

Hydroxymethylation and Polycondensation Reactions in Urea–Formaldehyde Resin Synthesis

Peep Christjanson,¹ Tõnis Pehk,² Kadri Siimer¹

¹Department of Polymer Materials, Tallinn University of Technology, Tallinn, 19086, Estonia

²National Institute of Chemical Physics and Biophysics, Tallinn, 12618, Estonia

Received 15 March 2005; accepted 29 September 2005

DOI 10.1002/app.23782

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Formaldehyde–urea (F/U) reaction products with molar ratios of 1.8, 2.1, and 2.4 were synthesized at pH 8.3, and the last one also at pH 4.5 using 45% formaldehyde aqueous solution. For obtaining the resin, the synthesis of F/U 2.1 was continued by acid-catalyzed condensation at pH 4.5 and posttreatment with second part of U (F/U 1.05/1) at 70°C and pH 8.3. The products were analyzed using ¹³C-NMR spectrometry. Higher excess of F increases the dihydroxymethyl content on account of smaller dimethylene ether content. Certain ¹³C chemical shifts in carbonyl and methylene region of spectra were assigned to trishydroxymethylurea, being the main trisubstituted urea compound in hydroxymethylated product. Acid catalyst promotes the formation of methylene groups by polycondensa-

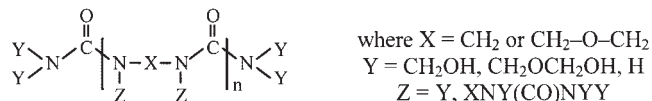
tion of hydroxymethyl groups, against the background of similar content of dimethylene ethers in both catalytic conditions. The ratio of linear/branched chains is emphasized in characterizing the resin structure. Higher hydroxymethyl content in acid-catalyzed polycondensation is an advantage of three-step synthesis technology. The amount of binding methylene and dimethylene ether groups linked only to secondary amino groups can be increased by transhydroxymethylation with subsequent polycondensation in posttreatment with U in suitable reaction conditions. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1673–1680, 2006

Key words: thermosets; resins; polycondensation; structure; NMR

INTRODUCTION

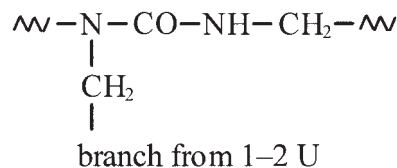
Urea–formaldehyde (UF) resins have been extensively used in industry for binding wood particles with adhesive spots or for lamination of wood plies with continuous adhesive film.¹ High reactivity and low cost are the main attractive properties of the application of UF resins. The problems arise from the reversibility of aminomethylene bond causing the low resistance of UF resins against water and formaldehyde (F) emission from hardened resins. To overcome that, very low formaldehyde/urea ratio (down to 1.03) in synthesis is used, as a compromise between lower F emission and poor mechanical properties of adhesive joints. Despite that, in-door conditions are preferred for UF resins' use.

Regardless of the fact that UF resin is synthesized only from two reactive components, the broad variety of reactions in synthesis, storage, and curing makes this object quite attractive for research. Chemical structure of UF resins can be described as hydroxymethylated methylene (methyleneether) urea.



Many researchers regard ¹³C-NMR spectroscopy as the best analytical tool for the quantitative determination of functional groups in UF polycondensates.^{2,3} In fact, it is not possible to determine exactly the oligomeric species to which these groups are linked. Despite that, the average macromolecule is described as consisting of 6–7 linearly bound structural units of which 3–4 are substituted with branches having 1–2 ureas, and containing about 6 functional end groups of which 2–3 are bishydroxymethyl groups.^{4,5}

The preferred fragment of UF resin can be represented as follows:



Some peculiarities of UF resin structure formation are as follows:

- Trifunctionality of U in reaction with F is observed in weak acid resin formation conditions.^{6,7} Strong acid conditions mostly are avoided for

Correspondence to: P. Christjanson (peep.christjanson@ttu.ee).

restricting the formation of uronic structures causing the higher F emission, lower reactivity and mixing ability of resins.^{8,9,10}

- The branching of macromolecules with methylenes adjacent to trisubstituted amino groups occurs only in acid condensation.¹¹
- The formation of dimethylene ethers in alkaline hydroxymethylation of U was known much time before the use of NMR analysis.¹²
- The substitution degree in U decreases because of methylene formation during acidic polycondensation, causing the liberation of F from hydroxymethyl and dimethylene ether groups.^{12,13}
- The equilibrium between methylene and dimethylene ether binding groups prevails over other structure characterizing factors. In case of methanol containing F solution, the methoxymethylene groups should be considered as part of ether constituent.¹¹
- The low amount of crosslinking groups in the structure of resins should be divided uniformly. Acidic polycondensation can be regarded as a part of polycondensation. The migration of bound F from resinous part to secondary added U (transhydroxymethylation), alongside the U reaction with free F, is an obligatory structure forming stage.^{5,11}
- The conditions of posttreatment with U are important, as higher temperature ($>60^{\circ}\text{C}$) promotes the migration of hydroxymethyls and subsequently the reactions between functional groups of resinous and monomeric parts.¹⁴
- Insufficient migration in posttreatment favors, at storage of green resin, the formation of methylene diurea, which in excess is not a very desired component in resin.^{11,14}

