The Structure of Urea–Formaldehyde Resins*

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Synopsis

Fourier transform infrared (FTIR) spectroscopy has been used as a modern analytical tool to elucidate the structure of urea–formaldehyde (UF) resins. Several low molecular weight condensation products of urea and formaldehyde were synthesized and characterized. Structural differences were observed for prepolymers prepared in alkaline and acidic media. Plausible mechanistic routes are proposed to explain the prepolymer structural differences prepared in different experimental conditions. The structural elucidation of the UF resins is considerably increased and improved by using absorbance magnification to further enhance the observed signals.

INTRODUCTION

In order to understand the structure of urea–formaldehyde (UF) resins, several analytical tools and techniques including carbon-13 solution NMR,[1–7] nitrogen-15 NMR,[8] Raman spectroscopy,[9] and infrared spectroscopy[10] have been applied as they become available, yet the structure is still ambiguous. Due to the evolution of the formaldehyde from cured UF resins, the use of such resins is limited. Understanding the mechanism and source of the evolution of toxic formaldehyde from these resins is a challenging issue which can only be surmounted by increased knowledge of the molecular structure and its dependence on the polymerization process.

On the basis of experimental studies of the condensation of urea with the formaldehyde and from the kinetic data of formation of UF resins, several authors[11–15] have proposed different types of structures for these resins. Many recent studies have been reported[1,2,10]; yet, today, the actual structure of UF resin remains ill-defined.

Due to the complexity of the structure of UF resin and the presence of many components, the observed IR bands are weak and broad.[10] The conventional dispersive IR spectrometer has limited use in establishing the molecular structure by analyzing such bands.

In an attempt to elucidate the structure of UF resin, Fourier transform infrared (FT-IR) spectroscopy has been used. By the use of FT-IR and the ability of computer to analyze the data, structure elucidation will be considerably increased and improved by using absorbance magnification to enhance the observed signals.

It is assumed that a thorough and systematic contribution to the elucidation of the structure of UF resins would stem from the preparation and

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characterization of UF resin intermediates, and their associated absorption band assignments. With that spirit, several intermediate model compounds whose presence was identified by chromatographic methods[16] are synthesized and their known structure used to make further improvements in the band assignments. A freeze-drying sample preparation procedure, which yields improved FT-IR spectra compared to normal sample preparation method, is also developed.

EXPERIMENTAL

The model compounds were prepared in the laboratory or purchased. They are listed in Table I together with their source or method of preparation.

Eleven different urea–formaldehyde prepolymers were synthesized by the condensation of urea and 37% aqueous formaldehyde in acidic and alkaline media. Their chemical (feed) composition with the identification numbers are given in Table II.

General Method of Preparation of UF Resins in Alkaline Media

Urea was added with agitation to a 37% aqueous formaldehyde solution (Fischer Sci. Co.) buffered with triethanol amine in a 500-mL three-necked flask equipped with stirrer, reflex condenser, and thermometer. The urea was dissolved in formaldehyde solution and maintained at a temperature between 20 and 25°C. While the urea was in solution, the pH was adjusted to the desired value with triethanol amine/5N formic acid. The reaction mixture was heated to reflux, using a heating mantle attached to a 1KVA variable transformer. The batch was refluxed between 98 and 102°C with vigorous agitation for about 45 min. After refluxing 5 min, a sample was withdrawn and cooled to room temperature for pH and viscosity tests. The viscosity was checked every 10 min by using a Brookfield viscometer and the readings were plotted, viscosity vs. time, until a value of 17–19 cP was anticipated by extrapolation. When the desired viscosity was reached, heat was removed, and the batch was then cooled with cold water. Triethanol amine was added to raise the pH to between 7.3 and 8.0. The resin was concentrated under vacuum until a viscosity of 150–250 cP was reached. The final pH of the prepolymer was between 7.3 and 8.0.

The UF6 prepolymer was prepared by condensing urea with 37% aqueous formaldehyde at a pH value of 3.2 ± 0.2. No pH adjustment was made after the condensation reaction.

In another set of studies, five different prepolymers were synthesized keeping the pH constant and varying the feed ratio. Prepolymers UF1 through UF7 were freeze-dried. Formulations and experimental parameters are summarized in Table II.

The infrared absorbance spectra of semisolid prepolymers were taken as thin films between KBr discs. Absorbance spectra were obtained at 2 cm^{-1} resolution between 3600 and 600 cm^{-1} on a Digilab FTS-20E FTIR spectrometer using 200 sample and reference beam scans (co-added interferograms). The ratio of ether, methylol, and $>N—CH_2—N<$ groups in differ-

TABLE I
Synthesis or Source of Model Compounds

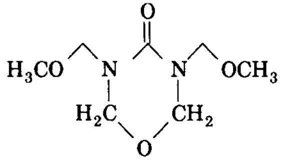
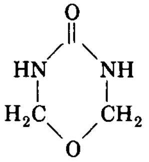
Model compound	Formula	Source	Ref.
Monomethylol urea	$H_2N—CO—NH—CH_2OH$	Lab made	33
Dimethylol urea	$HOH_2C—NH—CO—NH—CH_2OH$	Lab made	33
Monomethylol urea methylether	$H_2N—CO—NH—CH_2—OCH_3$	Lab made	29
1,3-Dimethyl urea	$H_3C—NH—CO—NH—CH_3$	Sigma Chem. Co	
Methyl urea	$H_3C—NH—CO—NH_2$	Aldrich Chem. Co.	
Dimethylol urea dimethylether	$(H_3CO—H_2C—NH)_2—CO$	Lab made	33
Dimethylol uron dimethylether		Lab made	34
Uron		Lab made	33
Methylene diurea	$H_2N—CO—NH—CH_2—NH—CO—NH_2$	Lab made	33
Dimethyloloxy methylenediurea	$HOCH_2—NH—CO—NH—CH_2—O—CH_2—NH—CO—NH—CH_2OH$	"	29
Trimethylene tetraurea	$H_2N—CO—NH—(CH_2—NH—CO—NH)_2—CH_2—NH—CO—NH_2$	"	29
Pentamethylene hexaurea	$H_2N—CO—NH—(CH_2—NH—CO—NH)_4—CH_2—NH—CO—NH_2$	"	29

TABLE II
Amounts of Reagents in Different UF Resins

Resin	Amounts (mol) of Urea	Amounts (mol) of Formaldehyde	pH	Viscosity (Brookfield) (cP)
UF1	1.0	1.3	8.0 ± 0.2	a
UF2	1.0	1.5	8.0 ± 0.2	a
UF3	1.0	1.7	8.0 ± 0.2	a
UF4	1.0	1.85	8.0 ± 0.2	a
UF5	1.0	2.2	8.0 ± 0.2	a
UF6	1.0	1.7	3.2 ± 0.2	a
UF7	1.0	1.6	7.5 ± 0.2	a
UF8	1.0	1.85	7.3 ± 0.2	185 ± 50
UF9	1.0	1.7	7.5 ± 0.2	180 ± 50
UF10	1.0	1.3	8.0 ± 0.2	250 ± 50
UF11	1.0	1.6	7.6 ± 0.2	250 ± 50

[a] Freeze-dried samples.

ent UF resins was calculated from the following general equation:

$$R = \frac{A\ (\text{asymmetric CH stretch of pertinent reactive moiety})}{A\ (\text{total symmetric and asymmetric CH stretch})}$$

where R is the relative amount of components present and A is the peak area for the specific functional moiety.

