

Effect of Different Catalysts on Urea-Formaldehyde Resin Synthesis

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ABSTRACT: Four catalysts (H_2SO_4 , HCl , H_3PO_4 , and $\text{NaOH}/\text{NH}_4\text{OH}$) were studied in the preparation of melamine modified urea-formaldehyde (UFM) resins. ^{13}C -nuclear magnetic resonance spectroscopic analysis of the UFM resins at different synthesis stages revealed the polymer structure and detailed reaction mechanism. Three acidic catalysts (H_2SO_4 , HCl , and H_3PO_4) enhanced the resin polymerization through the formation of various contents of methylene, ether linkages, and urons. H_3PO_4 yielded the most terminal ether linkages at the first stage and enhanced polycondensation by depleting all free urea and glycols to form the most linear methylene linkages NHCH_2NH in the end. However, at the initial synthesis stage, $\text{NaOH}/\text{NH}_4\text{OH}$ catalyzed the formation of UFM prepolymer to a limited extent with a large amount of free urea left, and therefore produced the final polymer with relatively more substituted methylolureas and linear ether linkages. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40644.

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INTRODUCTION

The wood products industry, especially the structural and non-structural panel sectors, has heavily relied on the use of urea-formaldehyde (UFM),^{1–4} melamine-formaldehyde,^{5,6} phenol-formaldehyde,⁷ and melamine-urea-formaldehyde (MUF) synthetic resins.^{8,9} Novel UFM resin modified by a small amount of melamine has attracted interest because of its long-term bond strength, moisture resistance, low formaldehyde emission, and cost.^{10,11} Recently, melamine-modified UF resin draws more attention to the preparation of novel resin with liquefied wood with MUF¹² and self-healing MUF microcapsules,¹³ and performance improvement by modifying resin with poly(amido-amine)s dendrimers,¹⁴ PolyFox PF-151N polymer,¹⁵ mimosa tannin resin,¹⁶ and nanoclay.¹⁷

Our previous studies showed that different catalysts displayed various effects on UFM resins and particleboards.¹¹ This suggests that resin structure is a substrate characteristic relevant to the properties of UFM resin bonded forestry products and must be monitored not only to deconvolute the factors affecting glue bond performance, formaldehyde emission, and thermal behavior in curing but also to help develop a deeper understanding of the molecular-level mechanisms that these catalysts employed. A vital component of this is to generate reliable structural models of UFM resins in different synthesis stages.

These results can be then used in further research such as computational methods applied model for the generation of new optimized forestry based products and novel materials glued by UFM resin.

In addition, research on synthesis mechanism is far from adequacy, especially on the detailed reaction and molecular structural changes of the multistep synthesis procedure for wood adhesive-type UF resin modified by melamine. To address this need, this article focused on the effect of different catalysts on the mechanisms of resin synthesis and the intermediate structural change using ^{13}C -nuclear magnetic resonance (NMR) spectroscopy. Three stages of resin preparation were subdivided, and the chemical structural change in each stage was studied. The detailed reaction mechanism obtained from this article could help pave the way for future optimization of resin synthesis and further applications.

EXPERIMENTAL

Preparation of UFM Resins

Four resins with different catalysts (H_2SO_4 , HCl , H_3PO_4 , and $\text{NaOH}/\text{NH}_4\text{OH}$) (50/50 w/w, solids content) were prepared with the same F/U/M molar ratio of 1.38/1/0.074 in the laboratory, based on previous work.¹¹ Each resin synthesis was replicated twice and included three stages to prepare.

