

Structure formation in urea-formaldehyde resin synthesis

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Abstract. The structure formation in acid promoted polycondensation and particularly in alkaline post-treatment with urea was studied by ¹³C NMR spectroscopy in the three-step synthesis of urea-formaldehyde resins. Trishydroxymethyl urea was identified as the constituent of the mixture of hydroxymethylated urea derivatives obtained in alkaline conditions. The formation of methylenes linked to secondary or tertiary amino groups occurs only in acidic conditions by branching chains in the reaction with mono- and 1,3-bishydroxymethyl urea. Bishydroxymethyl groups do not take part in acid promoted polycondensation. The final structure of resins depends mostly on the migration of formaldehyde from bishydroxymethyl groups to urea with formation of monohydroxymethyl urea as the first preferred compound. A greater amount of oligomers with methylenes adjacent to secondary amino groups and containing singly bonded urea is a sign of a thorough heat treatment. A steady content of methylenes linked to tertiary amino groups is observed in heat treatment and ageing of resins.

Key words: thermosets, urea-formaldehyde resins, polycondensation, ¹³C NMR spectroscopy, structure.

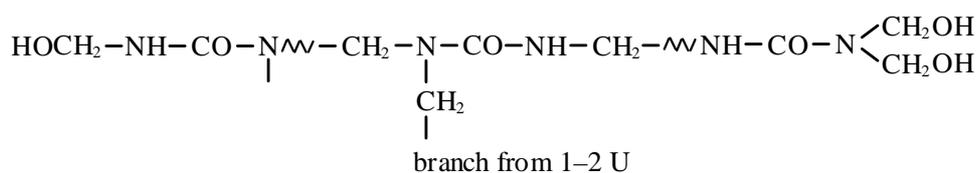
INTRODUCTION

Urea-formaldehyde (UF) resins are the main binders for wood composite boards, such as particleboards, fibreboards, or hardwood plywood [1]. In the use of UF resins, water solubility, good adhesion, high curing rate, and low cost are the attractive properties. Their drawbacks are low water resistance and emission of formaldehyde from wood boards, resulting from the low stability of the amino-

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methylene bond. The key parameter in the decrease of formaldehyde emission is lowering the formaldehyde/urea (F/U) ratio in the synthesis of UF resins to 1.05. This leads to a reduction in the content of crosslinking groups in cured UF resins, lowering the strength and water resistance of adhesive joints in boards.

Although the UF resins are synthesized only from two reactive components (urea and 45–50% aqueous solution of formaldehyde), the variety of reactions in synthesis, storage, and curing make them quite an attractive object for research. Changing synthesis conditions of resins provides relatively good possibilities of designing the structure and technical properties of resins [2–6]. Very broadly, the chemical structure of UF resins can be specified as poly(methylene methylene ether hydroxymethylureas). This definition leaves the details of structure undetermined and, in fact, we have a mixture of different linear and mostly branched macromolecules characterized by the average molar mass (or molar mass between branches) and the content of different functional groups. The fragment statistically occurring most frequently can be pictured as follows:



Despite the use of highly recognized ^{13}C NMR for the characterization of resins, their quantitative analysis is limited by the content of different functional groups [7, 8]. The differences in chemical shifts are obtained according to mono- or disubstitution in amino groups, e.g. 1-hydroxymethyl and 1,1-bishydroxymethyl groups or methylenes (methylene ethers), linked to the secondary or the tertiary amino group. At the same time, it is not possible to determine exactly the oligomeric species to which these groups are linked. The low functionality of U is a problem in resin formation conditions. The well-known trifunctionality of U described as a property of amide of amino acid cannot be realized in synthesis due to reversibility and sterical hindrances. So the actual functionality attainable in the synthesis conditions of UF resins is about 2.5 [6]. The formation of cyclic compounds (e.g. bishydroxymethyl urons) is avoided because of their adverse influence on water compatibility and resin reactivity [9]. Trishydroxymethylurea (TMU) cannot be the main compound of alkaline hydroxymethylation product in the synthesis of UF resins, as the proper molar ratio of F/U in the limits of 2.1–2.4 gives only a slight shift in the equilibrium between monohydroxymethylurea (MMU), bishydroxymethyl (mostly 1,3) urea (BMU), and TMU on the background of unreacted F and condensation products (mostly dimethylene ethers).