RESULTS

Monosubstituted Urea Derivatives

In the NH stretching region, urea derivatives of the type $H_3C—NH—CO—NH_2$, methyl urea (MU), three bands around 3432, 3324, and 3230 cm^{-1} are present. The bands at 3432 and 3230 cm^{-1} of methyl urea may be assigned by analogy to the NH_2 group of the asymmetric and symmetric stretching mode of the NH group and the band at 3324 cm^{-1} to the secondary (bonded) NH group. In the region between 1540 and 1700 cm^{-1}, there are mainly three absorptions at 1670–1685, 1611, and 1546 cm^{-1} for monomethylolurea methylether (MME), and two absorptions each at 1635–1660 and 1582 cm^{-1} in methyl urea (MU) and at 1656 and 1574 cm^{-1} in monomethylolurea (MMU) (see Fig. 1). The band at 1655–1666 cm^{-1} should be ascribed largely to the C=O stretching mode generally termed the amide I. The band at 1550–1575 cm^{-1} is ascribed to the NH deformation (amide II) of the secondary amide group. The assignments for monosubstituted ureas are shown in Table III.

In case of MU (see Table III), the author ascribed the band at 1656 cm^{-1} to the C=O stretching mode, while the band at 1637 cm^{-1} is assigned to the NH_2 deformation. In MME the 1682 cm^{-1} band is assigned to the C=O stretching. A medium absorption band for NH_2 deformation is observed at 1610 cm^{-1}. However, in MMU a C=O stretching band is observed at 1656 cm^{-1} and no absorption in the 1600–1640 cm^{-1} region is observed for NH_2 deformation. This absence is probably because of the hydrogen-bonded struc-

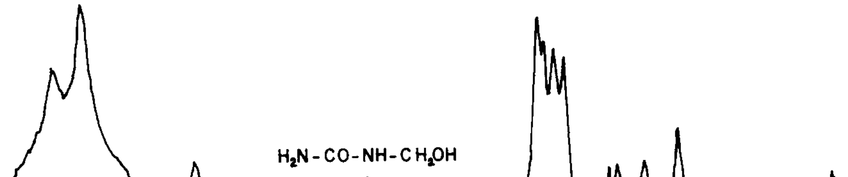
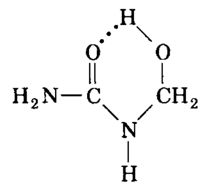


Fig. 1. Infrared absorption spectra of (a) monomethylol urea, (b) dimethylol urea, and (c) methylene diurea.

ture of the MMU as proved by Becher.[17] This is shown as:



In all the monosubstituted urea derivatives, the amide II of the secondary amide group is observed in the 1546–1580 cm^{-1} region. The amide III band (secondary amide) is found in the region of 1350–1360 cm^{-1} indicating the essentially NH deformation character of this bond. A band in the region of 750–780 cm^{-1} in all the model compounds can be attributed to the out-of-plane deformation of C=O in the $>N-CO-N<$ skeleton. However, the out-of-plane NH wagging mode absorbs broadly near 700 cm^{-1}.[18] The absorption band at 1464 cm^{-1} is assigned to the CH_2 group arising from the CH deformation according to Bellamy.[19] A medium absorption around 1400 cm^{-1} is assigned to twisting CH_2 mode of the methylene. This assignment is in agreement with other authors.[20]

Disubstituted Urea Compounds

As expected, in the distributed urea compounds a strong band at 3340–3350 cm^{-1} is observed for dimethylolurea dimethylether (DME) and methylene

TABLE III
Assignment of Infrared Bands in Monosubstituted Ureas[a]

Methylurea		Monomethylolurea			Monomethylolurea methylether	
Band (cm^{-1})	Assignment	Band (cm^{-1})	Assignment (Ref. 14)	Assignment (author's work)	Band (cm^{-1})	Assignment
3429s	νNH$_2$	3432s	νNH$_2$ & νNH	νNH$_2$	3355s	νNH
3332s	νNHY	3324s	νNH$_2$ & νNH	νNH	3000m	νCH of —OCH$_3$
2980w 2920w	νCH of CH$_3$	3260vw	—	νOH	2940m	νCH of CH$_2$
					2830w	CH def. and overtone of —OCH$_3$
1656 vs	Amide II	2900w 2958m 2985w	νCH$_2$	νCH of CH$_2$	1682vs	δNH$_2$
					1669m	Overtone of 1682 cm^{-1} band
1637vs	Amide I	1656vs	δNH$_2$ & νC=O	As in Ref. 14		
1582vs	Amide II	1574vs	νAsy. N—C—N	Amide II	1611m	νC=O
1422s	δCH, CH$_2$ & CH$_3$	1464m	δCH$_2$	As in Ref. 14	1546vs	Amide II(νC—N + δN—H)
1357s	Amide III	1432w	γOH	As in Ref. 14	1453vw 1439vw 1403w	δCH in CH$_2$ & —OCH$_3$
1170m	νC—N	1390w	γCH$_2$	As in Ref. 14	1350s	Amide III (δNH)
782m	νC—O out-of-plane	1359s	δNH	Amide III		
		1275w	τCH$_2$	OH def. of CH$_2$OH	1060vs	νC—O of —C—O—C— plus νC—O of CH$_2$OH
		1150w	νN—CH$_2$—O	νC—O of Ether		
		1110w	ρNH$_2$	As in Ref. 14		
		1013vs	—	νC—O of CH$_2$OH	900s	νN—CH$_2$—O, see Ref. 14
					780vw	νC—O out-of-plane

[a] s = strong; w = weak; m = medium; vs = very strong; vw = very weak.