Today, the three-step procedure for synthesis of UF resins is mostly used. The accumulation of maximum amount of hydroxymethyl groups occurs during alkaline reaction with excess of F. In case of finely elaborated synthesis, the precise constitution of hydroxymethylated ureas should be characterized. In this study, changing the U/F ratio in possible limits, three hydroxymethylated products were synthesized. The analysis was carried out by ^{13}C -NMR method, described previously.¹¹

It can be thought that the synthesis of UF resins is possible to accomplish without changing the pH during the process. Alkaline conditions in synthesis and storage never produce the branched structures through the tertiary substituted amino groups.¹¹ Despite the gelation, the cured adhesive gives only poor mechanical properties. Hence, the acid polycondensation is an inevitable procedure of resin synthesis. Very low pH (about 1) is not suggested, as the content of uron rings increases.⁸ For comparison, the reaction

product at pH about 4.5 was also prepared and analyzed. In this case, the excessive branching may be the problem. Some additional data about resin analysis were used for the discussion of the properties of first-formed hydroxymethylated products, in close connection with the constitution of final resins.

Unfortunately, the analysis can be performed on the level of different functional groups including only the short-range influence of substituents of neighboring atoms. The effects of the shape of chains and molar mass distribution remain out of discussion.

EXPERIMENTAL

Synthesis

Industrial grade 45% formaldehyde aqueous solution was used with a stirred reactor (1 L) to synthesize three hydroxymethylated products with F/U molar ratios of 1.8, 2.1, and 2.4. pH of F solution was adjusted to 8.2–8.3 with 20% NaOH solution, and temperature was raised to 40°C . The selected amount of reagent grade U was added in small portions for 15 min, bringing the temperature to 80°C . The hydroxymethylation was carried by heating for 30 min at the temperature of $(80 \pm 1)^{\circ}\text{C}$.

The molar ratio $\text{F/U} = 2.4$ was used to obtain the reaction product, without the first step hydroxymethylation. pH of F solution was adjusted to 4.5, and U was added in three portions (50, 25, and 25%) at 10-min intervals, maintaining the temperature near 80°C . Reaction was terminated by rapid cooling after 30 min procedure.

The hydroxymethylation product $\text{F/U} = 2.1$ was also used for obtaining the resin by traditional procedure. pH was adjusted to 4.5 with formic acid, and the polycondensation was accomplished at $(90 \pm 1)^{\circ}\text{C}$ for 100 min. After that, the reaction was terminated by setting the pH to 8.5 at rapid cooling to $60\text{--}70^{\circ}\text{C}$. Equal to the first one, the other portion of U was added, and heat-treatment for hydroxymethyl migration to secondary added urea was carried out at temperature 70°C for 2 h.

^{13}C -NMR spectroscopy

^{13}C -NMR spectra of synthesized products were obtained on a Bruker AMX500 NMR spectrometer with ^{13}C frequency at 125.77 MHz at 25°C from DMSO-d_6 solutions using a 5-mm ^{13}C - ^1H dual probehead. Spectra were accumulated into 32,000 data points and processed using exponential multiplication with 2 Hz line broadening into 128,000 spectra. For the resulting spectra, 25,000–35,000 scans were accumulated. All spectra were accumulated at identical conditions, using power gated Waltz decoupling with 25 degree measurement pulse and 1 s prepulse delay. Quantita-

TABLE I
Molar Distribution (%) of Structural Elements in F/U Reaction Products on the Basis of ^{13}C NMR Spectra

Assignment		Typical signal (ppm)	Alkaline hydroxymethylation			pH ~ 4.5	Resin F/U (1.05/1)
			Molar ratio F/U				
			2.4/1	2.1/1	1.8/1	2.4/1	
Methylenes		Σ	0	1.2	3.8	14.4	36.2
—NH—CH ₂ —NH—		47–48	—	0.8	2.8	6.4	19.3
—NH—CH ₂ —N <		53–54	—	0.4	1.0	7.7	14.9
>N—CH ₂ —N<		60–61	—	0	0	0.3	2.0
Hydroxymethyls		Σ	68.8	65.0	64.2	33.2	46.1
—NH—CH ₂ OH		65–66	50.0	49.2	50.1	22.0	41.7
—N(CH ₂)—CH ₂ OH } —N(CH ₂ OH) ₂ }		71–72	18.8	15.8	14.1	11.2	4.4
Dimethylene ethers		Σ	18.0	21.2	21.6	22.5	15.2
—NH—CH ₂ OCH ₂ —NH—		69–70	15.9	17.9	18.6	18.3	13.0
—NH—CH ₂ OCH ₂ —N(CH ₂)—		74.5–75.5	2.1	3.3	3.0	4.2	2.2
Methoxymethylenes		Σ	1.2	1.5	1.7	2.3	2.0
—NH—CH ₂ OCH ₃		73–74	0.3	1.0	1.4	2.2	1.3
—N(CH ₂)—CH ₂ OCH ₃ + urons		79–80	0.9	0.5	0.3	0.1	0.7
Methylene ether glycols		83–95	12.0	11.2	8.7	27.6	0.5
Carbonyl region	Free urea	162	0.9	2.2	4.5	0.8	17.9
	Monosubstituted urea	160–161	19.2	30.2	38.5	35.2	50.1
	Disubstituted urea	159–160	64.8	57.0	48.6	{64.0	32.0
	Trisubstituted urea	158.5–159.0	15.1	10.6	8.4		

tive information on changes of different structural elements was obtained by the manual integration routine of XWINNMR 2.1 software.