Table I. ^{13}C -NMR Assignment of Stage 1 UFM Resin

Functional group	Chemical shift (ppm)	Relative peak area (%)			
		H_2SO_4	HCl	H_3PO_4	NaOH/ NH_4OH
Total methylene linkages		28.68	26.38	21.87	22.28
HNCH ₂ NH	45-47	8.32	6.50	5.26	7.05
HNCH ₂ N(CH ₂)	53-56	16.85	15.12	13.15	15.23
N(CH ₂)CH ₂ N(CH ₂)	57-58	3.51	4.76	3.46	0
Total methylol groups		17.62	18.47	19.31	29.77
CH ₃ OH	51-52	5.62	7.00	8.07	5.15
HNCH ₂ OH	63	5.46	6.15	6.19	14.87
N(CH ₂)CH ₂ OH; N(CH ₂ OH) ₂	66-67	6.54	5.32	5.05	9.75
Total methylene-ether groups		32.80	32.27	34.79	35.00
HNCH ₂ OCH ₂ NH	69-70	5.66	7.10	8.58	12.58
NHCH ₂ OCH ₃	71-72	2.68	2.79	3.17	7.54
N(CH ₂)CH ₂ OCH ₃	73-75	3.99	4.64	5.02	5.36
N(CH ₂)CH ₂ OCH ₂ N	76-77	9.68	5.57	5.28	3.67
NCON(CH ₂ OCH ₃) ₂ ; ether urons	81.1	10.79	12.17	12.74	5.85
Total methylene glycols		20.9	22.88	24.03	12.95
HOCH ₂ OH	84-85	7.91	10.16	11.80	4.79
HOCH ₂ OCH ₂ OH;	88.7	8.68	9.82	9.00	5.31
HOCH ₂ O(CH ₂ O) _n CH ₂ OH	92-93	4.31	2.90	3.23	2.85
Urea carbonyl region					
Uron	153-154	23.65	17.61	13.64	0
Tetrasubstituted or uron urea	156-158	76.35	82.39	86.36	66.54
Di- or trisubstituted urea	159-160	0	0	0	4.66
Monosubstituted urea	160-161	0	0	0	0
Free urea	163-164	0	0	0	28.80

Stage 1: All of the formaldehyde solution (3 mol) and water were placed in a reaction kettle, and the pH was adjusted with four catalysts (H_2SO_4 and HCl: 1.25; H_3PO_4 : 1.60; and NaOH/ NH_4OH : 5.0). Urea (1 mol) was added over the course of 15 min. The reaction kettle was heated and maintained at 70°C for 30 min.

Stage 2: pH was adjusted to 5.0, and all melamine (0.16 mol) was added over the course of 15 min. The reaction was kept at 70°C till reaching the same cloudy point.

Stage 3: The solution temperature was raised to 80°C , and the second portion of urea (1.17 mol) was added in six equal parts in 60 min. No additional pH adjustment was made after adding

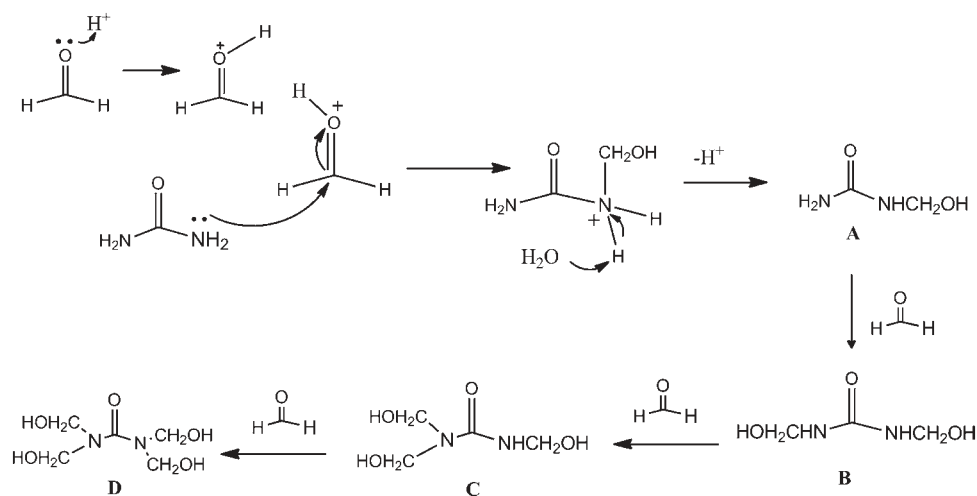


Figure 1. Proposed formation of mono-, di-, tri-, and tetramethylolurea by the addition of 3 moles formaldehyde to 1 mole urea.