TABLE IV
Assignment of Infrared Bands in Disubstituted Ureas[a]

1,3-Dimethylurea		Dimethylolurea		Monomethylolurea methylether	
Band (cm^{-1})	Assignment	Band (cm^{-1})	Assignment (Author's work)	Band (cm^{-1})	Assignment
3346vs	νNH	3384vs	νNH	3340vs	νNH
3180vw		3185vw			
3050vw	νCH of CH_2 & CH_3	3010vw	νCH of CH_2	2980w	νCH_2
2942w		2960m			
2900w					
2810vw	N—CH_3	1651vs	νC=O of amide I	2938m	ν—OCH_3
				2820w	
1635vs	Amide I	1601s	νasy. C—N amide II	1640vs	Amide I
1597vs	Amide II	1457s	δCH_2	1560vs	Amide II
1420s	Asy. def. of CH of CH_3 and N—CH_3	1391m	γCH_2	1453vw	Asy. & sym Def. —CH_3
				1439vw	
1269sb	Amide III	1301s	δOH plus amide III	1403m	νCH_2
1176m	νC—N	1050vs	νC—O—C as impurity	1320m	δNH and amide III
				1250s	
720mb	NH_2 wag. out-of-plane	1013vs	νC—O of —CH_2OH	1130s	—N—CH_2—O
		700m	γOH or NH	1007vs	
				1050m	νasy. C—O—C
				1030s	
				900s	νN—CH_2—O

[a] Spectra between 3600 and 600 cm^{-1}. vs = very strong; vw = very weak; w = weak; s = strong; sb = strong broad.

diurea. In dimethylolurea (DMU) a strong absorption band at 3384 cm^{-1} and a weak band at 3185 cm^{-1} are observed, due to the secondary amide NH group.

In all three disubstituted urea derivatives under investigation, bands at 1630–1650 cm^{-1} are assigned to C=O stretching mode (amide I) while the bands at 1550–1590 cm^{-1} are ascribed to the NH deformation mode (amide II). This is in agreement with the study of ^{18}O- and D–^{18}O-labeled derivatives.[21] A summary of band assignments is given in Table IV.

Compared to the monosubstituted urea derivatives, there is a shift in the amide III band frequency (see Fig. 1). This particular absorption is seen at 1256, 1250, and 1269 cm^{-1} for DME, DMU, and methylene diurea respectively. The infrared spectrum of methylene diurea (Fig. 1) shows a characteristic absorption at 1651 cm^{-1} for C=O stretching (amide I). However, the

TABLE V

Assignment of Infrared Bands for Urea Derivatives with Linear and Cyclic Ether Linkages[a]

Dimethyloloxy methylenediurea		Uron dimethylether	
Band (cm^{-1})	Assignment	Band (cm^{-1})	Assignment
3341vs	νNH	3382vw	νNH
2995vw	$\nu CH_2, CH_3$	2987vw	νasy. CH
2958m	—	2941m	—
1679vs	νC=O(amide I)	1673vs	νC=O of cyclic amide I
1557vs	Amide II (linear)	1503vs	Amide II of cyclic urea derivatives
1479w	δCH_2 in $N—CH_2—N$; CH_2O & OCH_3	1467s	νOCH_3
1446m	νOH	1391vs	CH mode of CH_2
1389m	CH mode in CH_2 & CH_3	1299vs	δOH (impurity)
1331vw	OH def.	1181vs	—
1314m	CH_2OH	1074vs	Asy. cyclic ethers
1242m	—	1019s	νC=O of CH_2OH (impurity)
1098m	—	908vs	$\nu N—CH_2—O$
1023vs	Amide III	806vs	Sym C—O—C of cyclic ethers
880m	$\nu N—CH_2—O$	751m	νC=O out-of-plane

[a] vs = very strong; vw = very weak; m = medium; w = weak.

intensity of the asymmetric stretching vibration of amide II at 1601 cm^{-1} decreased compared to the same band with MMU. As in MMU, the DMU compound also showed a characteristic absorption for the aliphatic ether group at 1050 cm^{-1}, which exists as an impurity.

Linear and Cyclic Urea Derivatives with Ether Linkage

The presence of linear and cyclic ether linkages in the UF prepolymer as well as derivatives after curing is presumed but not proven. To aid in the establishment of the presence of such ether type linkages, model compounds such as dimethyloloxy methylenediurea (DMMU) and dimethylol uron dimethylether (DUDE) were synthesized. The band assignments for these compounds are summarized in Table V. A representative absorption spectrum is shown in Figure 2.

In the case of DMMU, the linear monosubstituted amide, both NH bending and C—N stretching modes absorb strongly at 1557 cm^{-1}. The absorption band at 1098 cm^{-1} is due to the aliphatic ether linkage and a broad, strong peak around 1020–1040 cm^{-1} is due to C—O stretching of the methylol group. These assignments agree with the sharp absorbance bands at 1050 and 1013 cm^{-1} for ether and the $—CH_2OH$ group in the DMU compound.

