.5–3.7	$A'_{3.5}$	triplet
$(\text{CH}_3\text{CO})_2\text{O}$	2.0	—	singlet
CH_3COO —	1.9	—	singlet
$(\text{CH}_3)_2\text{SO}$ (DMSO)	2.5	—	singlet
Pyridine (1)	6.6–7.5	—	broad multiplet
Pyridine (2)	7.8–8.5	—	broad multiplet

* A : NMR peak area of the original samples; A' : NMR peak area of the acetylated samples; A'' : NMR peak area of the ethoxylated samples; *Solvent systems*: for original samples, DMSO; for ethoxylated samples, DMSO; for acetylated samples, pyridine-acetic anhydride-acetic acid.

peaks due to $\text{C}_3\text{H}_7\text{CH}_2\text{O}$ — and $\text{C}_3\text{H}_7\text{CH}_2\text{OAc}$ at 3–3.3 and 3.5–3.7, respectively. The difference in the peak areas at 4.7 between the acetylated ($A_{4.7}$) and nonacetylated ($A'_{4.7}$) samples can therefore be used to determine the protons in the hydroxyl groups or to calculate the total number of methylol groups, in either water-dispersible or butylated UF resins, as follows:

$$X = 6 \frac{(\text{DMSO})}{A_{2.5}} A_{4.7} - \frac{(\text{Ac})}{A_{2.0}} A'_{4.7}.$$

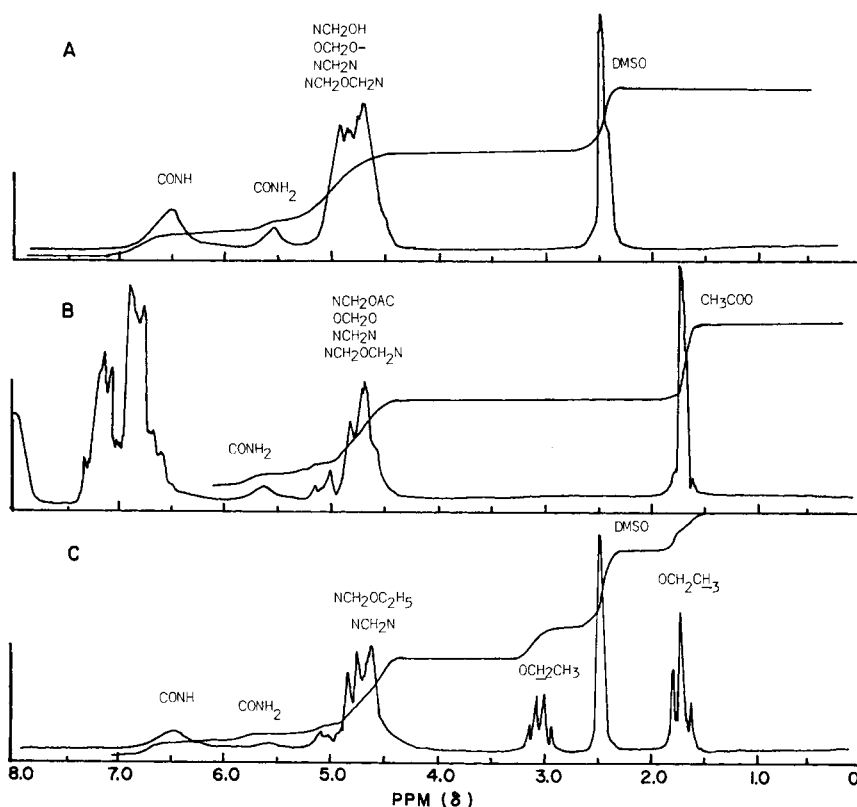


Fig. 1. NMR spectra of water-dispersible UF resins: (A) untreated; (B) acetylated; (C) ethoxylated, with ether splitting.