The decisive peculiarity in UF synthesis lies in the different realization of trifunctionality of U in the hydroxymethylation reaction and polycondensation [10]. It means that the compounds with tertiary amino groups in alkaline conditions are mostly formed with bishydroxymethyl groups, but in acid conditions branching through substitution in the reaction with hydroxymethyls

occurs as well. Methylene formation causes another mechanism of substitution in U that leads to the liberation of F from hydroxymethyl or dimethylene ether groups. It seems that the ratio between methylene and dimethylene ether binding groups obtained in acid polycondensation [e.g. 2] that does not change in the storing of resins [10] is quite independent from other structural characteristics. Only in the case of methanol containing F solution (37–45%) should the methoxymethylene groups formed be considered as part of the ether constituent [10, 11].

Without any special proof it is clear that the low content of crosslinking methylene (dimethylene ether) groups in cured binders should be distributed as uniformly as possible. The synthesis strategy envisages the post-treatment with the second part of U, which reacts with free F remaining after the condensation step. Part of U remains unreacted acting further as a scavenger for liberated F. It means that in the post-treatment the formation of the monomeric or low molecular mass part occurs as consisting of free U, its hydroxymethyl derivatives (mostly MMU), methylene diurea (MDU), or oligomers. The amounts of resinous and monomeric parts can be regulated by the ratio of U added first and second.

The deepness of acid polycondensation is controlled by the suitable viscosity level. Variations in the pH, temperature, and time within technologically possible limits do not cause essential changes in the structure of resins. At the same time acidic polycondensation can be regarded as only part of the structure formation of the final resin. A quite intensive migration of bound F from polycondensate to U added second (transhydroxymethylation) also occurs [5, 10]. Reversibility of F-containing bonds is a specific feature of UF resins, compared to melamine-formaldehyde resins and ultimately also to phenol(resorcinol) formaldehyde resins [1]. The temperature and time of alkali promoted post-treatment with U added second can be changed. The different extent of migration of hydroxymethyls essentially influences the final structure of resins and their behaviour in storage as the division of functional groups between resinous and monomeric parts is changed [10].

Hence the purpose is to obtain a resin consisting of optimum amounts of resinous and monomeric parts with a balanced content of functional groups. This should guarantee a high stability and curing rate of resins as well as the minimum formaldehyde emission at an acceptable level of mechanical properties of boards.

In this study the three-step procedure for the synthesis of UF resins was used. The technology without alkaline hydroxymethylation by stepwise decrease in the F/U ratio in acid polycondensation was not regarded as the best [12]. The influence of different initial F/U ratios in hydroxymethylation was also discussed previously [6, 13]. In this study the ratio $F/U = 2.1$ was used. The main attention is paid to the structure formation in acid promoted polycondensation and to changes in the structure of final resins due to different post-treatment conditions. The analysis was carried out by the ^{13}C NMR method, described previously [10]. The changes in the content of different functional groups are caused by short-range influences of substituents of the neighbouring groups. The long-range effects of the shape and size of chains on the chemical shifts can be considered only indirectly.

EXPERIMENTAL

Synthesis

As raw materials, industrial grade 45% formaldehyde aqueous solution and urea were used. All syntheses for this study were carried out in a stirred reactor. For obtaining the hydroxymethylated product with the F/U initial ratio of 2.1/1, the pH of the F solution was adjusted to 8.2–8.3 with 20% NaOH solution, and the temperature was raised to 40°C. The urea was added in small portions during 15 min, bringing the temperature to 80°C. The hydroxymethylation was ended by heating during 30 min at 80±1°C. The hydroxymethylated urea was analysed and used for subsequent polycondensation. For that, the pH was adjusted to 4.5 with formic acid and the acid promoted reaction was accomplished at 90±1°C. The time (about 100 min) was adjusted by controlling the increase in viscosity during polycondensation to terminate the reaction at an optimum viscosity level. Three polycondensation products prepared in the same conditions were analysed. For obtaining the resin, the pH was adjusted to 8.5 at rapid cooling to 60–70°C, and another portion of U, equal to the first one, was added (F/U = 1.05). Heat treatment at different temperatures (60–80°C) for 1.5 h (at 80°C for 1 h) for hydroxymethyl migration to U added second was carried out. After that, the dry solids content of the resins was set to 68.5–69.5% by vacuum drying the resins at a temperature not exceeding 40°C. Analysis of resins heat treated at 65–75°C was also carried out after storage during one month.