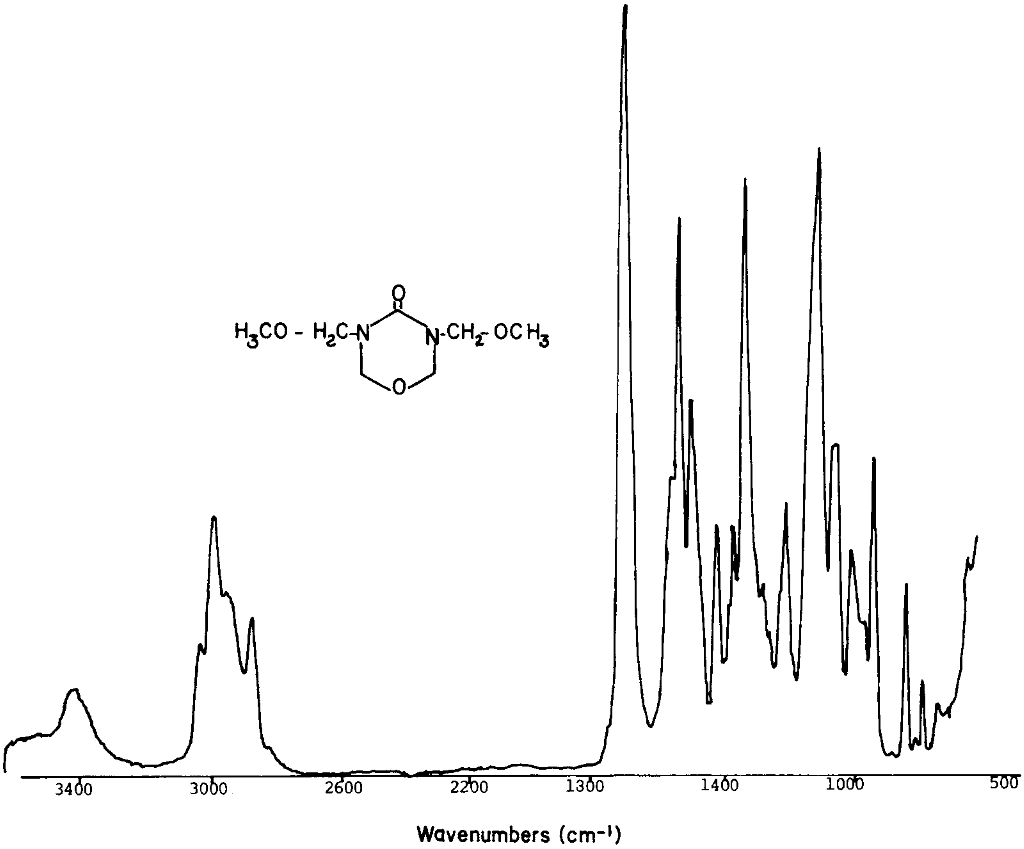


Fig. 2. Infrared absorption spectrum of dimethyloluron dimethylether (DUDE).

In DUDE, the strong absorption band around 1500 cm^{-1} is assigned to the amide II group. A strong absorption band around 1300 cm^{-1} is attributed to the bending of the OH of the CH_2OH group. This is probably due to the incomplete dehydration of dimethylol compound which is formed as an intermediate during the synthesis of DUDE. The asymmetric stretching vibration of the cyclic ether is observed at 1074 cm^{-1}. A strong absorption band at 806 cm^{-1} is observed for cyclic ether linkages.[18b]

Interpretation of Urea-Formaldehyde Prepolymer Spectra

Due to the multiplicity of structure in the polymer, the absorption frequencies are very broad and overlapped. In all the prepolymers, the spectra obtained at 3600-2000 cm^{-1} region have very little useful information. This broadening is due to the presence of byproducts in the resin, such as water and excess formaldehyde, which allow hydrogen bonding with the reactive functional groups such as $—CH_2OH$, NH_2, and —NH. However, spectra obtained from the freeze-dried prepolymers give sharper characteristic absorption peaks in this region. A representative infrared absorption spectrum of freeze-dried and non-freeze-dried UF7 prepolymer is shown in Figure 3.

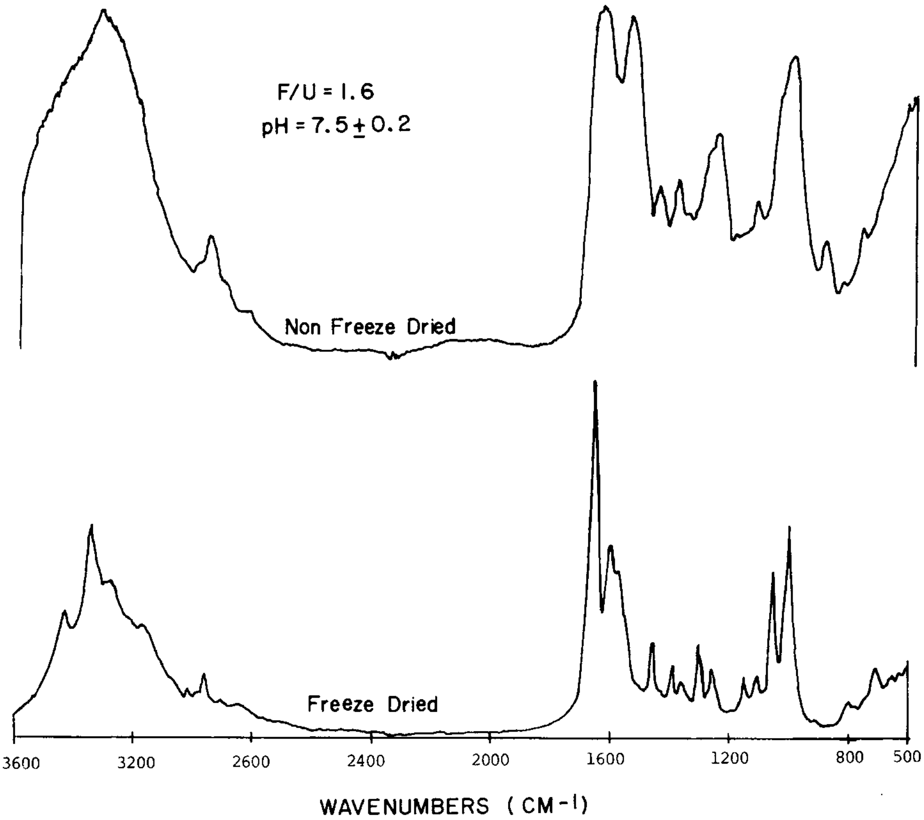


Fig. 3. Infrared absorption spectra of freeze-dried and non-freeze-dried UF7 prepolymer.

The assignments of absorption bands in UF prepolymers are tabulated in Table VI.

3500–3100 cm^{-1} Region

In the UF7 resin (see Fig. 3), a medium absorption peak is seen at 3440 cm^{-1}, which is characteristic of the NH stretching mode for the free —NH_2 group. The —NH stretching of the bonded —NH group is observed at a lower frequency near 3340 cm^{-1}. In the absorption spectra of the other resins, a broad band with a high noise level is seen in this region indicating less of the amino structure is present. Compared to the UF9 prepolymer (see Fig. 4), the freeze-dried UF7 prepolymer gives a stronger, more distinct band at 3340 cm^{-1}, indicating that the amount of bonded NH is higher compared to the free NH_2.