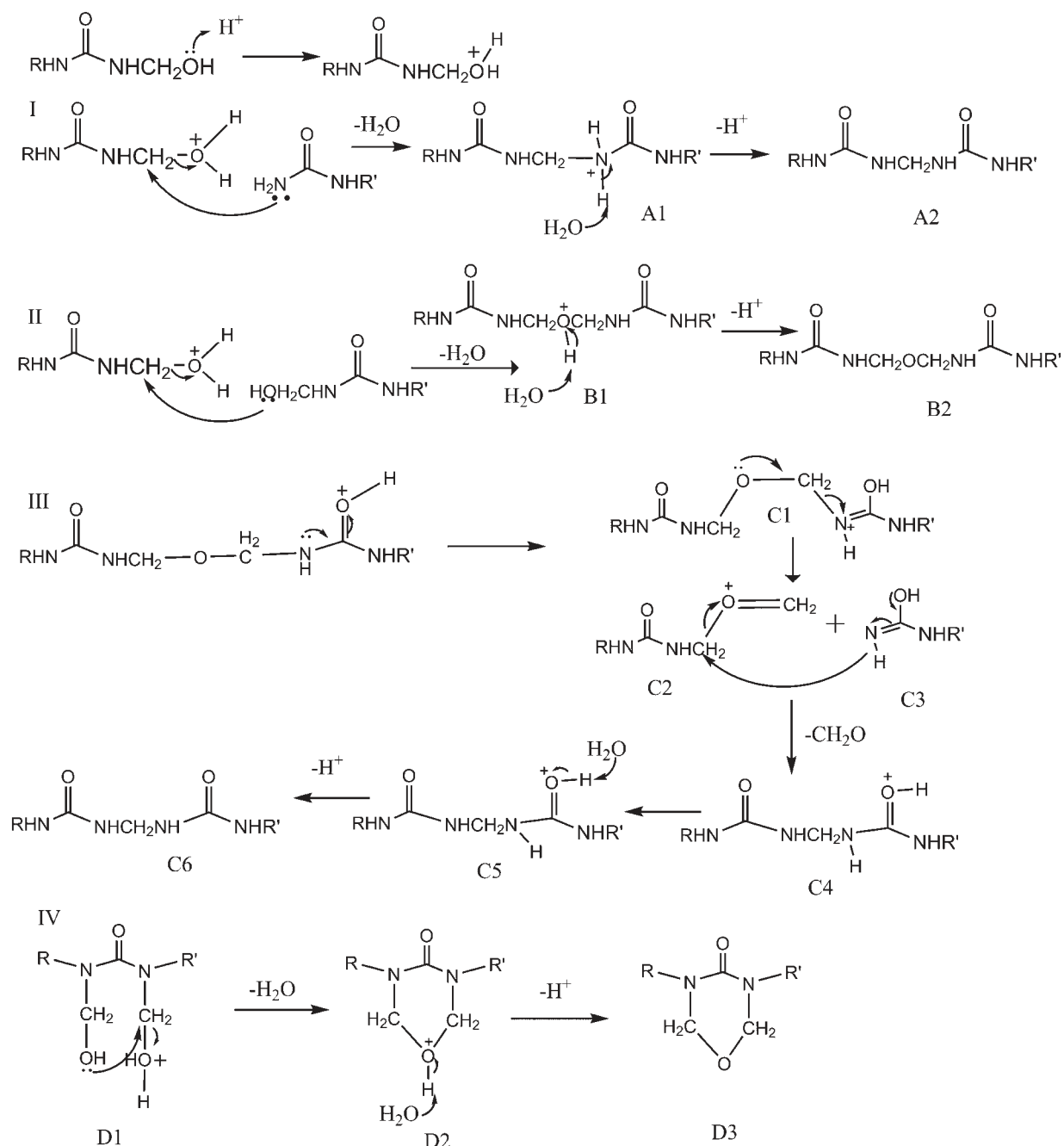


Figure 2. Proposed formation of methylene and methylene ether linkages and uron structure.

