

Synthesis–Structure–Performance Relationship of Cocondensed Phenol–Urea–Formaldehyde Resins by MALDI-ToF and ^{13}C NMR

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ABSTRACT: Matrix assisted laser desorption ionization time of flight (MALDI-ToF) mass spectrometry has consistently confirmed on a number of PUF resins that phenol–urea cocondensates exist in phenol–urea–formaldehyde (PUF) resins. A noticeable proportion of methylene-linked phenol to urea cocondensates were detected in all the PUF resins tried, alongside methylene bridges connecting phenol to phenol and urea to urea. The PUF, PF, and UF oligomers formed were identified. Variations of the PUF preparation procedure did always yield a certain proportion of the mixed phenol to urea cocondensates. Their relative proportion was determined and related the synthesis procedure used. Comparison of the MALDI-ToF results with a ^{13}C NMR investigation showed that in a real PUF resin in which phenol to urea cocondensates were identi-

fied the methylene bridge NMR signal at 44 ppm, characteristic of phenol to urea unsubstituted model compound cocondensates, does not appear at all. This confirmed that this peak cannot be taken as an indication of the existence of phenol and urea condensation under actual resin preparation conditions. The peak indicating cocondensation in PUF resins in which the phenolic nuclei and urea are substituted appears instead at 54.7–55.0 ppm. Thermomechanical analysis has again confirmed that the resin gel times greatly accelerates with increasing urea molar content. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1182–1194, 2008

Key words: adhesives; MALDI; resins; structure–property relations; synthesis

INTRODUCTION

Phenol–formaldehyde (PF) thermosetting resins are extensively used as exterior-grade adhesives in the wood industry, particularly in the wood panels industry.¹ The wood panels industry relies heavily on the use of these synthetic resins as adhesives, bonded products constituting the majority of the wood products on the market today. Over many years, excellent formulations have been developed for these resins for wood applications. Although some trial and error industrial research has been and is still carried out in the field of resin formulations, nonetheless resin knowledge has progressed to such an extent that scientific principles are used today to develop resins of ever improving performance. In recent years, the increase in the cost of phenol because of the increasing cost of oil has prompted research in resin engineering to decrease the cost of PF resins whereas maintaining or even improving their performance.^{1–11} The development

of phenol–urea–formaldehyde (PUF) resins is one among several different approaches developed for this purpose. Considerable amount of research has been carried out on PUF resins synthesis, properties, and characterization of reaction products.^{9–13} The start of their extensive industrial utilization goes back now to the late 1990s.^{9–13}

Low condensation phenol–formaldehyde (PF) resins coreacted under alkaline conditions with up to 42% molar urea on phenol during resin preparation were found to yield PUF resins capable of faster hardening times than equivalent pure PF resins prepared under identical conditions and presenting better performance than the latter^{10,11} when used as adhesives for wood particleboard. Part of the urea was found by ^{13}C NMR to be copolymerized to yield the alkaline PUF resin whereas, especially at the higher levels of urea addition, unreacted urea was still present in the resin. Nonetheless, there are still some doubts by other authors as regards the copolymerization of phenol and urea through formaldehyde in these resins.¹⁴ It is for this reason that an extensive investigation on the effect of PUF resins formulation and synthesis on the products obtained has been carried out, to confirm or dispel such doubts. The different PUF resins and their

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intermediates, including the resins which other authors alleged to lack of phenol-urea condensation,¹⁴ were examined in depth by ¹³C NMR, moreover, with the use of the more pointed and modern MALDI-ToF technique.

Since its introduction by Karas and Hillenkamp in 1987,¹⁵ Matrix-Assisted Laser Desorption/Ionization (MALDI) mass spectrometry has greatly expanded the use of mass spectrometry toward large molecules and has revealed itself to be a powerful method for the characterization of both synthetic and natural polymers.^{16–24} Fragmentation of analyte molecules on laser irradiation can be substantially reduced by embedding them in a light absorbing matrix. As a result intact analyte molecules are desorbed and ionized along with the matrix and can be analyzed in a mass spectrometer. This soft ionization technique is mostly combined with time-of-flight (ToF) mass analyzers. This is so as ToF-MS present the advantage of being capable to provide a complete mass spectrum per event, for its virtually unlimited mass range, for the small amount of analyte necessary and the relatively low cost of the equipment. This technique has already been used to determine the series of oligomers prepared in PF, MUF, and other polycondensation resins and to solve questions at the molecular level for these resins that could not be solved by ¹³C NMR.^{22–27}

This article then deals with following the different chemical species formed and their distribution through the preparation of several different PUF resin formulations by analyzing the relevant fractions by ¹³C NMR and MALDI-ToF Mass Spectrometry.