3100–2900 cm^{-1} Region

In the UF7 prepolymer, a medium absorption peak is observed about 3015 cm^{-1}. In the case of linear and cyclic ethers, in model compounds such as DMMU and DUDE (see Table II), a distinct, weak absorption band appears around 2995 cm^{-1} which is characteristic of the C—H stretching mode of the

TABLE VI
Assignment of Absorption Bands in Urea-Formaldehyde Prepolymers[a]

Frequency (cm^{-1})	Comments	Assignment (lit.[10])	Assignment (Author's work)
3440–3445	Medium	Not available	νNH mode in free NH_2
3340–3345	Strong	Not available	νNH mode of bonded NH_2
3015–3020	Medium to weak	Not available	νasy. CH mode of the $-CH_2-O-CH_2-$
2960–2970	Strong	Not available	νsy. CH mode of CH_2 of ether, CH_2OH, and $N-CH_2$
2900–2910	Weak	Not available	νasy. CH mode of $-CH_2OH$
1660–1630	Very strong in all prepolymers	Amide I mainly C=O; C—N and NH deformation	Amide I mainly due to C=O stretching
1600–1550	Strong in all polymers	Amide II (C—N and NH def.)	Amide II, mixture of C—N and NH def; the contribution of NH def. is higher
1470–1460	Weak	CH mode in CH_2O; $N-CH_2-N$	Most likely due to CH bending in CH_2 of $N-CH_2-N$
1400–1390	Weak	CH mode in CH_2	νCH of CH_2OH
1370–1360	Medium	Not available	νC—N mode
1300–1305	Strong	OH def. in CH_2OH plus cyclic amide III	OH def. of CH_2OH
1260–1265	Medium	Amide III bond for sec. amide	Amide III
1150–1130	Medium	Aliphatic ether C—O stretch plus C—N stretch in sec. amide	νasy. $>N-CH_2-N<$
1060–1065	Very strong	Not available	νC—O of ether
1000–1005	Very strong	C—O stretch in methylol	OH def. of CH_2OH
800–780	Medium	Not available	Sym. cyclic νC—O of —C—O—C—
720–700	Medium	Not available	νC—N of $-NH-CH_2-NH-$

[a] The spectra recorded between 3600 and 600 cm^{-1}.

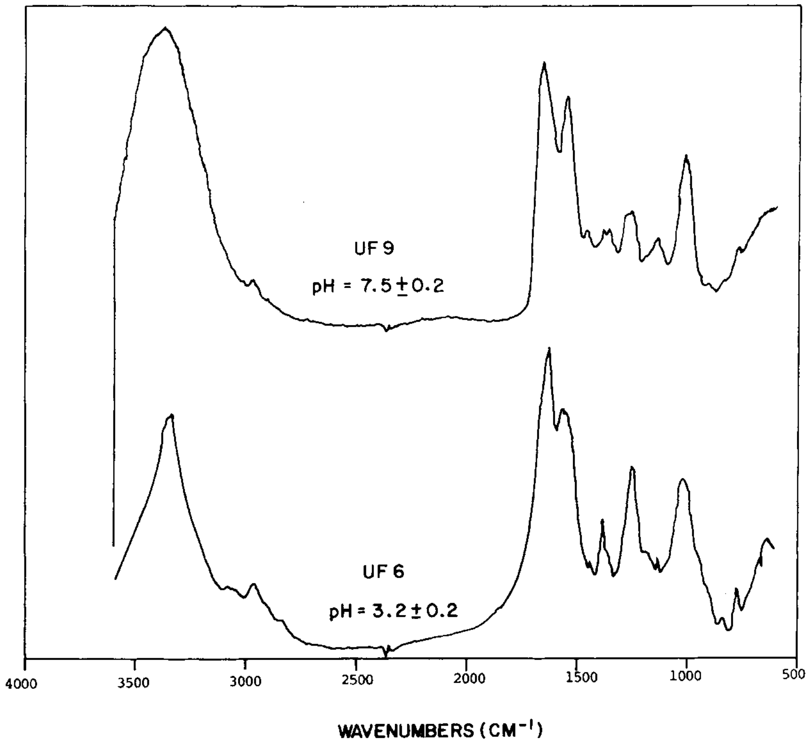


Fig. 4. Infrared absorption spectra of prepolymer: (a) UF9 at pH 7.5 ± 0.2 and (b) UF6 prepared at pH 3.2 ± 0.2. The F/U ratio in both the resins is 1.7.

$—CH_2—O—CH_2—$ group. On the basis of model compounds, this band at 3015 cm^{-1} is assigned to the asymmetric CH_2 stretching of the $—CH_2—O—CH_2—$ group. A sharp strong band appears at 2960 cm^{-1}, which is a combination of the asymmetric CH stretching modes of ether, alcohol, and $>N—CH_2—N<$ groups. As expected, the symmetric stretching mode is more intense than the asymmetric mode. A weak yet distinct absorption band appears around 2900 cm^{-1}. The author assigns this peak to the asymmetric CH stretching of the $—CH_2OH$ (see Table VI). The asymmetric stretching frequency of the $>N—CH_2—N<$ is probably weak and badly overlapped so that it does not appear as a distinct band in this region. However, such distinct bands are not observed in the rest of the resins. This is probably due to the high conversion of the $—CH_2OH$ in the polymers.

1660-1630 cm^{-1} Region

A very strong absorption band is observed at 1650 cm^{-1} in all lab-made prepolymers. In urea and the monosubstituted urea derivatives, such as monomethylolurea (see Table 1), a doublet is seen around 1600–1630 cm^{-1}.

The absorption band at the higher wavenumber is assigned to the C=O stretching of amide I; the peak at the lower frequency is assigned to the NH_2 deformation mode. However, in disubstituted urea compounds, such as methylene diurea (1635 cm^{-1}), 1,3-dimethylurea (1640 cm^{-1}), and in derivatives with linear ether linkages DMMU (1674 cm^{-1}) a strong absorption band appears which the author assigned to the C=O stretching mode of amide I (see Table VI). In the case of urea and the monosubstituted urea derivatives, the contribution of the NH mode of the free NH_2 group to the C—O stretching of amide I is very large. Thus, a doublet is seen in this region. But in case of the disubstituted urea derivatives, where there are no free $—NH_2$ groups, the contribution of the NH mode of free NH_2 is minimal. Thus, only a singlet is seen. A distinct single absorption band appears at 1660–1630 cm^{-1} for all of our resins, indicating a high conversion of the NH_2 group. This peak is mainly due to the C=O stretch of amide I.

1600–1550 cm^{-1} Region

The amide II band at 1500–1560 cm^{-1} is very strong in all UF prepolymers. This absorption band is observed in our model compounds, MMU and DMU solids, which contain secondary amides. The frequency of the amide II band is sensitive to the configuration between the C=O and NH groups in the amides.[22,23] According to the normal coordinate analysis and calculations of potential energy distribution using monomethylol urea and dimethylol urea,[24,25] the amide II band observed is the strong band in the 1550–1560 cm^{-1} region, which has been estimated to arise from 61% (C—N) and 30% (N—H). Pshenitsyna et al.[24] observed a similar band shift when the secondary amide was converted to tertiary amide.