melamine. The reaction was terminated at the end of 60 min by cooling to room temperature within 10 min.

¹³C-NMR Measurement

Fourier transform ¹³C-NMR spectra were obtained on a Varian Inova spectrometer at a relaxation delay of 5 sec with inverse proton decoupling. The chemical shifts were calculated by defining a ¹³C chemical shift using a capillary tube with a *d*-DMSO insert in an NMR tube for locking and chemical shift referencing. At the end of three synthesis stages, resin samples were taken out for analysis. NMR spectra were integrated, and

functional groups were quantified according to previous studies.^{4,6–9}

RESULTS AND DISCUSSION

Resin Reaction Mechanism at Stage 1

The effect of four catalysts on resin synthesis after a 30 min reaction with a molar ratio U/F = 3/1 is presented in Table I. The initial backbone was built with different amounts of chemical groups. Under strong acidic conditions (pH = 1.25–1.60), three acid catalysts yielded similar prepolymer structures. H₂SO₄ provided the most total methylene linkages (—CH₂— connecting a second amide and a tertiary amide), most

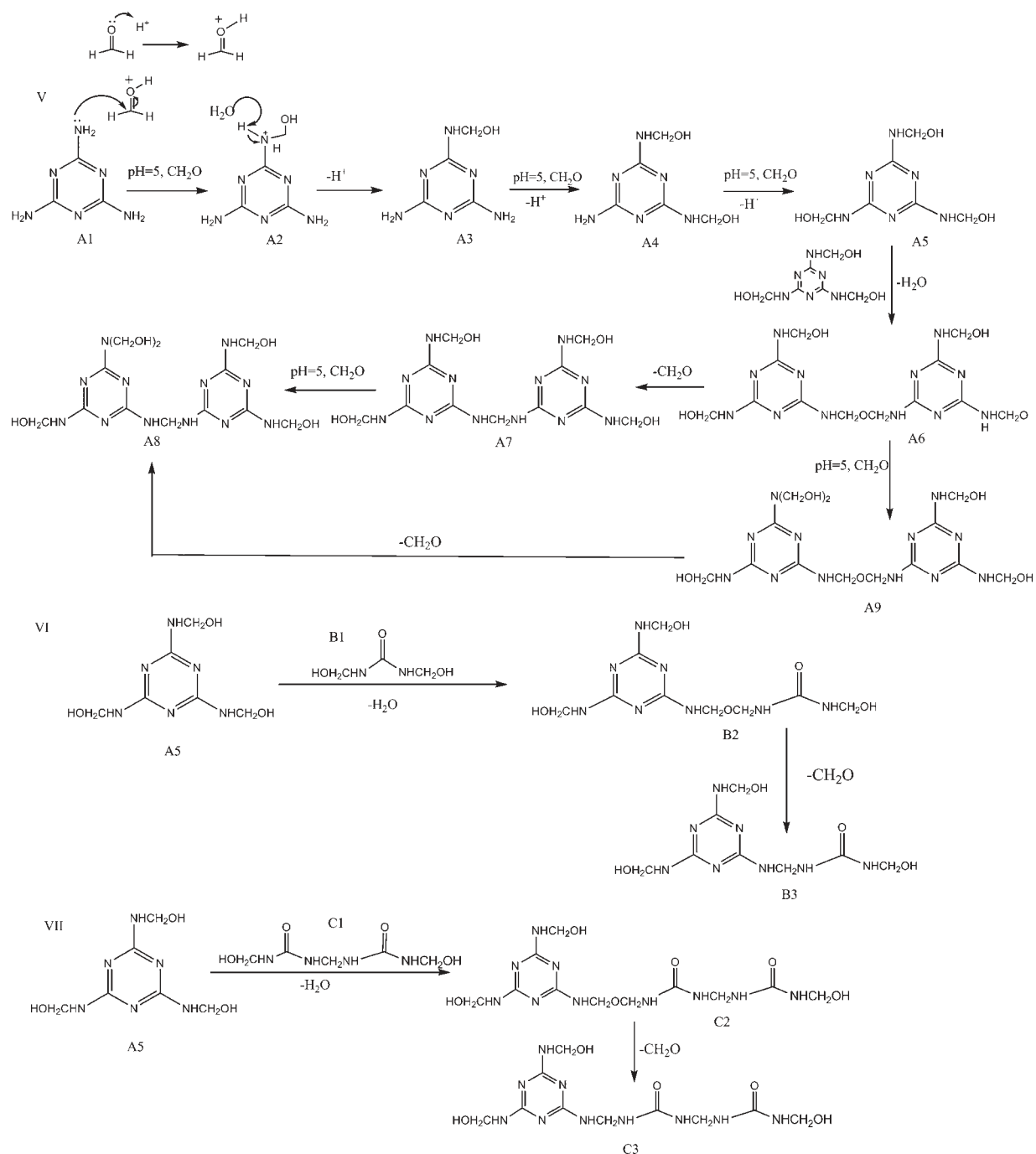


Figure 3. Proposed mechanism and polymer structures after adding melamine.

—CH₂OCH₂— attached to tertiary amides (76–77 ppm), and high uron¹⁸ content but the least total methylol groups and methylene glycols; H₃PO₄ produced the most methylene–ether linkages (—CH₂OCH₃ attached to tertiary amide and uron), methylol groups (CH₃OH), tetrasubstituted urea, and methylene glycols (formaldehyde), but few methylene linkages and uron; HCl did not provide any noticeable effect on the various resin chemical groups except the most HOCH₂OCH₂OH. Compared with the three acid catalysts in weak acid (pH = 5), NaOH/NH₄OH generated the relatively largest number of methylol

groups (—CH₂OH connecting a secondary and tertiary amide), methylene–ether groups (—CH₂OCH₃ attached to secondary amide), free urea, and di- or trisubstituted urea but few methylene glycols and tetrasubstituted urea and no uron.

In the initial reaction stage H₂SO₄ catalyzed the reaction to form the most branched methylene and ether linkages (—CH₂OCH₂—), H₃PO₄ yielded the most terminal ether linkages (—CH₂OCH₃), and NaOH/NH₄OH improved the reaction to a limited extent, which formed linear methylene and ether