EXPERIMENTAL

Control PF resin preparation

About 1.0 mol of phenol was mixed with 0.35 mol NaOH as a 30% water solution and 1.2 mol of formaldehyde (as a 37% formalin solution) in a reactor equipped of mechanical stirring, heating facilities, and reflux condenser. After stirring for 10 min at 30°C, the temperature was slowly increased to reflux (94°C) over a period of 30 min and under continuous mechanical stirring and kept at reflux for further 30 min. About 0.5 mol of formaldehyde (as a 37% formalin solution) were then added. The reaction mix was now at pH 11 and the reaction was continued at reflux until the resin achieved a viscosity (measured at 25°C) of between 0.5 and 0.8 Pa s. The resin was then cooled and stored. Resin characteristics were then pH = 11, resin solids content = 50% ± 1%.

PUF resins formulations

PUF1 resins were prepared at F : P : U molar ratios of 2.1 : 1 : 0.48. The preparation procedure was as

follows: 1 mol of phenol was mixed with 0.35 mol NaOH as a 30% water solution and 1.4 mol of formaldehyde (as a 37% formalin solution) in a reactor equipped of mechanical stirring, heating facilities and reflux condenser. After stirring for 10 min at 30°C, 0.48 mol urea were then added, and the temperature was increased to reflux (88 ~ 90°C) over a period of 20 min and under continuous mechanical stirring and kept at reflux for further 40 min. About 0.7 moles of formaldehyde were then charged. The reaction was continued at reflux up to the required viscosity or stopped after further 40 min. Resins PF4 to PF10 were based on this preparation procedure with the variations indicated in Table I. Resins PUF2 and PUF3 were prepared according to the procedure outlined by previous authors.¹⁴

MALDI-ToF-MS

The spectra were recorded on a KRATOS Kompact MALDI 4 instrument. The irradiation source was a pulsed nitrogen laser with a wavelength of 337 nm. The length of one laser pulse was 3 ns. The measurements were carried out using the following conditions: polarity-positive, flight path-linear, mass-high (20 kV acceleration voltage), 100–150 pulses per spectrum. The delayed extraction technique was used applying delay times of 200–800 ns.

MALDI-ToF sample preparation

The samples were dissolved in acetone (4 mg/mL). The sample solutions were mixed with an acetone/water solution (10 mg/mL acetone-water mix) of the matrix. As the matrix 2,5-dihydroxy benzoic acid was used. For the enhancement of ion formation, NaCl was added to the matrix. The solutions of the sample and the matrix were mixed in equal amounts and 0.5–1 μL of the resulting solution were placed on the MALDI target. After evaporation of the solvent, the MALDI target was introduced into the spectrometer.

¹³C-NMR analysis

The liquid ¹³C NMR spectrum of the PUF resin used was obtained on a Brüker MSL 300 FT-NMR spectrometer. Chemical shifts were calculated relative to (CH₃)₃Si(CH₂)₃SO₃Na dissolved in D₂O for NMR shifts control.²⁸ The spectra were done at 62.90 MHz for a number of transients of approximately 1000. All the spectra were run with a relaxation delay of 5 s and chemical shifts were accurate to 1 ppm. In this article, only one of the PUF NMR spectra is reported and discussed as an example of what found with all of the other resins spectra.