A considerable shift is seen in the case of the UF7 prepolymer (see Fig. 3) in the 1600–1550 cm^{-1} region. A sharp peak appears at 1600 cm^{-1}. This peak is characteristic of NH_2 deformation of the primary amide. A very weak shoulder band is seen around 1580 cm^{-1}. This is characteristic of the NH deformation mode (amide II) of secondary, noncyclic amides. This indicates that the NH absorption mode of the secondary amide II is present in all of lab-prepared prepolymers and is clearly seen in UF7. In UF8, a shoulder appears in this region. This observation is consistent with recently published results.[10]

1470–1460 cm^{-1} Region

In all the prepolymers and model compounds, a weak absorption band at 1470–1460 cm^{-1} is observed. This absorption is most likely due to the CH_2 bending mode of the $—CH_2—N$ group. This assignment is in agreement with the literature.[19,24,26,27] The intensity of this peak varies in all polymers and reflects the amount of $—CH_2—N\langle$ present in each of the prepolymers.

1400–1360 cm^{-1} Region

All the prepolymers give a strong absorption band around 1390 cm^{-1} with a shoulder peak at 1360 cm^{-1}. Two distinct bands with high intensity at 1390 and 1360 cm^{-1} appear in the UF6 prepolymer. In the case of the UF10 resin, a weak doublet is observed. On the basis of our model compounds, MU and DU, the band at 1390 cm^{-1} is assigned to the CH stretching of the CH_2OH group. The medium band at 1360 cm^{-1} is attributed to the C—N stretching for all of the UF prepolymers. The relative intensity of bands at 1390 and 1360 cm^{-1} is a clear indication of the amount of CH_2OH and the C—N present in the prepolymer. However, a weak band around 1380–1400 cm^{-1} was assigned to the CH mode in CH_2 and CH_3 by Myers.[10]

1300–1260 cm^{-1} Region

A strong, broad band is observed at 1300–1260 cm^{-1} for the UF7 resin. However, a sharp band at 1260 cm^{-1} with a shoulder at 1300 cm^{-1} appears in all the prepolymers. A very strong band at 1300 cm^{-1} and a medium distinct peak at 1260 cm^{-1} appear in the case of the UF7 prepolymer. Disubstituted urea model compounds show a very strong absorption band around 1300 cm^{-1} (see Table IV), and the author ascribes this band to the —OH deformation of CH_2OH. The OH deformation absorption for primary alcohols occurs at about 1300 cm^{-1}.[18c] In the disubstituted urea compound, the amide III band appears at 1259 cm^{-1}. In the dialkyl ureas, the peaks in the 1330–1240 cm^{-1} region are assigned to the amide III band on the basis of the amide III–III′ shift to the 1000–900 cm^{-1} on deuteration. The potential energy distribution of amide III in dimethylol urea showed 52% (N—H) and 24% (C—N).[28] On the basis of the available data, it is concluded that medium band absorption at 1260 cm^{-1} is due to amide III in our polymers (see Table VI).

1150–1130 cm^{-1} Region

A moderately strong absorption band appears between 1150 and 1130 cm^{-1} in our polymer spectra, and also in the mono and disubstituted model compounds. This peak is assigned to asymmetric stretching of $>N-CH_2-N<$. In the literature[10] this peak has been assigned to the C—O stretch of aliphatic ether.

1060–970 cm^{-1} Region

A broad, strong band with a shoulder peak around 1060 cm^{-1}, with maximum peak intensity at 1020 cm^{-1}, is observed in all the prepolymers except in UF7. Myers[10] discussed the possible assignment of this peak to ether, amide, or the hydroxyl groups. In our UF7 prepolymer, two strong, distinct absorption peaks appear at 1060 and 1000 cm^{-1}. Most of the simpler aliphatic ethers absorb near 1125 cm^{-1}, and overall the $CH_2—O—CH_2$ gives rise to a strong band at 1140–1085 cm^{-1}.[18c, 19b] In the linear urea derivatives with ether linkages such as dimethyloloxymethylene diurea, a strong band at 1050 cm^{-1} is observed. In case of tertiary cyclic urea derivatives with cyclic ether linkages, the asymmetric stretching vibration of the ether is observed at 1074 cm^{-1}. Thus it is clear that linear and/or cyclic aliphatic ether absorptions are not frequently observed below 1050 cm^{-1}. On the basis of our model compounds, the absorption peak at 1060 cm^{-1} is assigned to the ether group. However, on the basis of his evidence Myers[10] concluded that the band at 1030–1050 cm^{-1} is assigned in UF polymers to the amide linkage. The spectra for mono- and dimethylol urea compounds, show a distinct peak with maximum absorption at 1000 cm^{-1}. In UF7 prepolymer, a strong peak appears at 1000 cm^{-1} (see Fig. 5). On the basis of our model compounds this band is ascribed to the C—O stretch of CH_2OH. This assignment is supported by Chabert's[29] assignment for the band a 1000–1020 cm^{-1} for $—CH_2OH$ in mono- and dimethylol urea polymers. Becher[17] indicates that peaks at 1000 cm^{-1} in dimethylol urea and a 1015 cm^{-1} band in monomethylol urea are due to the $—CH_2OH$ group.

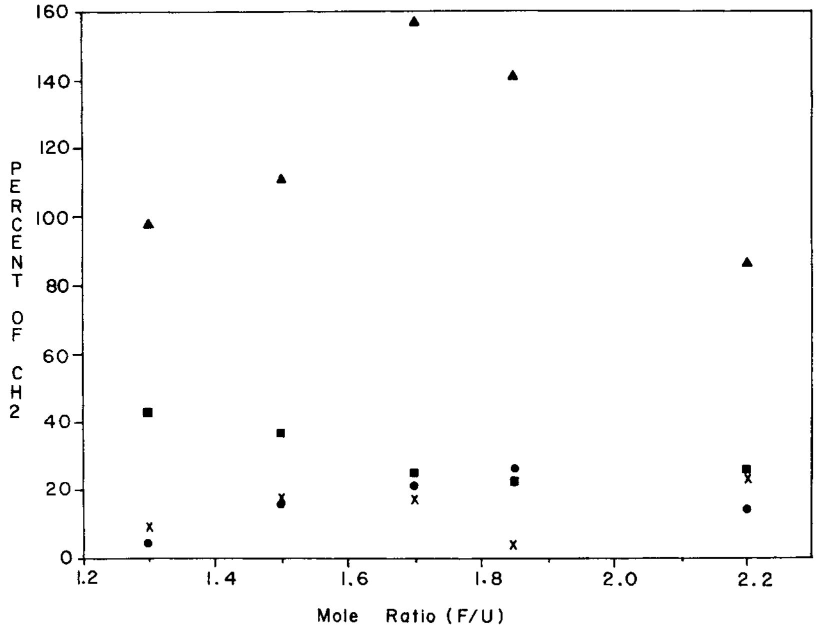


Fig. 5. The plot of percent of reactive functional moieties of the freeze-dried prepolymers vs. the mole ratio: (▲) N—CH_2—N; (●) ether; (×) methylol; (■) symmetric cyclic ether.