Table II. ^{13}C -NMR Assignment of Stage 2 UFM Resin

Functional group	Chemical shift (ppm)	Relative peak area (%)			
		H_2SO_4	HCl	H_3PO_4	NaOH/ NH_4OH
Total methylene linkages		32.34	26.84	30.15	21.08
HNCH ₂ NH	45-47	11.73	9.37	11.50	4.92
HNCH ₂ N(CH ₂)	53-56	18.10	17.47	16.41	14.08
N(CH ₂)CH ₂ N(CH ₂)	57-58	2.51	0	2.24	2.08
Total methylol groups		16.99	22.34	18.89	23.22
CH ₃ OH	51-52	4.46	7.46	6.46	8.08
HNCH ₂ OH	63	7.57	9.09	7.83	8.98
N(CH ₂)CH ₂ OH; N(CH ₂ OH) ₂	66-67	4.96	5.79	4.60	6.16
Total methylene-ether groups		33.22	36.36	31.87	32.53
HNCH ₂ OCH ₂ NH	69-70	7.05	11.59	6.90	9.92
NHCH ₂ OCH ₃	71-72	4.03	4.64	5.11	3.74
N(CH ₂)CH ₂ OCH ₃	73-75	4.37	4.42	3.83	5.34
N(CH ₂)CH ₂ OCH ₂ N	76-77	10.08	8.33	5.62	2.67
NCON(CH ₂ OCH ₃) ₂ ; ether urons	81.1	7.69	7.38	10.41	10.86
Total methylene glycols		17.45	14.46	19.09	23.17
HOCH ₂ OH	84-85	4.94	4.37	5.87	10.63
HOCH ₂ OCH ₂ OH;	88.7	6.69	5.84	9.34	9.08
HOCH ₂ O(CH ₂ O) _n CH ₂ OH; H(OCH ₂) _n CH ₂ OCH ₃	92-95	5.82	4.25	3.88	3.46
Urea carbonyl region					
Uron	153-154	22.28	12.33	11.70	0
Tetrasubstituted or uron urea	156-158	50.26	61.64	73.94	100
Di- or trisubstituted urea	159-160	6.74	0	0	0
Monosubstituted urea	160-161	0	0	0	0
Free urea	163-164	20.72	26.03	14.36	0

prepolymer structures with substantial free urea residue. Most of the methylene-ether groups in the four catalyzed resins were formed in the first synthesis stage by a condensation reaction among methylol groups, which could result in the formation of UFM resin oligomers with various molecular weights. Furthermore, under the high F/U = 3/1 mole ratio and strong acidic condition (pH range from 1.25 to 1.60), the uron-type methylene-ether, uron-CH₂-urea, and uron-CH₂OH structures were extensively formed in three acidic catalyzed resins.

In brief, at the initial stage under strong acidic pH, urea and formaldehyde form a UF polymer as a backbone structure and then co-react with melamine. The proposed reaction mechanism and prepolymer structure are shown in Figures 1 and 2. Considering excessive formaldehyde to urea (mole ratio = 3 : 1) and urea with four functional groups, the addition reaction may occur under the strong acidic condition in the initial synthesis stage, but the following synthesis stage may consist of a series of reactions including addition and condensation reaction as shown in Figure 1. The UF prepolymer favors the formation of methylene linkage and a cyclic uron compound. In the first synthesis stage, urea will be hydroxymethylated by the addition of formaldehyde to the amino groups. The reaction will lead to mono-, di-, tri-, and tetramethylolureas. Considering the steric

hindrance and relatively weaker nucleophilicity of trimethylolurea, there would be relatively little tetramethylolurea [Figure 1(D)] in the initial synthesis stage. The following stage of UFM prepolymer synthesis would consist of the condensation of methylolureas to low-molecular-weight polymers. The increase in molecular weight of the UF prepolymer will be a combination of reactions leading to the formation of methylene bridges [Figure 2(A2)] between amino nitrogen by the reaction of methylol groups in methylolureas and amino groups in urea; methylene ether linkages [Figure 2(B2)] by the reaction of two methylolureas; methylene linkages [Figure 2(C6)] from methylene ether linkages by the elimination of formaldehyde; and uron [Figure 2(D3)] by dehydration reaction forming stable five-member rings.

Resin Reaction Mechanism at Stage 2

The four catalysts provided different prepolymer structures after the addition of melamine (Table II). It could be seen under the same molar ratio and pH = 5 that H_2SO_4 yielded the most methylene linkages both in linear and branched structures, uron, and di- or trisubstituted urea, but the least methylol groups and tetrasubstituted urea. HCl produced the most ether linkages (mostly linear ether -NHCH₂OCH₂NH-), linear methylol group (-NHCH₂OH), and free urea, but the least