RESULTS AND DISCUSSION

Hydroxymethylation in case of different formaldehyde/urea ratio

The main approach to influence the structure of UF resins involves the change in F/U ratio and pH in the first step reaction. An excess of F is needed for getting the high concentration of hydroxymethyl groups. Only in this case it is possible to obtain the resins with suitable technical characteristics, e.g., reactivity and processability. On the basis of integral intensities in ^{13}C -NMR spectra, the distribution of F between different compounds in the region of 40–100 ppm was determined (Table I). In carbonyl region (150–165 ppm), the resolution depends on substitution differences in urea. Some useful ratios and amounts of different species have been calculated (Table II).

The ratio F/U of 1.8/1 is already out of optimum technology because of high condensation rate, and a somewhat altered technology should be used in resin synthesis to minimize turbidity.¹⁴ Contrary to that, molar ratio of F/U higher than 2.5/1 leaves great amount of free F in hydroxymethylation. Because of equilibrium reaction, the trishydroxymethylurea as pure compound can be obtained only with a great excess of F and has nothing common with the actual F/U ratio in resin synthesis. The following polycon-

densation rate is too low and should be raised with lower pH. It is not suitable, as the amount of uron rings increases. So, the best attention is given to the F/U molar ratio between 2 and 2.5. The initial weak acid condition should be considered as variant. Molar ratio of 2.4/1 was suitable for comparison of the products synthesized by both catalytic conditions. Very high polycondensation rate should be mitigated with initial large excess of F (here 4.8/1) and by gradual addition of U in small portions.⁷ Despite that the accumulation of hydroxymethyl ureas is quite low. The acid polycondensation without preliminary alkaline hydroxymethylation fosters the trisubstitution in U by the formation of branched chains. Compatibility with water and adhesion properties of resins are lower (e.g. Ref. 1).

Because of the equilibrium reaction, quite a great amount of F remains unbound with U (Table I), and an increase in bound F is, to a great extent, not suitable. The resolution in the range of 83–91 ppm occurs, depending on different polymerization degree of poly(methylene ether) glycol. Thus, the distinct methylene ^{13}C chemical shifts are assigned for methylene glycol (83.5 ppm), for dimethylene ether glycol and hydroxymethyls of oligomers (87–87.5 ppm), and for in-chain methylene ether groups (91 ppm) (Fig. 1). The ratio of integral intensities of signals refers to different polymerization degree and is strongly dependent on dimethylene ether glycol amount. The amounts of hydroxymethyls and in-chain methylene ethers in different products are similar (44–53% and 16–21% ac-

TABLE II
Some Characteristics of Urea/Formaldehyde Reaction Products

Assignment	Alkaline reaction			pH ~ 4.5	Resin (1.05/1 ^a)
	2.4/1 ^a	2.1/1 ^a	1.8/1 ^a	2.4/1 ^a	
Ratio —NH—CH ₂ OH/—N(CH ₂ OH) ₂	2.7	3.1	3.6	2.0	9.5
Ratio —CH ₂ OH/—CH ₂ —O—CH ₂ —	3.8	3.1	3.0	1.5	3.0
Ratio —CH ₂ —/—CH ₂ —O—CH ₂ —	0	0.06	0.18	0.64	2.4
Ratio —CH ₂ OH/—CH ₂ — + —CH ₂ —O—CH ₂ —	3.8	2.9	2.5	0.90	0.90
Ratio —N(CH ₂ OH) ₂ /—CH ₂ — + —CH ₂ —O—CH ₂ —	1.05	0.71	0.56	0.30	0.09
Ratio >N—CH ₂ —/—NH—CH ₂ —	0.33	0.29	0.25	0.48	0.32
Same, without —CH ₂ OH	0.18	0.21	0.19	0.49	0.59
HO—CH ₂ —NH—CO—N (%F)	7.4	6.2	4.8	4.2	2.8
Same, in TMU, %F	6.3	5.0	4.7	—	—
—N(CH ₂ OH) ₂ in TMU (%F)	12.6	10.1	9.3	—	—
Ratio mono/di + tri	0.24	0.45	0.68	0.55	1.6
Ratio tri/di	0.23	0.19	0.17	—	—
Ratio mono/di	0.30	0.53	0.79	—	—
1,1-BMU (%U)	7.5	6	4.5	—	—
Signal at 159.1 ppm (1,3-BMU) (%U)	39	31	21	—	—
NH ₂ —CO—NH— (160 ppm) (%U)	4.9	7.2	8.6	—	—
Dimethylene ethers (159.2–159.3 ppm) (%U)	16	17	18	—	—
Signal at 160.3 ppm (MMU) (%U)	14	23	27	—	25