800–780 cm^{-1} Region

A medium absorption band appears around 800 cm^{-1} in our cyclic model compound and in all our UF polymers. The author ascribes this band to symmetric (cyclic) —C—O—C stretch for six-membered cyclic compounds.[18c]

720–700 cm^{-1} Region

A medium absorption band is observed at 720–700 cm^{-1} only in the UF7 prepolymer. On the basis of our model compounds the peak is assigned to C—N of NH—CH_2—NH group.

DISCUSSION

The —CH symmetric and asymmetric stretching modes are chosen as ideal for the qualitative estimation of ethers (linear and cyclic), methylol, and $>N—CH_2—N<$ groups present in the prepolymers. On the basis of model compounds, the band at 3015 cm^{-1} is assigned to the asymmetric CH stretching mode of the —CH_2—O—CH_2— group. A sharp strong band is observed around 2960 cm^{-1} which is a combination of the symmetric —CH stretching modes of ether, methylol, and $>N—CH_2—N<$ groups. The symmetric stretching mode is more intense than the asymmetric mode. A weaker yet distinct absorption band around 2900 cm^{-1} is assigned to the symmetric CH stretching mode of the —CH_2OH (see Table VI). For example, the ratio of ether and methylol contents in different UF resins is obtained from the following equation:

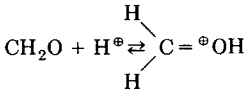
$$R = \frac{A_{3015}}{A_{2960}} \times 100 \text{ (for methylene ether)}$$

$$R = \frac{A_{2900}}{A_{2960}} \times 100 \text{ (for methylol)}$$

R is the relative amount of components present and A_{3015}, A_{2900}, and A_{2960} are the areas of asymmetric CH stretching of ether, methylol, and the combination of ether, methylol, and $>N-CH_2-N<$ groups, respectively. Such qualitative analysis of each functional group moiety present in the prepolymer is possible with the features associated with FT-IR, such as spectrum magnification, uniform base line correction, and peak area measurement between specific wavenumbers in all recorded spectra. Such features are very helpful in analyzing the differences in the absorption frequencies of many characteristic groups in prepolymers prepared when the feed composition is kept constant and the pH is changed (see Fig. 4). For example, the UF6 prepolymer was condensed under very acidic media (pH 3.2 ± 0.2) and UF9 at slightly alkaline condition with pH of 7.5 ± 0.2. The feed composition of urea and formaldehyde in both the polymers is 1 and 1.7 mol, respectively. A dramatic change in the intensity of the amide II band at 1550 cm^{-1} is observed when the UF6 and UF9 final resins are compared. A significant change in the peak intensity and peak area is observed in the CH_2 bending mode of the CH_2OH group at about 1440 cm^{-1}. The relative amounts of ether, methylol and $>N-CH_2-N<$ content for UF6 is found to 1.4, 5.5, and 38.5, respectively. For UF9, the relative amounts of ether is 2.3, methylol 50.0, and $>N-CH_2-N<$ 6.9. Such structural differences may have a very significant effect on the end product properties. These important differences in the contents of reactive moieties can be explained as follows:

Acid Catalyzed UF Resins

In acidic condition it is more likely that the protonation occurs on the oxygen atom of formaldehyde, that is,

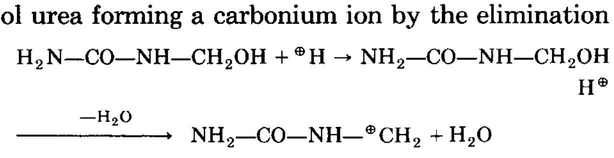


$$CH_2O + H^{\oplus} \rightleftarrows \begin{matrix} H \\ \\ H \end{matrix}\!\!>C=^{\oplus}OH$$

While discussing the protonation of formaldehyde it is important to note that the Cannizzaro reaction is favored as the explanation for the acidic character of aqueous formaldehyde solutions. The first step is probably the addition of protonated formaldehyde to urea to form a monomethylol urea:

$$NH_2-CO-NH_2 + CH_2=^{\oplus}OH \rightarrow \underset{\text{(monomethylol urea)}}{NH_2-CO-NH-CH_2OH} + {}^{\oplus}H$$

Further step growth condensation may proceed by further protonation of monomethylol urea forming a carbonium ion by the elimination of water:



$$H_2N-CO-NH-CH_2OH + {}^{\oplus}H \rightarrow NH_2-CO-NH-CH_2\underset{H^{\oplus}}{OH}$$

$$\xrightarrow{-H_2O} NH_2-CO-NH-{}^{\oplus}CH_2 + H_2O$$

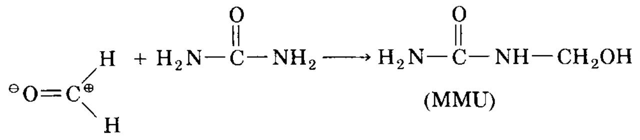
The monomethylol urea with reactive carbonium ion may further react with available urea to give methylenediurea:

$$NH_2{-}CO{-}NH{-}{}^{\oplus}CH_2 \xrightarrow{H_2N{-}CO{-}NH_2} NH_2{-}CO{-}NH{-}CH_2{-}NH{-}CO{-}NH_2$$

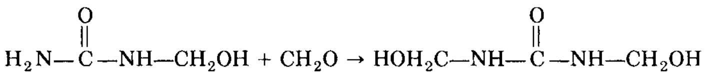
Thus under acidic condition, the $>N{-}CH_2{-}N<$ structure is highly favored as the spectra reflect (Fig. 4). Also with the final prepolymer, the concentration of the CH_2OH group is very low. This inference is easily seen in the absorption spectrum of the UF6 resin. In UF6, the intensity of absorption band at 1440 cm^{-1} is very low, which is characteristic of the CH_2 bending mode of CH_2OH group. Further confirmation is evident from the low intensity of the absorption peak at 1000 cm^{-1}, which is ascribed to the OH deformation of the CH_2OH group. With the low concentration of free methylol groups, the possibility of a $-CH_2OH$ group reacting with another $-CH_2OH$ group, forming a $-CH_2{-}O{-}CH_2-$ linkage is very low. This observation is clearly noticed in the low intensity of the absorption band at 1060 cm^{-1}, which is characteristic of the $-C{-}O{-}C-$ group.