In butylated resins, the number of free butanol (W) and of butylated methylol groups (V) are given by

$$W = 3 \frac{(\text{Ac})}{A'_{2.0}} A'_{3.0}$$

$$V = 3 \frac{(\text{Ac})}{A'_{2.0}} A'_{3.5}$$

The ethoxylation of the water-dispersible UF resins is accompanied by ether splitting. Consequently, each ether group in the polymer backbone and in the hemiformal side chain gives rise to two ethoxy groups, and each methylol gives rise to one ethoxy group. These are picked up at 3–3.2 as a quartet. For butylated resins, it is more convenient to accomplish the same analysis by butoxylation, the butoxy group showing up at 3–3.2 as a triplet. The total number of ether groups (U) attached to the —NH group can then be obtained as follows:

$$U = \frac{3(\text{Ac})}{A'_{2.0}} A'_{4.7} - 8(\text{urea}) + 2(\text{NH}) + 2(\text{NH}_2) + X.$$

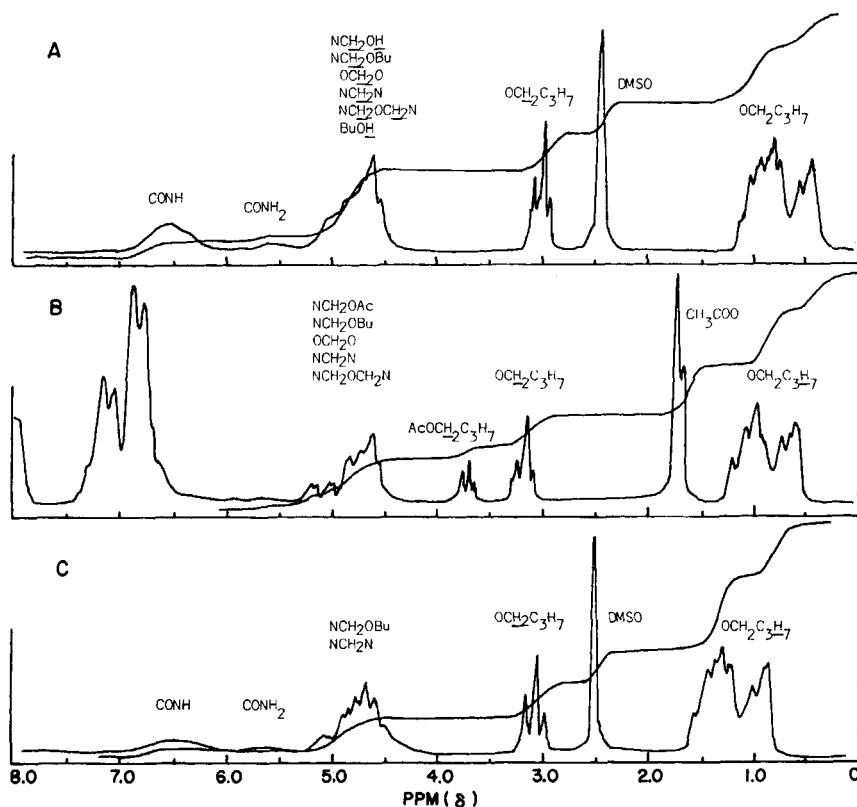


Fig. 2. NMR spectra of butylated UF resins: (A) untreated; (B) acetylated; (C) butoxylated, with ether splitting.

Using X , U , V , and W , the number of hemiformal groups (Y) can be calculated:

$$Y = 3 \frac{(\text{DMSO})}{A''_{2.5}} A''_{3.0} - X - 2U - V - W.$$

From the number of $-\text{NH}$ groups, the CH_2OH groups, and the total number of CH_2O groups in the ether and hemiformal chains, it is now possible to calculate the total number of $-\text{CH}_2$ linkages (Z):

$$Z = 8(\text{urea}) - 2(\text{NH}) - 4(\text{NH}_2) + U.$$

DISCUSSION

Previous analytical results on UF resins have shown that these resins contain methylol, methylene, dimethylene ether, amide, and butoxy (whenever a butylated UF has been investigated) groups. These groups have been determined quantitatively or semiquantitatively by infrared spectroscopy and quantitatively by volumetric and colorimetric techniques.