¹³C NMR spectroscopy

The ¹³C NMR spectra of synthesized products were obtained on a Bruker AMX500 NMR spectrometer with ¹³C frequency at 125.77 MHz at 25°C from DMSO-d₆ solutions by a 5 mm ¹³C-¹H dual probehead. The spectra were accumulated into 32K data points and processed using exponential multiplication with 2 Hz line broadening into 128K spectra. For the resulting spectra 25 000–35 000 scans were accumulated. All spectra were accumulated under identical conditions using power gated Waltz decoupling with 25 degree measurement pulse and 1 s prepulse delay. Quantitative information on changes of different structural elements was obtained by the manual integration routine of XWINNMR 2.1 software.

RESULTS AND DISCUSSION

On the basis of integral intensities in ¹³C NMR spectra the molar distribution of F between various methylene containing functional groups in the region of 40–100 ppm was determined. The resolution taking place in the carbonyl region (150–165 ppm) depends on the substitution differences in urea. Some useful ratios and amounts of different species for the discussion were calculated. The

data showing the changes in the steps of structure formation are presented in Table 1. The influence of post-treatment conditions with U added second on the parameters characterizing the structure is shown in Table 2.

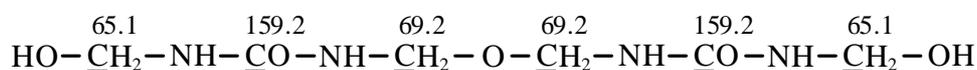
Table 1. Molar distribution of structural elements in F/U reaction products on the basis of ^{13}C NMR spectra

Assignment	Typical signal, ppm	Hydroxymethylated, F/U 2.1	Acid polycondensated, F/U 2.1	Heat treated at 65–75 °C, F/U 1.05/1	Ageing 1 month
Molar % of formaldehyde					
Methylenes, Σ		1.2	27.7–28.4	30.6–36.0	38–45
–NH– $\underline{\text{C}}\text{H}_2$ –NH–	47–49	0.8	6.7–7.4	15.1–19.5	22–27
–NH– $\underline{\text{C}}\text{H}_2$ –N<	53–54	0.4	17.9–18.7	14.7–15.5	15–16
>N– $\underline{\text{C}}\text{H}_2$ –N<	60–61	0	2.3–3.1	1.0–1.8	1–2
Hydroxymethyls, Σ		65.0	33.1–35.5	44.3–52.6	31–40
–NH– $\underline{\text{C}}\text{H}_2\text{OH}$	65–66	49.2	15.4–17.4	40.7–46.3	28–36
–N($\underline{\text{C}}\text{H}_2$)– $\underline{\text{C}}\text{H}_2\text{OH}$	71–72	15.8	17.7–18.1	4.0–6.5	3–4
–N($\underline{\text{C}}\text{H}_2\text{OH}$) $_2$					
Dimethylene ethers, Σ		21.2	13.0–14.0	11.4–15.3	15–17
–NH– $\underline{\text{C}}\text{H}_2$ –O– $\underline{\text{C}}\text{H}_2$ –NH–	69–70	17.9	8.1–8.8	9.0–13.3	13–15
–NH– $\underline{\text{C}}\text{H}_2$ –O– $\underline{\text{C}}\text{H}_2$ –N($\underline{\text{C}}\text{H}_2$)–	74.5–75.5	3.3	4.2–5.9	1.7–2.6	2–3
Methoxymethyls, Σ		1.5	2.6–3.1	3.1–4.4	3–4.5
–NH– $\underline{\text{C}}\text{H}_2$ –OCH $_3$	73–74	1.0	1.1–1.6	2.4–3.2	2.5–4
–N($\underline{\text{C}}\text{H}_2$)– $\underline{\text{C}}\text{H}_2$ –OCH $_3$ + urons	79–80	0.5	1.0–2.0	0.7–1.2	0.8–1.5
Methylene ether glycols	83–95	11.2	20.5–22.1	~0.2	~0.2
Molar % of urea					
Carbonyl region					
Free urea	162	2.2	0	16.2–23.1	12–15
Monosubstituted U	160–161	30.2	–	48–53	54–57
Disubstituted U	159–160	57.0	–	} 28–32	} 31–34
Trisubstituted U	158.5–159 (158.8)	10.6	–		
Ratio in –NH– $\underline{\text{C}}\text{H}_2\text{OH}$	65.6/65–66	12.5	38–40	6–10	6–7
Ratio in –NH– $\underline{\text{C}}\text{H}_2$ –NH–	48–49/47–49	17.3	64–69	22–30	18–21
Ratio in –NH– $\underline{\text{C}}\text{H}_2$ –O– $\underline{\text{C}}\text{H}_2$ –NH–	70/69–70	36.7	65–67	21–40	16–19
Ratio in –N($\underline{\text{C}}\text{H}_2\text{OH}$) $_2$	72/71–72	22.3	54–58	50–56	51–55
NH $_2$ – $\underline{\text{C}}\text{O}$ –NH– $\underline{\text{C}}\text{H}_2$ –NH–, % U	160.6–160.8	–	–	8–15	15–20
NH $_2$ – $\underline{\text{C}}\text{O}$ –NH– $\underline{\text{C}}\text{H}_2$ –O– $\underline{\text{C}}\text{H}_2$ –, % U	159.9–160.1	7.2	–	7–11	9–10
–NH– $\underline{\text{C}}\text{O}$ –NH– $\underline{\text{C}}\text{H}_2$ –O– $\underline{\text{C}}\text{H}_2$ –, % U	159.2–159.3	26.2	–	3–4	3–4
1,3-BMU, % U	159.1	31.0	–	6–8	5–6
MMU, % U	160.3	23.0	–	24–28	18–23