Table III. ^{13}C -NMR Assignment of Stage 3 UFM Resin¹¹

Functional group	Chemical shift (ppm)	Relative peak area (%)			
		H ₂ SO ₄	HCl	H ₃ PO ₄	NaOH/NH ₄ OH
Total methylene linkages		32.89	33.12	45.89	36.14
HNCH ₂ NH	45–47	21.19	20.12	32.82	18.75
HNCH ₂ N(CH ₂)	53–56	11.70	13.00	13.07	17.39
Total methylol groups		25.47	30.39	30.68	34.27
CH ₃ OH	51–52	9.39	8.77	9.98	10.36
HNCH ₂ OH	63	12.52	15.63	15.16	14.76
N(CH ₂)CH ₂ OH; N(CH ₂ OH) ₂	66–67	3.56	5.99	5.54	9.15
Total methylene-ether groups		30.27	25.18	23.43	17.07
HNCH ₂ OCH ₂ NH	69–71	15.25	13.46	13.16	15.42
N(CH ₂)CH ₂ OCH ₃	76–77	12.40	7.87	0	0
CH ₃ OCH ₂ NHCON(CH ₂ OCH ₃) ₂	81	2.62	3.85	10.27	1.65
Total methylene glycols		11.37	11.32	0	12.51
HOCH ₂ OCH ₂ OH; NCH ₂ OCH ₂ OH; HNCH ₂ OCH ₃ ; HOCH ₂ OCH ₂ OCH ₃	88–92	11.37	11.32	0	12.51
Urea carbonyl region					
Tetra-sub or uron urea	156–158	31.80	32.69	38.31	29.19
Di- or trisubstituted urea	159–160	22.62	25.19	38.63	31.85
Monosubstituted urea	161	19.25	15.44	23.06	18.20
Free urea	164	26.33	36.39	0	20.77

methylene and polyglycol groups. H₃PO₄ yielded the most linear glycols (HOCH₂OCH₂OH) but the least ether linkages. NaOH/NH₄OH gave the most total methylol groups (mostly CH₃OH and —CH₂OH attached tertiary amides), terminal ether linkages (—NCON(CH₂OCH₃)₂), total methylene glycols (mostly HOCH₂OH), and tetrasubstituted urea, but the least methylene linkages and no free urea.

Stage 2 revealed several interesting results: (1) Methylene glycols in H₂SO₄, HCl, and H₃PO₄ acidic catalyzed resins attacked the melamine and urea amide nitrogens to form more methylene linkages. (2) Methylene linkages, regarded as a measure of resin conversion degree, were higher in H₂SO₄ and H₃PO₄ catalyzed resins, indicating that they displayed higher catalytic activity in resin condensation. (3) H₂SO₄ and H₃PO₄ resulted in a decrease in methylol content and an increase in the methylene and ether content. However, HCl led to a decrease in glycols and an increase in the total methylol and ether groups. NaOH/NH₄OH decreased the total methylol groups and all free urea left at the initial stage to increase the ether and glycols, indicating its lower degree of condensation. (4) In the carbonyl region, three acid catalysts increased the amount of free urea but decreased the content of uron and its derivatives, whereas NaOH/NH₄OH produced only tetrasubstituted urea structures by depleting all free urea in the first stage. (5) Strong acidic catalysts H₂SO₄, HCl, and H₃PO₄ favored the polymerization reaction between melamine and UF prepolymer by increasing the branched-type methylene and ether linkages. In contrast, alkaline catalyst NaOH/NH₄OH retarded that reaction to some degree and just increased the branched ether linkages by co-condensation

between its methylols formed at the initial stage and melamine amino groups. (6) The cyclic uron structures formed under strong acidic condition were in equilibrium with the open dimethylol ureas. The increase in pH to 5.0 and the addition of melamine improved the rate of opening of the cycle and formed methylol ureas and methylene methylol ureas. Therefore, the amount of uron structures in resins with HCl, H₂SO₄, and H₃PO₄ catalysts decreased to different extents.