^a Molar ratio (F/U).

cordingly) and have no clear dependence on molar ratio. The content of methylene glycol is higher in case of lower molar ratio. In the presence of acid catalyst, more signals in ranges of 88–91 and 86–87.5 ppm are obtained (Fig. 2). Their assignment to certain oli-

gomers is complicated. On the whole, the acid catalyst promotes the depolymerization to methylene glycol (37%) and dimethylene ether glycol (18%), and the remaining part consists mostly of trimers and tetramers of methylene glycol (Fig. 2). The signals in the

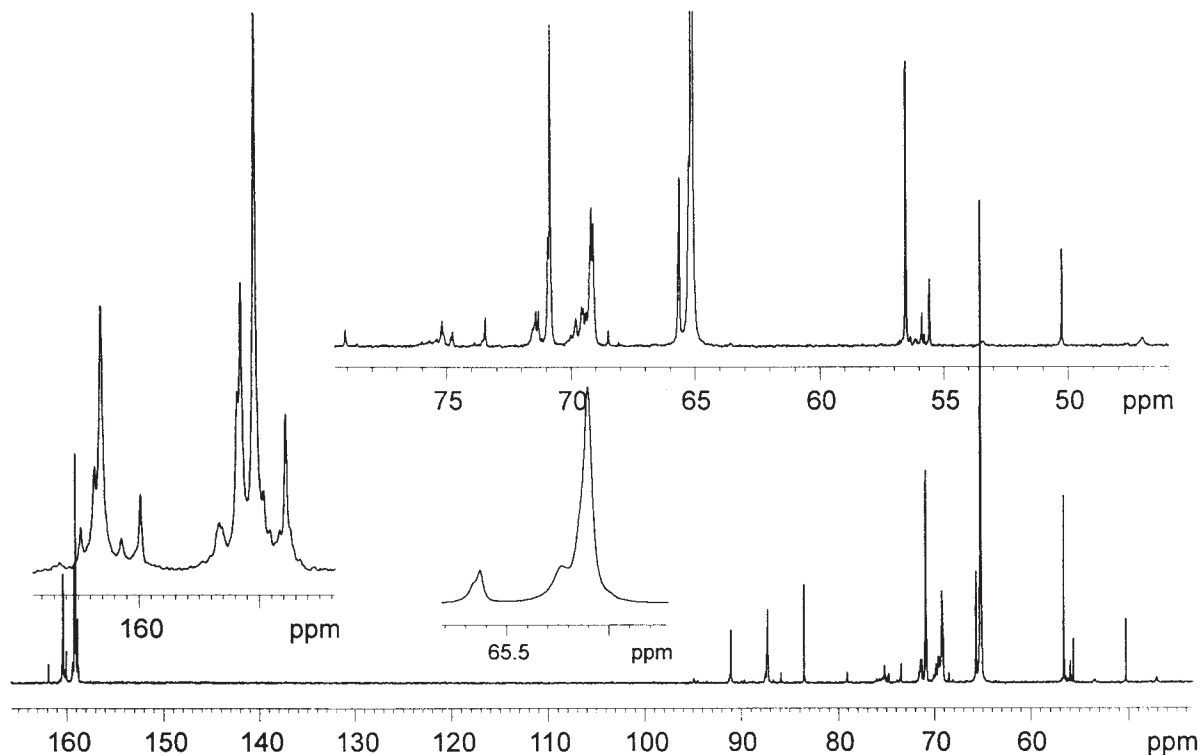


Figure 1 ¹³C-NMR spectrum in DMSO-d₆ of hydroxymethylated urea, obtained at pH 8.2–8.3 with formaldehyde/urea molar ratio of 2.1.