TABLE I
MALDI Fragmentation Peaks for a Pure PF Resin

M + Na ⁺ (exp.) Da	M + Na ⁺ (calc.)	Relative intensity	Unit type		
			A 106	B 136	
Dimers					
313.0	313	76	–	2	HOCH ₂ –P–CH ₂ –P–(CH ₂ OH) ₂
342.9 ^a	343	100	–	2	(HOCH ₂) ₂ –P–CH ₂ –P–(CH ₂ OH) ₂ and/or HOCH ₂ –P–CH ₂ OCH ₂ –P–(CH ₂ OH) ₂ ^a
357.1	357	37	–	2	HOCH ₂ –(CH ₂) ⁺ –P–CH ₂ OCH ₂ –P–(CH ₂ OH) ₂
374.9	374	26	–	2	(HOCH ₂) ₂ –P–CH ₂ OCH ₂ –P–(CH ₂ OH) ₂
Trimers					
430.9	432	7	–	3	⁺ CH ₂ –P–CH ₂ –P(–CH ₂ OH)–CH ₂ –P–(CH ₂ OH) ₂ ^a
449.2 ^a	449	28	–	3	HOCH ₂ –P–CH ₂ –P(–CH ₂ OH)–CH ₂ –P–(CH ₂ OH) ₂ ^a
479.3	479	100	–	3	(HOCH ₂) ₂ –P–CH ₂ –P(–CH ₂ OH)–CH ₂ –P–(CH ₂ OH) ₂ ^a
Tetramers					
551.1	551	22	2	2	(HOCH ₂) ₂ –P–CH ₂ –P–CH ₂ –P–CH ₂ –P–(CH ₂ OH) ₂ ^a
	or		1	3	HOCH ₂ –P–CH ₂ –P(–CH ₂ OH)–CH ₂ –P–CH ₂ –P–(CH ₂ OH) ₂ ^a
585.0	585	18	–	4	HOCH ₂ –P–CH ₂ –[P(–CH ₂ OH)–CH ₂ –] ₃ –OH ^a
615.6	615	56	–	4	(HOCH ₂) ₂ –P–CH ₂ –[P(–CH ₂ OH)–CH ₂ –] ₃ –OH ^a
Pentamers					
721.9	721.6	13	–	5	HOCH ₂ –P–CH ₂ –[P(–CH ₂ OH)–CH ₂ –] ₄ –OH ^a
752.0	751	34	–	5	(HOCH ₂) ₂ –P–CH ₂ –[P(–CH ₂ OH)–CH ₂ –] ₄ –OH ^a
781.5	781	6	–	5	(HOCH ₂) ₂ –P–CH ₂ OCH ₂ –P(–CH ₂ OH)–CH ₂ – [P(–CH ₂ OH)–CH ₂ –] ₃ –OH
Hexamer					
858.4	858	9	1	5	HOCH ₂ –P–CH ₂ –[P(–CH ₂ OH)–CH ₂ –] ₅ –OH ^a
888.3	887	2	–	6	(HOCH ₂) ₂ –P–CH ₂ –[P(–CH ₂ OH)–CH ₂ –] ₅ –OH ^a
Heptamers					
1024.7	1023	15	–	7	(HOCH ₂) ₂ –P–CH ₂ –[P(–CH ₂ OH)–CH ₂ –] ₆ –OH ^a
Octamers					
1101.2	1098	4	2	6	HOCH ₂ –P–CH ₂ –P–CH ₂ –[P(–CH ₂ OH)–CH ₂ –] ₆ –OH ^a
	or		1	7	P–CH ₂ –[P(–CH ₂ OH)–CH ₂ –] ₇ –OH ^a
1161.1	1159	11	–	8	(HOCH ₂) ₂ –P–CH ₂ –[P(–CH ₂ OH)–CH ₂ –] ₇ –OH ^a
Nonamers					
1297.5	1295	9	–	9	(HOCH ₂) ₂ –P–CH ₂ –[P(–CH ₂ OH)–CH ₂ –] ₈ –OH ^a
Decamers					
1433.7	1431	7	–	10	(HOCH ₂) ₂ –P–CH ₂ –[P(–CH ₂ OH)–CH ₂ –] ₉ –OH ^a
Undecamers					
1569.9	1567	4	–	11	(HOCH ₂) ₂ –P–CH ₂ –[P(–CH ₂ OH)–CH ₂ –] ₁₀ –OH ^a
Dodecamer					
1705	1703	3	–	12	(HOCH ₂) ₂ –P–CH ₂ –[P(–CH ₂ OH)–CH ₂ –] ₁₁ –OH ^a

Note that the predominant repeating unit is 136 Da.

^a Wherever there is an alternative between one –CH₂OH and one –CH₂OCH₂–, with the –CH₂OH always in the majority.