The results obtained from this NMR study (Table II) not only confirmed

the existence of the aforementioned functional groups, but also revealed the existence of hemiformal groups. Thus, it was found that in several resins the total concentration of combined formaldehyde exceeded the sum of concentrations of substituted amide groups. The difference was assigned to the only alternative, which was thought to be the hemiformal structure. The NMR quantitative results were compared with those obtained from volumetric techniques, and a good agreement was found as far as the concentrations of methylol groups and total formaldehyde are concerned. Furthermore, the previously reported indication that dimethylene ether linkages are formed usually under alkaline conditions⁹ was verified by our NMR work. Namely, the polymerization of dimethylolurea under alkaline conditions gave UF-2, which was found to contain no methylene groups (CH_2). However, the resin depolymerized under acidic ethoxylation and butoxylation, yielding corresponding $-\text{CH}_2\text{OEt}$ or $-\text{CH}_2\text{OBu}$ groups which were determined by NMR, and lead to the conclusion that the linkages consist of dimethylene ether groups.

TABLE II
Quantitative Determination of Functional Groups in Urea-Formaldehyde Resins*

Functional group	Concentration of functional group, moles/1000 g						
	UF-1	UF-2	UF-3	UF-4	UF-5	BUF-1	BUF-2
NMR analysis							
$[\text{CH}_2\text{OH}]$	1.65	1.20	1.05	0.40	0.54	0.070	0.245
$[\text{CH}_2\text{O}-]$	0	0	0	0.25	0.35	0.076	0.100
$[\text{CH}_2]$	0	0	0.40	0.50	0.40	0	0.040
$[\text{CH}_2\text{OCH}_2]$ by EtOH	0	0.25	0	0.08	0.08	—	—
$[\text{CH}_2\text{OCH}_2]$ by BuOH	—	0.20	0	—	—	0	0.020
$[\text{CH}_2\text{OBu}]$	—	—	—	—	—	0.670	0.540
$[\text{BuOH}]$	—	—	—	—	—	0.184	0.160
$[\text{NH}_2]$	0	0	0.27	0.24	0.10	0.020	0.115
$[\text{NH}]$	1.64	1.68	0.85	1.56	1.50	0.740	0.885
$[\text{N}]$	0	0	0	0	0	0	0
Volumetric Analysis							
$[\text{CH}_2\text{O}]$ total	1.67	1.75	1.78	1.51	1.70	0.830	0.970
$[\text{CH}_2\text{O}]$ free	0.03	0.02	0.08	0.20	0.30	0.014	0.025
$[\text{CH}_2\text{OH}]$	1.63	1.28	1.00	0.54	0.70	—	—

* For key to urea-formaldehyde resins, see text.

The resin produced by polymerizing dimethylolurea (UF-1) under acidic conditions, namely UF-3, was found to contain methylene linkages. Its ethoxylated derivative was found to contain ethoxy groups corresponding to the methylols in this resin, UF-3. Consequently, it can be concluded that the resin formed under acidic conditions contains no dimethylene ether groups and that the methylene linkages in the polymer do not cleave under the conditions of ethoxylation.

The two water-soluble resins, UF-4 and UF-5, and the two butylated resins, UF-6 and UF-7, may be considered typical of the variety of resins used in industry.

Table II shows that UF-5, with a higher formaldehyde content than UF-4, contained a higher concentration of methylol and hemiformal groups and a lower concentration of methylene and unsubstituted amide groups. The above structure difference of UF-4 and UF-5 was reflected in the higher stability and lower reactivity of UF-5. It is interesting to note that the concentration of ether groups is very low for both resins.

Of the butylated resins, BUF-1, with higher butanol content, contained a higher concentration of butoxy groups and a lower concentration of methylol, hemiformal, and unsubstituted amide groups. This resin (BUF-1) was found to contain no methylene or dimethylene ether groups. Together with the high concentration of butoxy groups, the resin shows a higher xylene tolerance.