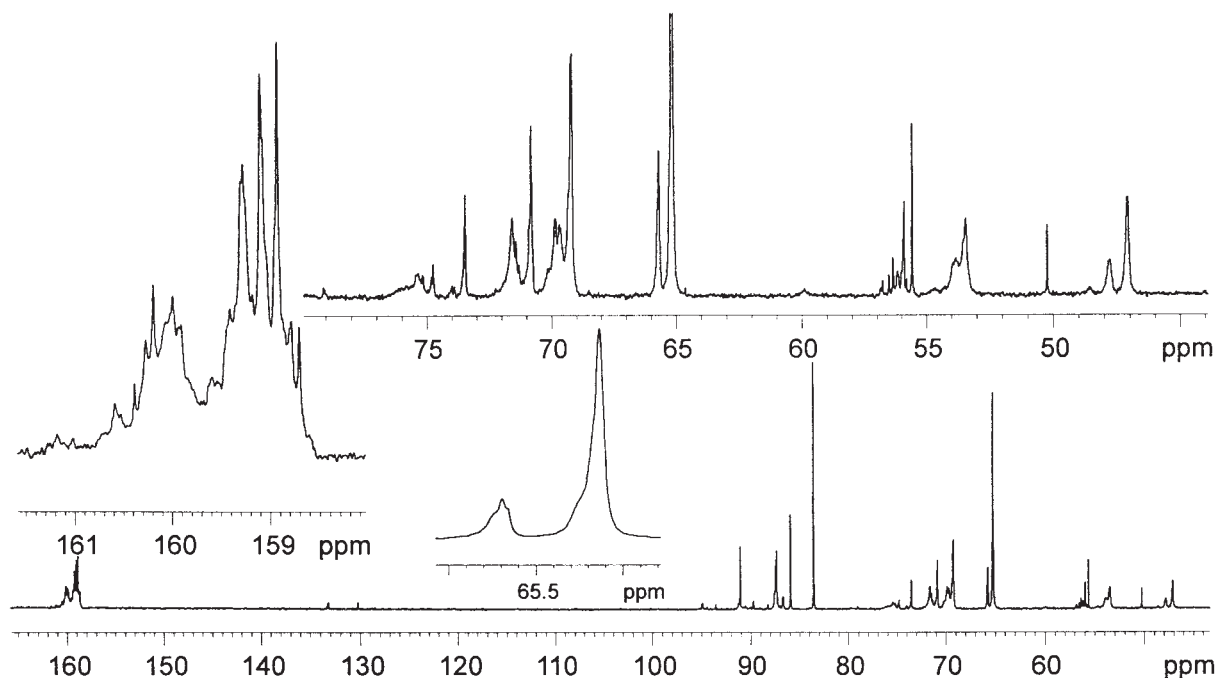


Figure 2 ^{13}C -NMR spectrum in DMSO-d_6 of reaction product, obtained with formaldehyde/urea molar ratio of 2.4 at pH 4.5.

range of 94–95 ppm (1.5–2%) belong to methoxymethylenes because of the use of F solution containing some amount of methanol. It is clear that, in the synthesis of UF resins, the rate of reactions depends on the concentration of F solution, but no direct relationship between oligomeric constitution of poly(methylene ether) glycol and synthesis characteristics was observed.

Surely, 1,3-bishydroxymethylurea (BMU) is the main constituent of hydroxymethylated product because of the preferred substitution in both amino groups of urea. Actually, quite complicated mixture of different compounds is formed. There are some distinct characteristics depending on molar ratio of F/U (Table I). The whole amount of hydroxymethyl groups increases with greater F/U ratio. The peculiarity is that it happens only with hydroxymethyls linked to the tertiary amino group. The amounts of other hydroxymethyl groups are quite different (Table II). Unfortunately, because of very small difference in chemical shifts, it is not possible to get the amounts of BMU and monohydroxymethylurea (MMU) directly from the signal at 65.1 ppm (Fig. 1) or to divide this amount between hydroxymethylureas and end groups of chains. Also, it can only be supposed that hydroxymethyls linked to trisubstituted amino groups are in monomers or in polymeric chains. The in-chain hydroxymethyl groups are also possible in principle. In case of weak acid reaction due to subsequent polycondensation, the content of hydroxymethyl groups is about two times lower, and the relative amount of hydroxymethyls linked to trisubstituted amino groups is higher.

A certain amount of methoxymethylene groups is formed on account of methanol added sometimes as the stabilizing component to F solution. No methoxymethylene groups have been noticed in synthesis using the industrial grade 50% F solution kept at 60°C (e.g. Ref. 14). Evidently this F solution contains no methanol. In our case, 45% F solution was used, which may contain the different amounts (up to 4%) of methanol. Quite low amount of methoxymethylene groups, in this case (Table I), does not essentially influence on the results. Some amount of methoxymethylene groups (up to 0.5%) can also arise from F reduction in resin synthesis.

Polycondensation

In resin synthesis conditions, pure hydroxymethylation is not possible. The formation of methylene groups is clearly preferred only in strong acid conditions (e.g., pH = 1). Both alkaline and weak acid conditions favor the formation of dimethylene ethers (Table I). Certainly the amount of methylenes, linked to tertiary amino groups, increases in acid catalysis as the sign of higher branching. There is a diminishing tendency in the amount of dimethylene ethers, with increase in F/U ratio in alkaline conditions (Table I). Mostly, ethers are formed during the polycondensation of BMU. It means that greater F/U ratios promote the formation of bishydroxymethyls from dimethylene ethers. From the other side, the direct participation of bishydroxymethyls in the formation of dimeth-