Thermomechanical analysis

A PF resin control (P : U : F molar ratio = 1.24 : 0 : 1.75) and PUF resins of P : U : F molar ratios of, respectively, (1.0 : 0.24 : 1.75), (0.8 : 0.44 : 1.75), (0.7 : 0.54 : 1.75), (0.6 : 0.64 : 1.75), were tested dynamically by thermomechanical analysis (TMA) on a Mettler apparatus. Total molar ratio was maintained constant for all the resins at (P + U) : F = 1 : 1.41. Triplicate samples of beech wood alone, and of two beech wood plys each 0.6 mm thick bonded with each system, for a total samples dimensions of 2161.2 mm were tested in nonisothermal mode between 40°C and 220°C at a heating rate of 10°C/

min with a Mettler 40 TMA apparatus in three points bending on a span of 18 mm exercising a force cycle of 0.1/0.5 N on the specimens with each force cycle of 12 s (6 s/6 s). The classical mechanics relation between force and deflection $E = [L^3 / (4bh^3)][F / (f)]$ allows the calculation of the Young's modulus E for each case tested.

RESULTS AND DISCUSSION

The MALDI-ToF results in Table I and Figure 1 show the oligomers formed in a phenol–formaldehyde resin. This resin was used as a control to compare it with the results obtained with phenol–urea–

Probe PF – Aceton/H₂O -- NaCl; Massenbereich: 200-1900 Da

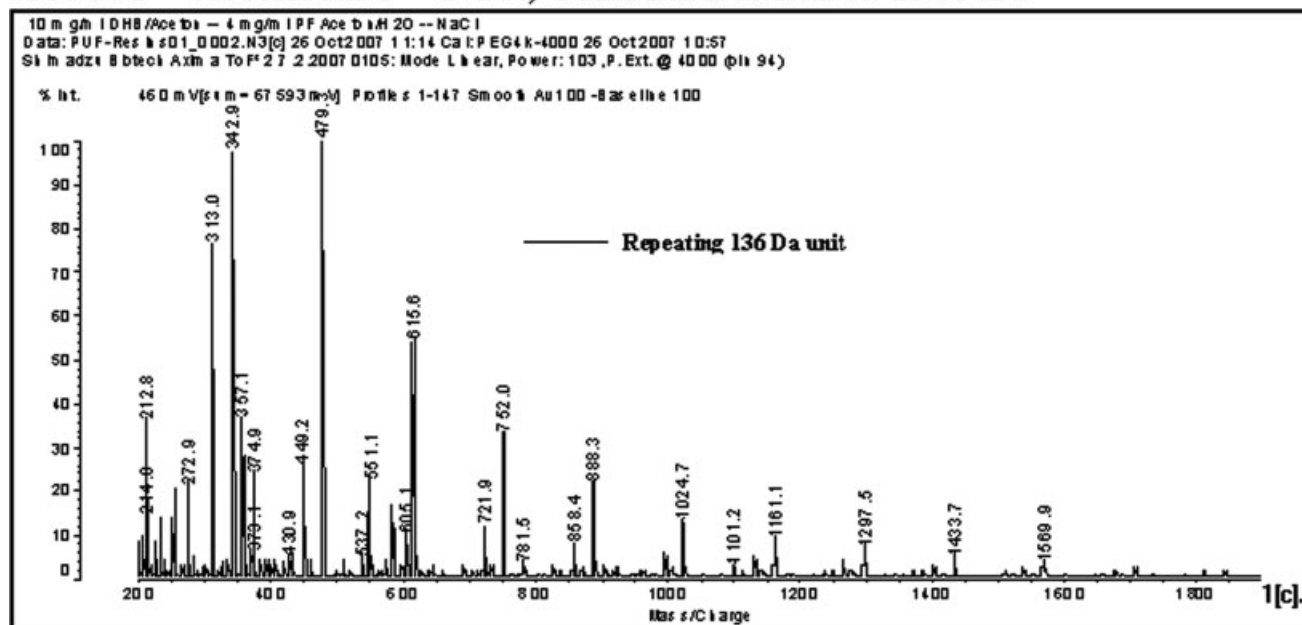


Figure 1 MALDI-ToF fragmentation peaks of control PF resin.