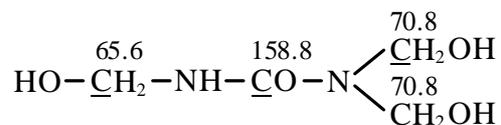
– Indeterminable.

It is often said that the purpose of hydroxymethylation is to obtain 1,3-bis-hydroxymethyl urea (BMU). Actually quite a complicated mixture consisting of mono-, di-, and trisubstituted U compounds is formed. The main monosubstituted U compound is MMU (about 23% of U), unambiguously identified by typical signals at 160.3 ppm ($-\text{CO}-$) and 65.1 ppm ($-\text{CH}_2\text{OH}$). Another mono-substituted U compound identified by the signals at 160.0 ppm ($-\text{CO}-$) and 69.1–69.2 ppm ($-\text{CH}_2-\text{O}-\text{CH}_2-$) can be pictured as follows: $\text{NH}_2-\text{CO}-\text{NH}-\text{CH}_2-\text{O}-\text{CH}_2-\text{NH}-\text{CO}-\text{NH}_2$.

Due to the F excess and alkaline conditions, dimethylene ether formation is the favoured mechanism of condensation. Low intensities at 47–49 ppm ($-\text{NH}-\text{CH}_2-\text{NH}-$) and 160.8–160.6 ppm for singly bonded U verify the insignificant content of methylene containing compounds including MDU. As expected, BMU is the most often occurring compound of the hydroxymethylated mixture. Its content can be evaluated by the signal at 159.1 ppm in the carbonyl region (about 31% of U). Unfortunately, due to very small differences in chemical shifts, it is not possible to get the amounts of BMU and MMU directly from the signal at 65.1 ppm or to divide the hydroxymethyl content between hydroxymethylureas and end groups of chains. The condensation of BMU by the formation of dimethylene ether groups is the most preferred mechanism of condensation in the hydroxymethylated mixture. The appearance of disubstituted urea linked to hydroxymethyl and dimethylene ether groups or only to the latter is a source of new carbonyl signals at 159.2–159.3 ppm (about a quarter of U). Hence, the predominant compound can be identified as follows:



The signals at 159.3 and 69.5–69.8 ppm also refer to longer chains. The distinct signal for trisubstituted U at 158.8 ppm belongs to TMU. It covers about 10% of U. Clearly assigned signals in the methylene region support the conclusion:

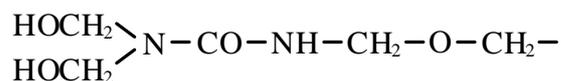


The somewhat greater relative intensities of signals in the methylene region (20–30%) show that more complicated variants of trisubstituted U compounds of the following structure can also be present:



The extension with chains containing dimethylene ether groups is one variant giving the signals at 74.5–75.5 ppm. The structure of the signal at 71–72 ppm

shows that there can be also some other species (about 3.5% of F) containing bishydroxymethyl groups. One variant is 1,1-bishydroxymethyl urea, but the end groups of chains are possible as well:



It is clear that the carbonyl signal from that kind of trisubstituted U compounds moves to the lower field but because of the coincidence with others it cannot be exactly assigned. Despite the presented speculations the amount of compounds with bishydroxymethyl groups besides TMU remains low and is not the main point in the determination of constituents of the hydroxymethylation product.

A certain amount of methoxymethylene groups is formed due to the use of the aqueous solution of F containing some amount of methanol as the stabilizing component. These groups (up to 4% of F) form easily in alkaline conditions and prove to be very stable in the following steps of synthesis.

Polycondensation

The polycondensation products with the used initial F/U ratio (2.1) carried to the proper viscosity level at the determined pH have quite similar constitutions (Table 1). Acid promoted polycondensation processes lead to another substitution model in U. It means that the amount of F not bound in compounds with urea increases about two times. Mostly F liberates from dimethylene ether groups. Surprisingly, bishydroxymethyl groups are not subjected to polycondensation in weak acid conditions. Due to a higher free F level, their equilibrium amount even has an increasing tendency. Certainly, they are linked also to more complicated structures as proved by the change in the ratio of signals at 71–72 ppm (Table 1). At the same time, the content of hydroxymethyl groups in the trisubstituted U compounds remains constant by the signal at 65.6 ppm, forming now up to 40% of the decreased hydroxymethyl content.

Unfortunately the spectrum in the carbonyl region gives few possibilities for thorough conclusions (Fig. 1). Despite that, the distinct signals at 158.8–158.9 ppm support the concept about low reactivity of bishydroxymethyl groups. Methylene formation is the main condensation reaction in acidic conditions. Due to the low content of free amino groups (mostly in MMU) after hydroxymethylation, the direct reaction between hydroxymethyls and amino groups can be regarded as only one possibility for methylene formation. The reaction between hydroxymethyls with subsequent release of F from dimethylene ether is another one. In comparison with disubstitution, the most favoured in acidic conditions is trisubstitution in U. It means that the content of methylenes linked to secondary amino groups remains low (signal at 47–49 ppm) and repeated substitution in one

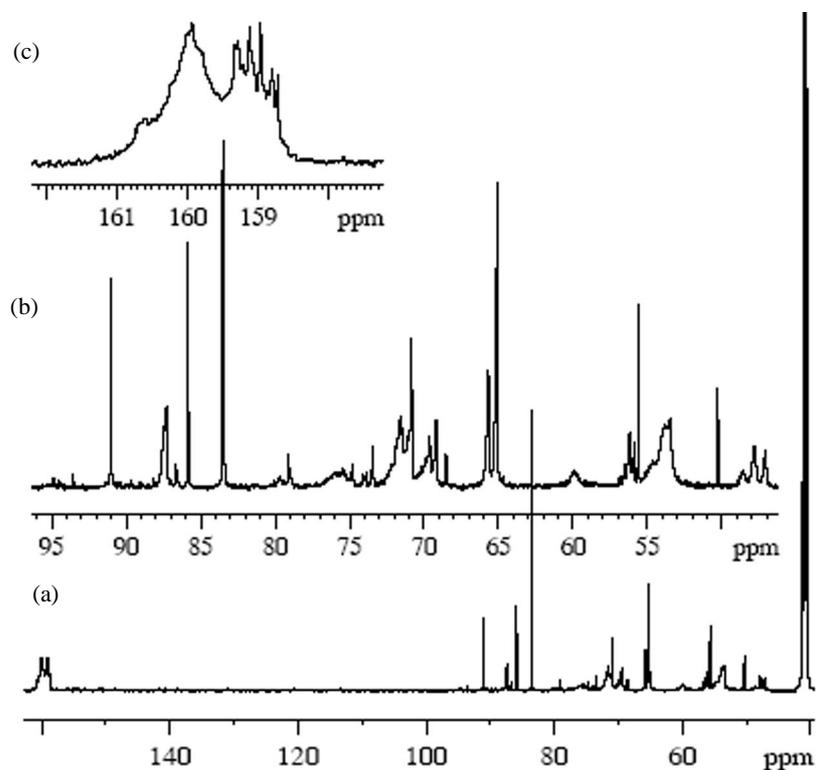
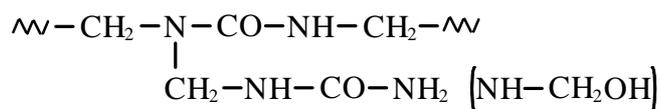
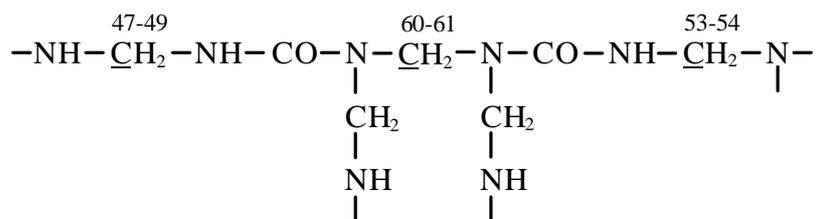