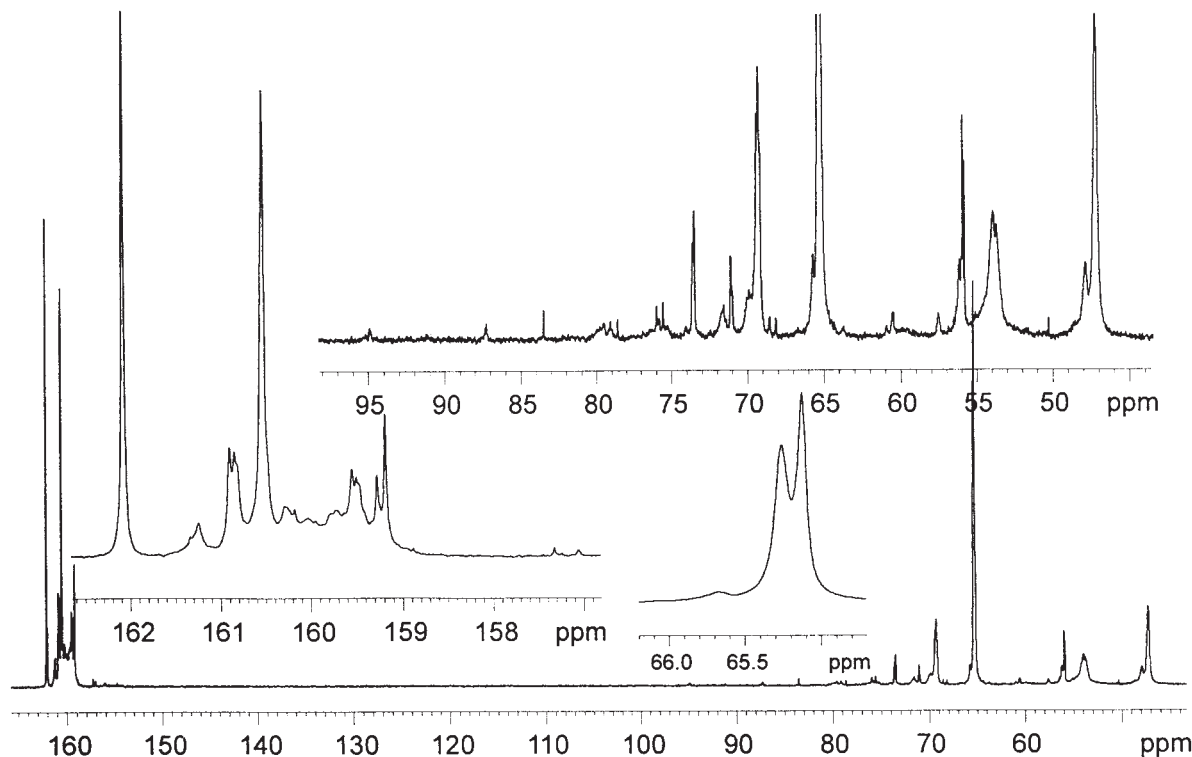
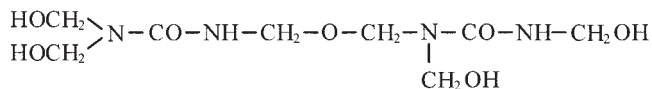


Figure 3 ^{13}C -NMR spectrum in $\text{DMSO}-d_6$ of resin obtained from hydroxymethylated urea (Fig. 1) after polycondensation at pH 4.5 and posttreatment at pH 8.5 with second part of urea.

ylene ethers should be low because of preferred F release. The trend to polycondensation in alkaline conditions is mostly connected with the substitution degree in U. Remarkable here is the similar content of dimethylene ethers in both catalytic conditions. Hence, the catalytic conditions influence mostly on the formation of methylene groups from the hydroxymethyl groups, on the background of different amounts of methylene ether glycols. The probabilities of hydroxymethylation and polycondensation reactions are best revealed by the ratio of different functional groups (Table II).

Predominantly, in alkaline conditions, the monosubstitution in amino groups of U occurs (e.g., BMU and MMU). The majority of trisubstituted U occurs as trishydroxymethylurea (TMU). In addition, the chains end with hydroxy- or bishydroxymethyl groups. All functional species include some amount of that linked to tertiary amino group (Table I). One example can be pictured as follows:



The ratio of integral intensities of signals for all methylene containing groups linked to tertiary and secondary amino groups decreases with the lower F/U ratio (Table II). This ratio is not very characteristic because

of the decisive role of the content of bishydroxymethyl groups, which is greater in case of higher F/U ratio. The mentioned ratio is higher in acid-catalyzed reaction, because of increased amount of methylene groups linked to tertiary amino group (Table I; 8% from F).

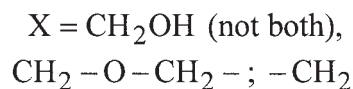
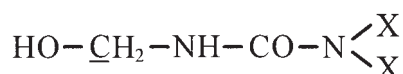
Assignments of ^{13}C signals for urea in carbonyl region of spectra

Integral intensities of ^{13}C signals for urea carbonyls are assigned according to the substitution differences. In Figure 3, the carbonyl region of ^{13}C spectrum is presented for the resin obtained by the classical three-step synthesis procedure. The content of free urea can be calculated quite exactly on the basis of signal at 161.8 ppm. The separation to monosubstituted urea and di/trisubstituted urea compounds is not so certain. The distinctive chemical shift at 159.9 ppm was chosen for the following calculations.