formaldehyde resins in which variations of formulations based on single or multiple successive additions of formaldehyde, urea, and phenol were carried out. Figures 2–5 show the MALDI ToF spectra of, respectively, PUFs 1, 5, and 9 the formulations of which are defined in Table II, and of intermediate A of PUF1 (Table II). The PUF oligomers species present are shown in Table III and their relative pro-

portions for the four different PUF resins are shown in Table IV. The results in Table III show that the oligomers formed in PUF resins are of three types, namely pure urea–formaldehyde (UF) species, pure phenol–formaldehyde (PF) species, and mixed cocondensed phenol–urea–formaldehyde (PUF) species. The repeating units indicated on some of the spectra are mainly the ones of molecular weight at

Probe PUF1 – Aceton/H₂O -- NaCl; Massenbereich: 200-900 Da

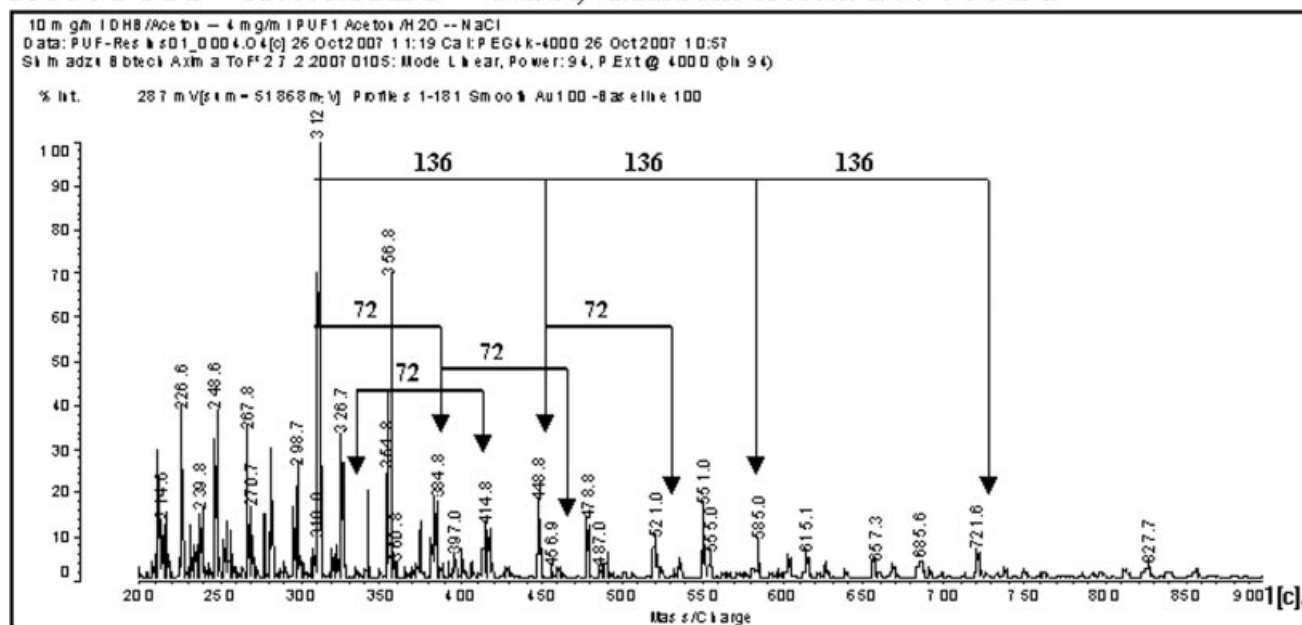


Figure 2 MALDI-ToF fragmentation peaks of finished PUF1 resin.