In summary, melamine co-reacts with prepolymers formed in resin synthesis Stage 1 under a weak acidic condition (pH = 5.0). Also, excessive free formaldehyde in resin synthesis Stage 1 could also react with melamine to initially form hydroxymethyl-melamines in dimers, trimers, and so forth. The proposed reaction mechanism and final resin polymer structures are presented in Figure 3. The major consideration is the formation of methylene linkage and cyclic uron as a result of strong acid-catalyzed UF prepolymer as a backbone to co-react with the melamine to form a UFM polymer, and thereby to control formaldehyde emission. The increase in the UFM polymer chain would be a combination of reactions leading to the formation of methylene ether linkages by the reaction of two methylolmelamines [Figure 3(A6)]; methylene linkages from methylene ether linkages by the elimination of formaldehyde [Figure 3(A7)]; methylene ether linkages [Figure 3(B2)] by the reaction of methylolmelamines [Figure 3(A5)] and methylolureas [Figure 3(B1)]; and methylene linkages [Figure 3(C3)] from methylene ether linkages [Figure 3(C2)] derived from methylolmelamines and UF prepolymers.

Resin Reaction Mechanism at Stage 3

Second portion of urea was added into the prepolymer formed in Stage 2 under the same F/U/M molar ratio of 1.38/1/0.074 and pH = 5. The detailed information of functional groups in four resins are listed in Table III. The addition of urea enhanced polymerization reaction via reacting with the ending site methylol groups in the methylolureas and methylolmelamines and further reacted with free and regenerated formaldehyde in the resin. To analyze and elaborate the resin structure change during the three synthesis stages, the glycol groups were separated from the total ether groups. H₂SO₄ produced the most total ether linkages (mostly —CH₂OCH₃ connecting tertiary amide) but the least methylene and methylol groups. HCl yielded the most free urea and —NHCH₂OH structures. H₃PO₄ gave the most total methylene linkages (mostly linear methylene connecting two secondary amides), various substituted urea, and terminal ether groups but no glycols and free urea. NaOH/NH₄OH produced the most total methylol groups (mostly CH₃OH and methylol attached to tertiary amide), total glycols, linear ether linkages, and methylene connecting a secondary amide and a tertiary amide.

Compared with the resin prepolymer structure formed at Stage 2, it was interesting to note that (1) the four catalysts caused further decrease of total glycols and increased the total methylene linkages; (2) methylene–ether linkages, especially most of methylene methyl ethers, formed in the second stage were partly changed to methylene groups by splitting off some formaldehyde; (3) the increase in linear —NHCH₂OH groups in the four resins could result from the reaction between free formaldehyde and the final urea; (4) NaOH/NH₄OH produced the highest content of branched methylol groups after the addition of final urea, which led to a tighter resin network; (5) most of the urea added in resins with HCl, H₂SO₄, and NaOH/NH₄OH catalysts was not copolymerized but just added to decrease the formaldehyde emission by reacting with free formaldehyde and formaldehyde released from the rearrangement of ether bridges. However, H₃PO₄ enhanced polycondensation by depleting all free urea and glycols to form the most linear methylene linkages NHCH₂NH.

CONCLUSIONS

Four catalysts (H₂SO₄, HCl, H₃PO₄, and NaOH/NH₄OH) played different roles in synthesizing UFM resin. At the first stage, three acidic catalysts improved the formation of UFM oligomers to a large extent but NaOH/NH₄OH did not have a clear effect on polymerization. At the second synthesis stage, the

catalysts led to a rearrangement of UF oligomers and formed more complex structures with the addition of melamine. At the last synthesis stage, the addition of final urea reacted with prepolymers formed in the second stage in the resins with H₂SO₄, HCl, and NaOH/NH₄OH catalysts to a limited extent, but the H₃PO₄ catalyst depleted the final urea and resulted in the formation of the most methylene linkages, displaying a significant influence on polymerization.

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