The presence of methylene and dimethylene ether groups in BUF-2 shows that the resin polymerized during butylation under acidic conditions. That is, the initial concentration of butanol was not sufficient to depress the competing condensation reaction. As a result of this and a lower degree of butoxylation, BUF-2 showed a much lower xylene tolerance than BUF-1. The presence of dimethylene ether groups in BUF-2 is interesting since it should not have been expected under acidic conditions. However, it is conjectured that they have been formed by the following reaction:



Furthermore, it is interesting to note that in all resins the concentration of disubstituted amide groups was zero. Apparently, the formaldehyde content in all these resins was not sufficiently high for the formation of tri- and tetramethylolureas.

Notation

The following concentrations are expressed in number of moles per 100 g resin:

(NH ₂)	concentration of unsubstituted amide groups
(NH)	concentration of monosubstituted amide groups
(N)	concentration of disubstituted amide groups
(X)	concentration of methylol groups
(Y)	concentration of hemiformal groups
(Z)	concentration of methylene groups
(U)	concentration of dimethylene ether groups
(V)	concentration of butylated methylol groups
(W)	concentration of free butanol
(urea)	concentration of urea segments
(Ac)	concentration of acetyl groups
(DMSO)	concentration of dimethyl sulfoxide

The following NMR peak areas were obtained from the NMR spectra of the original samples:

- $A_{6.4}$ area of the NMR peak at 6.4 ppm
- $A_{5.6}$ area of the NMR peak at 5.6 ppm
- $A_{4.7}$ area of the NMR peak at 4.7 ppm
- $A_{2.5}$ area of the NMR peak at 2.5 ppm

The following NMR peak areas were obtained from the NMR spectra of the acetylated samples:

- $A'_{4.7}$ area of the NMR peak at 4.7 ppm
- $A'_{3.5}$ area of the NMR peak at 3.5 ppm
- $A'_{3.0}$ area of the NMR peak at 3.0 ppm
- $A'_{2.0}$ area of the NMR peak at 2.0 ppm

The following NMR peak areas were obtained from the NMR spectra of the ethoxylated samples:

- $A''_{3.0}$ area of the NMR peak at 3.0 ppm
- $A''_{2.5}$ area of the NMR peak at 2.5 ppm

We wish to thank the National Research Council of Canada for partial support of the project through an IRAP grant.

References

1. H. J. Bercher, *Chem. Ber.*, **89**, 1593 (1956).
2. H. J. Bercher, *Chem. Ber.*, **89**, 1951 (1956).
3. Naoki Yoshimi, Tsuyoshi Yamanchi, Masayoshi Yamao, and Shigeyuki Tanaka, *Kogyo Kagaku Zasshi*, **65**, 1131 (1962).
4. Masao Inoue and Michiharu Kawai, *Nogoyashi Kogyo Kenkyusho*, **16**, 1 (1957).
5. Masatada Hamada, *J. Chem. Soc., Japan, Ind. Chem. Sect.*, **58**, 286 (1955).
6. M. Cheme, D. Morel, and M. Dubourgeau, *Papeterie*, **87**, 264 (1965).
7. C. Di Bello and E. Celon, *J. Chromatogr.*, **31**, 77 (1967).
8. G. Valk and K. Schliefer, *Textilindustrie*, **69**, 783 (1967).
9. G. Zigeuner, *Fette, Seifen, Anstrichm.*, **56**, 973 (1954).
10. J. F. Walker, *Formaldehyde*, Reinhold, New York, 1964, p. 489.
11. P. P. Grad and R. J. Dunn, *J. Anal. Chem.*, **25**, 1211 (1953).
12. S. Kappelmeier, C.P.A. Amer. Chem. Soc. Meeting, Boston, 1958.
13. J. I. De Yong, **72**, 653 (1953).
14. M. H. Swann and G. G. Esposito, *J. Anal. Chem.*, **30**, 107 (1958).
15. J. Van Zuylen, *J. Oil Colour Chem Ass.*, **52**, 861 (1969).
16. R. H. Glauert, *Ind. Chem.*, 392 (August 1957).
17. S. M. Smetz, *J. Polym. Sci.*, **3**, 371 (1951).

Received March 1, 1971

Revised April 8, 1971