Probe PUF1A – Aceton/H₂O -- NaCl; Massenbereich: 200-900 Da

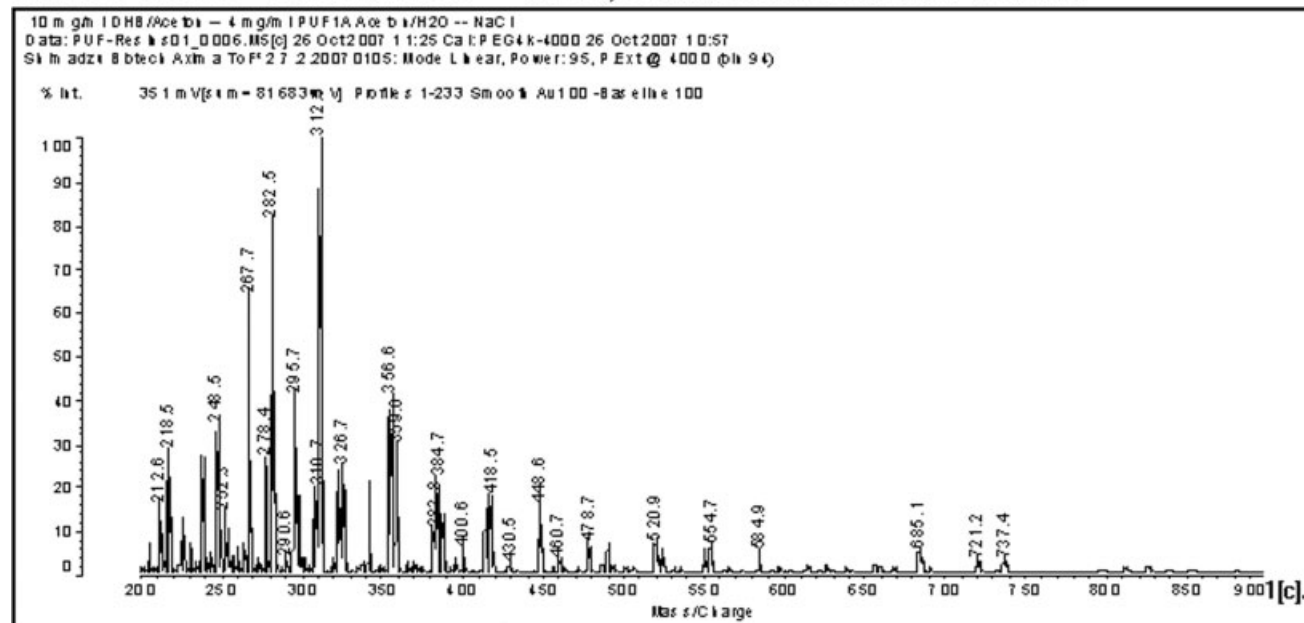
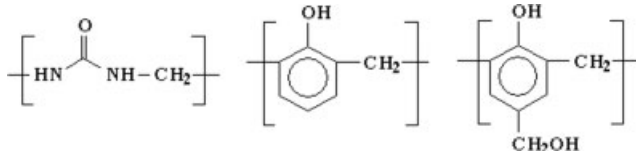


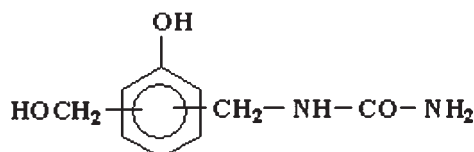
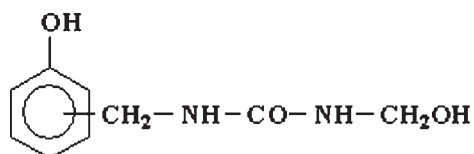
Figure 3 MALDI-ToF fragmentation peaks of first sample (sample A) of PUF1 resin.

72 Da for the UF segments, and the 106 Da but mainly the 136 Da for the PF segments, namely



Although in Table III there are several species which can be interpreted either as pure PF oligomers or cocondensed mixed PUF oligomers there are some species which can only be interpreted as mixed, cocondensed PUF oligomers, confirming that cocondensation between the two species actually occurs in these resins, even when the preparation formulation of the resin changes as much as what done passing from Resin 1 to Resin 9.

Among the peaks in Table III and Figures 2–4 that can only be explained by the existence of mixed cocondensed PUF species are the peaks at 248.6 Da, 384.8 Da, 414.8 Da, 521.0 Da, and 667.3 Da. The simpler of these species at 248.6 Da has either of the two following structures



where the hydroxymethyl group can be situated either on the urea or on the aromatic nuclei of the phenol. The high frequency in which the 136 Da repeating unit appears in the case of PF and PUF resins indicates, however, that the structure with the hydroxymethyl group situated on the phenolic aromatic nuclei is the most likely one to exist, or at least is in the majority.