Fig. 1. ¹³C NMR spectrum in DMSO-d₆ of the polycondensation product at pH 4.5 with the molar ratio of formaldehyde/urea of 2.1. a – spectrum in the region of 40–170 ppm, b – the region of ¹³C methylene signals, c – the region of ¹³C carbonyl signals.

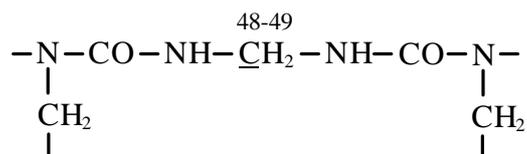
of the amino groups of U in the chain occurs. The most preferred structural fragment of polycondensate can be pictured as follows:



Branching probably occurs as substitution in the secondary amino group in the reaction with MMU or BMU. The presence of small amounts of methylenes linked only to tertiary amino groups (signal at 60–61 ppm) shows that the following amino groups of both ureas in the chain are disubstituted:



The ratio of the signal from methylenes adjacent to secondary amino groups (47–49 ppm) changes in polycondensation. The principle of resolution in that region is not fully understandable but it can be supposed that the signal at 48–49 ppm increases mostly from methylenes in chains containing also a branch at the next amino group:



The resolution in the carbonyl region occurs by substitution differences to mono-, di-, and trisubstituted U compounds. At the same time, the different substituents cause an overlapping of signals mostly for di- and trisubstituted compounds (Fig. 1). Typical signals for hydroxymethylated U compounds (BMU, TMU) and dimethylene ethers appear in the region of 158.8–159.3 ppm. Their integral intensities (except TMU) according to constitution (Table 1) are essentially lower than in the hydroxymethylated product. The preferred formation of various combinations of methylene-containing trisubstituted U compounds is revealed in the appearance of broad signals in the region of 159.5–160 ppm. The content of monosubstituted U compounds is low and the typical signals at 160.0–160.6 ppm are partly overlapped by other, more intensive signals.

Post-treatment with urea added second

The main concept in reducing the toxicity of UF resins lies in the low final molar ratio of F/U (here 1.05). It means that after the alkalization of the polycondensate, half of U was added. An almost quantitative reaction of free F (about 0.45 mol) occurs already at cooling (Table 1). Because of the high content of unreacted U (about 30% of U) and reactive hydroxymethyl groups (about 50% of F), numerous reactions take place in the storage of resins. It means that resins of different ageing time can have different technical properties and are quite unstable [10]. The best option is not to leave the resins without additional thermal treatment. The temperature of post-treatment can thoroughly change the resins of quite similar constitution after polycondensation (Table 2). In the case of 45% F solution, the optimum dry solids content (about 69%) is obtained after vacuum drying. In principle, it is supposed that equal conditions of drying (<40°C) in all cases have the same effect on the constitution.

The post-treatment conditions are mostly responsible for the formation of the monomeric part in resins. The formation of MMU is the prevailing first-step reaction in addition to secondary U (Fig. 2).