Base Catalyzed UF Resins

In the case of the prepolymers, such as UF9, prepared in a slightly alkaline media of pH 7.5, there is an electrophilic attack by formaldehyde on a nucleophilic urea, forming monomethylol urea (MMU):


(MMU)

MMU will then further react with another molecule of formaldehyde giving rise to dimethylol urea (DMU):



$$H_2N{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH{-}CH_2OH + CH_2O \rightarrow HOH_2C{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH{-}CH_2OH$$

(DMU)

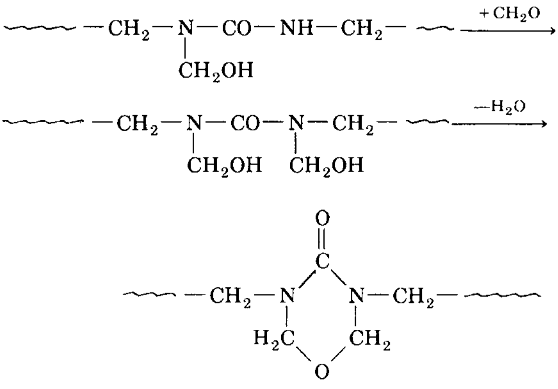
Thus, the step-growth condensation is random, giving rise to the mixture of MMU and DMU. Consequently, in the polymer the concentration of free methylol groups is very large but very little $>N{-}CH_2{-}N<$ is formed. This is clearly observed in the UF9 absorption spectrum (see Fig. 4). The intensities of absorption bands of $-CH_2$ of $-CH_2OH$ at 1460 cm^{-1} and OH deformation of $-CH_2OH$ at 1000 cm^{-1} are very large. Due to the large concentration of free methylol groups in the polymer prepared in less acidic and slightly alkaline media, the chance of a $-CH_2OH$ group reacting with another molecule of $-CH_2OH$ to give an ether linkage is very high. This is clearly seen in the intensity of absorption band at 1060 cm^{-1}, which is characteristic of C—O stretching of the $-C{-}O{-}C-$ group.

Effect of Composition Change

A great deal of information is obtained in the case of freeze-dried prepolymers in which the feed ratio is changed and the pH is kept constant, UF1–UF5 (see Table II). In Figure 5 the percent change of CH stretching of $>\mathrm{N{-}CH_2{-}N}<$; ether, methylol, and cyclic ether is plotted against the mole ratio of F/U. It is obvious from Figure 5 that the methylol and ether content increases as the feed ratio increases. The maximum content of ether and methylol is found in the prepolymer of F/U ratio of 1.85. With further increase of mole ratio, for example, F/U = 2.2, the ether and methylol content decreases. Chiavarini et al.'s[30] proton NMR analysis shows that the percentage of $>\mathrm{N{-}CH_2OH}$ decreases and $\mathrm{{-}CH_2O{-}}$ increases as the feed ratio (F/U) increases. However, on the basis of infrared studies, Myers[31] concludes that the higher the ratio of F/U, both ether and methylol content will increase. It is interesting to note that the percent of cyclic ether is higher when the mole ratio of F/U is lower (F/U = 1.3) and the content decreases as the feed ratio increases (see Fig. 5). Another important observation is the change in $>\mathrm{N{-}CH_2{-}N}<$ content of different polymers. The $>\mathrm{N{-}CH_2{-}N}<$ content increases as the feed ratio increases. After F/U = 1.75 the content of $>\mathrm{N{-}CH_2{-}N}<$ starts decreasing. Proton NMR quantitative results[30] showed a decrease as F/U increases. The decrease in $>\mathrm{N{-}CH_2{-}N}<$ content after F/U = 1.75 could be explained on the basis that as F/U increases the formation of tetramethylol urea increases.[32]

Cyclic and Linear Ether Linkages

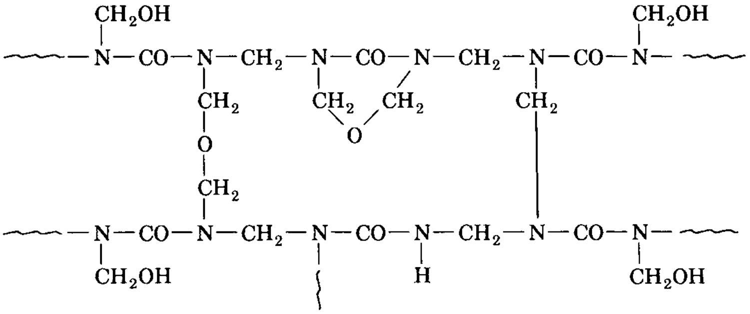
The formation of cyclic and linear structures with ether linkages cannot be overlooked. In all of the observed absorption spectra of the UF resins, a medium absorption band appears around the 800 $\mathrm{cm^{-1}}$ region which is assigned to cyclic ether. Thus, it is obvious that irrespective of the pH and mole ratios of the initial feed composition of urea and formaldehyde, a certain amount of cyclic urea compound may form during the condensation reaction. This can be explained as the amide group of $\mathrm{{-}NH{-}CH_2OH}$ in the growing polymer chain reacting with formaldehyde to form a dimethylol compound and finally into a cyclic ether compound by the elimination of water. This is shown in Scheme 1.



Scheme I

From Figure 4 it is inferred that, in the final resin, prepared in acidic media with pH < 5.0, the number of ether linkages is very low. In the case of final resins prepared at pH > 7.5, the ether bonds being formed are the result of an elimination of water molecule from the condensation of two methylol groups, resulting a linear ether linkages in the growing polymer chain (see Discussion: Base Catalyzed UF Resins).

Overall, a space-network final prepolymer results with a structure that can be represented in a simplified manner as shown in Scheme 2:



Scheme 2

Further studies were made in the thermal degradation of UF resins prepared under different conditions. Using the above spectral assignments, new insights into the structural degradation process have been developed to account for the formaldehyde emission from the cured resins. These results will be published later.

CONCLUSIONS

FT-IR spectroscopy has provided insight into the very complex structure of the urea-formaldehyde resin. The general structure of the intermediate mono, di, linear and cyclic urea derivatives were well characterized. The dependence of urea and formaldehyde addition and/or condensation reaction(s) on pH and mole ratio could be conveniently followed. The relative changes in the functional groups such as $>N—CH_2—N<$, methylol, linear, and cyclic ether contents could be detected. Based on the methods of preparation of polymers and their characterization by FT-IR, an overall structure of UF resin has been proposed.

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