The simpler constitution of hydroxymethylation products allows to use the carbonyl region more successfully. The signal at 158.8 ppm for trisubstituted urea (Fig. 1), almost not met in spectra of UF resin, belongs to TMU. This conclusion is drawn by the coincidence of chemical shifts for typical components in both products—for MMU at 160.3 ppm and for BMU at 159.1 ppm (Figs. 1 and 3). In the spectrum of UF resin, where the trisubstituted U occurs in more

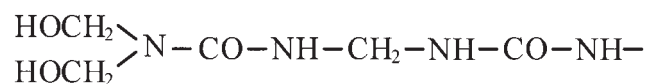
complicated species, the typical signals appear in lower field and are not resolved from other signals (Fig. 3). In the calculation of the constitution on the basis of carbonyl region, it was presumed that TMU is the only component containing trisubstituted U (Table I). The resolution to mono- and disubstituted U is quite clear (Fig. 1). In the presence of acid catalyst (Fig. 2), the spectrum is more complicated. It is not comparable with others, as quite a high content of dimethylene ether and methylene groups is obtained at high F excess (ratios in Table II). Here, there is even the problem of evaluating the amount of monosubstituted urea, not to mention the resolution of di- and trisubstituted urea.

The increase in F/U ratio results in lower content of free and monosubstituted urea and higher content of di- and trisubstituted urea (Table I). The increase in content of TMU is more pronounced. Knowing the amount of TMU from the carbonyl region, some other contents can be calculated approximately. The presence of TMU is revealed, in methylene region, by two signals for hydroxymethyls with twofold difference in intensity (Fig. 1). The content of bishydroxymethyl groups for TMU (Table II) obtained from carbonyl region covers 64–67% from hydroxymethyls linked to trisubstituted amino group (Table I). Hence, the signal at 70.8 ppm (Fig. 1) can be assigned to TMU. From TMU content, the amount of hydroxymethyl adjacent to secondary amino group (65.6 ppm in Fig. 1) is directly known. It covers more than 80% of the content of mentioned groups (Table II). The remaining part belongs to end group of branched structure pictured as follows:



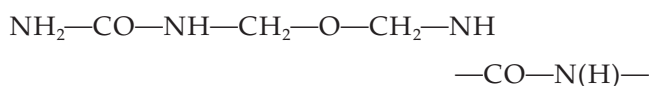
The extension with chains containing dimethylene ether groups is one variant giving the signals at 74.5–75.5 ppm (Fig. 1). From the structure of signal at 71–72 ppm, it can be concluded that there should also be some other species containing hydroxymethyl group linked to tertiary amino groups. The content of these compounds was calculated as 1,1-bishydroxymethylurea (1,1-BMU) (Table II). Considering dimethylene

ether and methylene groups in hydroxymethylation product, one more complicated variant should be presented as well:

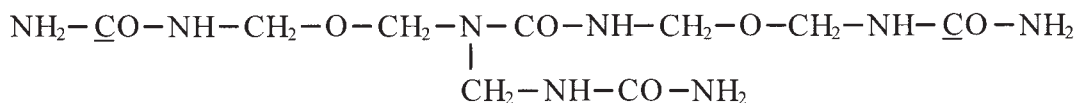


In principle, one can compare the amount of dimethylene ethers proceeding from methylene region (Table I) or carbonyl region by characteristic signals at 159.2–159.3 ppm (Fig. 1). Quite similar contents are obtained (Tables I and II). The contents of BMU and MMU can be evaluated from the carbonyl region (signals at 159.1 and 160.3 ppm), but are slightly overestimated because of uncomplete resolution from signals for other compounds.

MMU covers the most part of monosubstituted urea. We cannot see here (Fig. 1) the characteristic signal at 160.8 ppm for the other possible compound, methylenediurea (MDU), which is a typical compound in UF resin after treatment with secondary added U (Fig. 3). In acid-catalyzed product, the role of polycondensation is higher, and MDU is the constituent (Fig. 2). Also the structure of signal at 47–49 ppm² shows that acid promotes the formation of longer and more complicated chains besides MDU. The other significant signal can be met at 160 (incl. 160.1) ppm (Fig. 1), the integral intensity of which lessens with higher F/U molar ratio in alkaline reaction conditions (Table II). This signal is assigned to the end urea of chains and can be presented in the following way:



It is understandable, considering the trend in content of dimethylene ether groups in hydroxymethylation products. Since the chains are quite short, this amount can be evaluated as low, and dimethylene ethers mostly contain hydroxymethyl end groups. Otherwise, essentially greater signal intensity at 159.7–160.1 ppm is obtained in acid-catalyzed synthesis (Fig. 2). High amount of unbound F and greater condensation degree at the same F/U ratio lead to substantially higher content of monosubstituted U (Table I). At a two times lower hydroxymethyl content and high amount of dimethylene ether groups, the chains include branches that are terminated with singly bonded urea rather than with hydroxymethyl group. One of the commonly occurring structure can be presented in the following way:



Structure of UF resins

Despite the success in ^{13}C -NMR analysis, the question remains unsolved how to divide the hydroxymethyl groups between BMU and end groups of chains. The posttreatment with U increases the amount of MDU and methylene-containing oligomers (Fig. 3; by 160.8–160.6 ppm 12% from U) in resin. It causes relative increase in the intensity of signal at 47 ppm, in comparison with signals at 48–49 ppm in methylene region. The structure of signal from methylenes adjacent to secondary amino groups refers to the ratio of linear/branched chains. The signal at 48–49 ppm appears mostly from $-\text{NH}-\text{CH}_2-\text{NH}-$ fragment of chain containing also the branch linked to the following tertiary amino group of U.