The content of monosubstituted U compounds increases over half of the total U content (Table 2). This means that an essential part of the first-formed MMU is in further condensation with U converted to MDU, identified by signals at

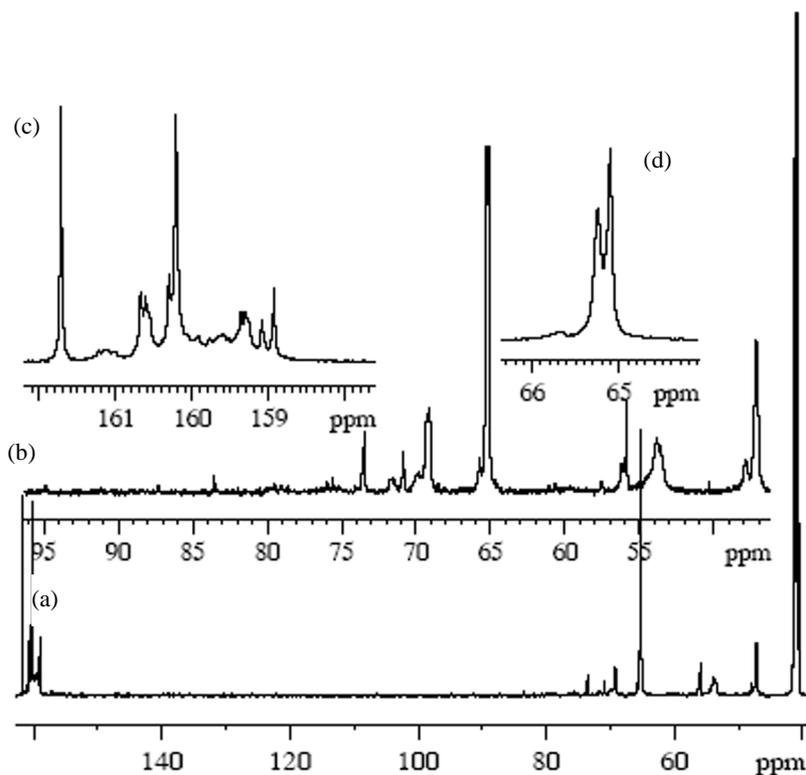


Fig. 2. ^{13}C NMR spectrum in DMSO-d_6 of resin with the molar ratio of formaldehyde/urea of 1.05 obtained in post-treatment with urea added second at 75°C . a – spectrum in the region of 40–170 ppm, b – the region of ^{13}C methylene signals, c – the region of ^{13}C carbonyl signals, d – the region of ^{13}C signals from hydroxymethyls ($-\text{NH}-\underline{\text{C}}\text{H}_2\text{OH}$).

160.8 ppm in the carbonyl region and 47.0 ppm in the methylene region. Other methylene containing linear oligomers are also present, characterized by end U molecules (carbonyl signals at 160.5–160.7 ppm) and by a change in the ratio of signals at 47–49 ppm. The relative increase in dimethylene ether signals at 69.1–69.2 ppm most likely shows the formation of dimethylene ether of diurea. The about threefold increase in the hydroxymethyl content (signal at 65–66 ppm) is not only the result of the reaction with free F. One of the most important temperature promoted processes is the migration of hydroxymethyl from bishydroxymethyl groups to the monomeric part. Actually this process occurs as transhydroxymethylation (Table 2). The content of about 4% of bishydroxymethyl groups seems to be the minimum but can be regulated with the conditions of thermal treatment. Lower intensities at 65.6 ppm and 71–72 ppm in the methylene region and disappearance of signals at 158.8–158.9 ppm in the carbonyl region also verify the small amount of compounds with bishydroxymethyl groups (e.g. TMU and others) in the final resins (Fig. 2).

The formation of methylenes linked to tertiary amino groups is not possible in alkaline conditions. Their content in thermal treatment shows a slightly decreasing tendency (Tables 1 and 2). The typical signals for trisubstituted U with the tertiary amino group linked to methylene groups appear mostly at 159.5–159.7 ppm in the carbonyl region. The increase in the methylene content during thermal treatment occurs due to the formation of methylenes linked to secondary amino groups mostly in the monomeric part (e.g. MDU). The content of BMU and its dimethylene ether-containing polycondensates does not essentially change in the thermal treatment.

It can be seen (Table 2) that the resins of various post-treatment temperatures differ in the extent of the migration of F from bishydroxymethyl groups. This process proceeds successfully already at the cooling of resins but can be promoted essentially by thermal treatment. It appears to be a useful phenomenon enhancing evenness of the distribution of F-containing functional groups in the resin. The increase in monosubstituted U compounds is the main change during post-treatment, leading also to a decrease in the free U content. The summary content of di- and trisubstituted U remains quite constant.

The changes in the storage of resins (Table 1) depend on the thoroughness of post-treatment. The main difference is that the temperature promoted migration from bishydroxymethyl groups becomes retarded at room temperature. The content of bishydroxymethyl groups of about 3–4% seems to be an equilibrium content that does not change at ageing. Hence the resins with a higher content of these groups continue a slow migration. Despite the different concentrations of reacting species, a slow condensation between MMU and free U by the formation of methylenes adjacent to secondary amino groups is the reaction occurring most often in the storing of resins. A good verification of this process is the increase in the amount of singly bonded U with a typical signal at 160.6–160.8 ppm. No change is seen in the content of methylenes linked to tertiary amino groups. Some additional dimethylene ether formation occurs in the storing of resins with the participation of hydroxymethyl groups. Quite a constant ratio of methylene and dimethylene ether groups (~2.5) on the background of other structural characteristics can be observed.

CONCLUSIONS

- Equilibrium between the various formaldehyde containing functional groups depending on different conditions of hydroxymethylation, polycondensation, and post-treatment is decisive in the structure formation of UF resins.
- Alongside with 1,3-bis- and monohydroxymethylureas, with the signals at 158.8 ppm in the carbonyl region and 70.8 and 65.6 ppm in the methylene region of the ^{13}C NMR spectrum, trishydroxymethylurea was identified as a constituent (about 10% of U) of the alkaline hydroxymethylated product.

- Bishydroxymethyl groups as end groups of chains or constituents of monomeric compounds are not subjected to polycondensation in weak acid conditions.
- In acid conditions polycondensation proceeds preferably with the formation of methylenes adjacent to secondary and tertiary amino groups as trisubstitution in urea is favoured compared to disubstitution.
- Branching of chains occurs in polycondensation by repeated substitution in one of the amino groups of urea mostly in the reaction with mono- or 1,3-bis-hydroxymethylurea.
- The products of the U/F reaction in technologically acceptable conditions are quite similar after acid promoted polycondensation but can be changed essentially by conditions of post-treatment with urea added second.
- Migration of formaldehyde from bishydroxymethyl groups to urea, which increases steeply the amount of monohydroxymethyl groups, is the most important temperature promoted process of post-treatment.
- Formation of methylenes linked to secondary amino groups including the reaction of first-formed MMU with urea is fostered in alkaline conditions of post-treatment.
- Appearance of signals at 160.5–160.8 ppm in the carbonyl region of the ^{13}C NMR spectrum is connected with the presence of compounds with singly bonded urea in methylene diurea or methylene containing oligomers.
- The structures with methylenes linked to trisubstituted urea obtained in acid polycondensation survive the post-treatment without any substantial changes.

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Struktuuri moodustumisest karbamiid- formaldehüüdvaikude sünteesil

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On uuritud karbamiid-formaldehüüdvaikude kolmeastmelisel sünteesil keemilise struktuuri moodustumist happelisel polükondensatsioonil ja eriti järgneval aluselisel järelkondensatsioonil lisakarbamiidiga ¹³C TMR spektroskoopia abil. Tertsiaarsete/sekundaarsete aminorühmadega seotud metüleenrühmad tekivad ainult happelises keskkonnas. Bishüdroksümetüülirühmad ei võta happelisest polükondensatsioonist osa, kuid mõjutavad oluliselt vaikude lõppstruktuuri, olles transhüdroksümetüülimisreaktsiooni põhiliseks allikaks järelkondensatsioonil lisakarbamiidiga. Pärast happelist kondensatsiooni järelkondensatsioonil ja vaikude vananemisel tekivad juurde ainult sekundaarsete aminorühmadega seotud metüleenrühmad.