The product obtained in weak acid conditions (Fig. 2) in technology of resin synthesis becomes more complicated in additional polycondensation. About two times higher amount of methylene groups is needed for normal rheological properties. The excess of methylenes adjacent to tertiary amino groups increases in acid-catalyzed polycondensation. It means that the resins obtained by polycondensation without preliminary accumulation of hydroxymethyl groups are of other structural characteristics. Practical experiences show that the resins do not suffer the long-time posttreatment with U and gather viscosity more quickly at storage.

The lowered F/U ratio in posttreatment (Table I) causes the migration of bound F to monomeric part. It is indispensable for obtaining the even distribution of crosslinking groups in final structure of cured resins. The content of 4–5% of hydroxymethyls, adjacent to tertiary amino groups (mostly bishydroxymethyls), is the sign of proper extent of migration of hydroxymethyls (Table I). The posttreatment increases the amount of monosubstituted U compounds, including MMU, MDU (Fig. 3; about 50%). The changes at 159.1–159.8 ppm (Figs. 2 and 3) refer to decrease in amount of di/trisubstituted U including BMU and dimethylene ethers (159.1–159.2(3) ppm), and appearance of methylene-containing structures with di/trisubstituted U having the characteristic signals for carbonyl groups at 159.5–159.8 ppm (Fig. 3). The reaction between MMU and U in combination with MDU (characteristic signal at 160.8 ppm) as well reduces the amount of free U in resin. Finally, it follows that the resins with alkaline hydroxymethylation step have another but more purposeful distribution of methylene groups (Table I and resins in Ref. 11).

CONCLUSIONS

1. The accumulation of high content of hydroxymethyl groups is possible only in alkaline hydroxymethylation with excess of F to U (2.4–2.1/1) before acidic polycondensation.
2. Higher excess of F increases the amount of bishydroxymethyl groups in place of the condensation of hydroxymethyl groups to dimethylene ethers.
3. Trishydroxymethylurea as constituent of hydroxymethylated mixture was identified by ^{13}C chemical shifts at 158.8 ppm in carbonyl region and at 70.8 and 65.6 ppm in methylene region of NMR spectra.
4. Dimethylene ether oligomers of hydroxymethylation product are ended mostly with hydroxymethyl groups and rarely with singly bound urea groups.
5. Only acid catalyst promotes the formation of branched chains with methylenes linked to tertiary amino groups.
6. Transhydroxymethylation from bishydroxymethyl groups to urea is the most important temperature-promoted process of posttreatment with secondary added urea.
7. The amount of methylene and dimethylene ether groups linked to secondary amino groups increases essentially in alkaline posttreatment by condensation between hydroxymethyl groups and amino groups of urea.

References

1. Dunky, M.; Pizzi, A. In *Adhesion Science and Engineering: Surfaces, Chemistry and Applications*; Pocius, A. V.; Dillard, D. A.; Chaudhury, M., Eds; Elsevier: Amsterdam, The Netherlands, 2002; Vol. 2, p 1039.
2. Tomita, B.; Hatano, S. *J Appl Polym Sci* 1978, 16, 2509.
3. Kim, M. G.; Amos, L. W. *Ind Eng Chem Res* 1990, 29, 208.
4. Kim, M. G. *J Polym Sci Part A: Polym Chem* 1999, 37, 995.
5. Kim, M. G. *J Appl Polym Sci* 2001, 80, 2800.
6. Soulard, C.; Kamoun, C.; Pizzi, A. *J Appl Polym Sci* 1999, 72, 277.
7. Park, B. D.; Kim, Y. S.; Singh, A. P.; Lim, K. P. *J Appl Polym Sci* 2003, 88, 2677.
8. Hse, C. Y.; Xia, Z. Y.; Tomita, B. *Holzforchung* 1994, 48, 527.
9. Gu, J. Y.; Higuchi, M.; Morita, M.; Hse, C. Y. *Mokkuzai Gakkai-shi* 1995, 41, 1115.
10. Gu, J. Y.; Higuchi, M.; Morita, M.; Hse, C. Y. *Mokkuzai Gakkai-shi* 1996, 42, 149.
11. Christjanson, P.; Siimer, K.; Pehk, T.; Lasn, I. *Holz als Roh- und Werkstoff* 2002, 60, 379.
12. de Jong, J. I.; de Jonge, J. *J Rec Trav Chim* 1952, 71, 643, 661, 891.
13. Siimer, K.; Pehk, T.; Christjanson, P. *Macromol Symp* 1999, 148, 149.
14. Kim, M. G.; No, B. Y.; Lee, S. M.; Nieh, W. L. *J Appl Polym Sci* 2003, 89, 1896.