Other peaks can either be interpreted as pure PF oligomers as well as mixed PUF oligomers. However, the repeating of the 72 and 136 Da units as shown in Figures 2 and 3 for the finished PUF1 resin and of its intermediate PUF1A indicate that this possibility is not likely and that these peaks are totally due to mixed cocondensed PUF oligomers. Thus, of these the 326.7 Da, 521.0 Da, 585.0 Da, and 827.7 Da peaks first do not occur in pure PF resins and second are from Figure 3 clearly formed by condensing PF oligomers having reacted with UF oligomers. For example, the 312.7 Da peak is clearly a pure PF oligomer (cf. Figs. 1 and 2), but only by adding to it 1 urea unit (72 Da) one can obtain the 384.8 Da species, only by adding to it 2 urea 72 Da units one can obtain the 448.8 Da species, and only by, respectively, adding to it 3 and 4 urea 72 Da units one can obtain the 521 and 585 Da species.

The other peaks in Tables III and IV could be formed by either PF or UF or mixed PUF species for which it cannot be excluded that they are mixes of all three cases. One cannot exclude either that cocondensed PUF species are present for these peaks too. The existence of definite mixed PUF oligomers as discussed earlier renders this most likely.

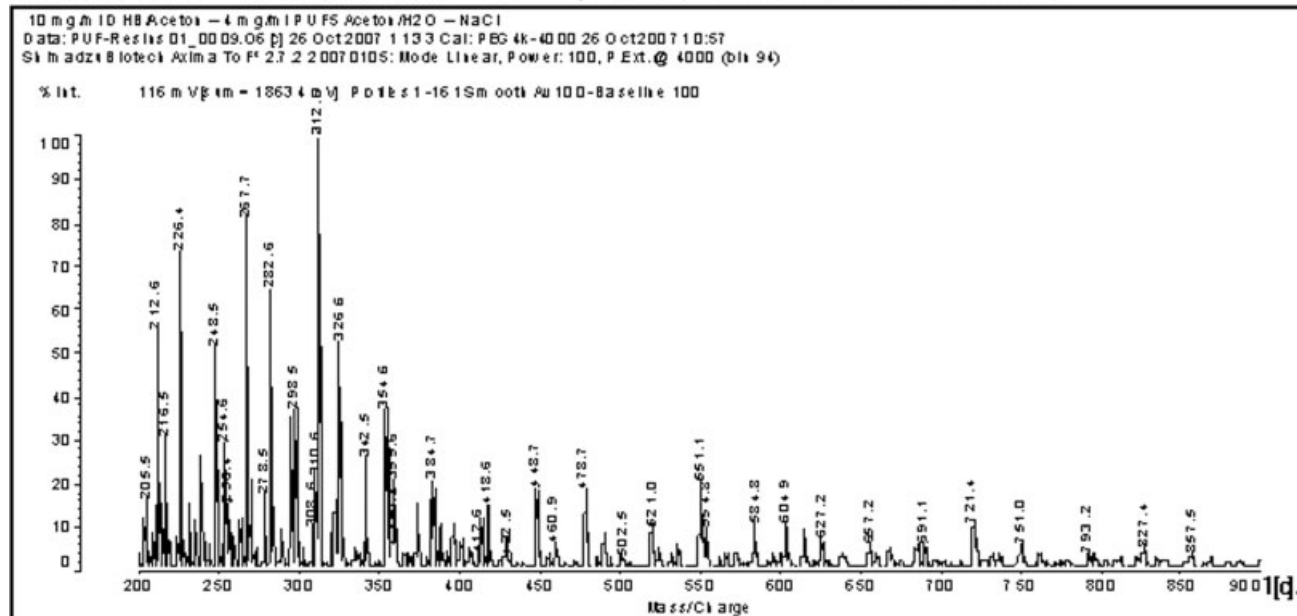
Probe PUF5 – Aceton/H₂O -- NaCl; Massenbereich: 200-900 Da

Figure 4 MALDI-ToF fragmentation peaks of finished PUF5 resin.

Calculating the relative proportions of cocondensed mixed PUF species for the final PUF1 resin from Table II results in a high relative proportion of 28% of mixed PUF species in relation to the UF and PF species present.

It is interesting to compare the results in Table IV as the formulation of the PUF changes. In Table I

are shown the differences in preparation procedures for the PUF1, PUF5, and PUF9 resins, where these have identical final molar ratios of F : P : U : NaOH = 2.1 : 1 : 0.48 : 0.35 but the formulations of which differ in number and sequence of addition of the materials. Thus, PUF1 is prepared by charging all the materials at the beginning of the reaction except

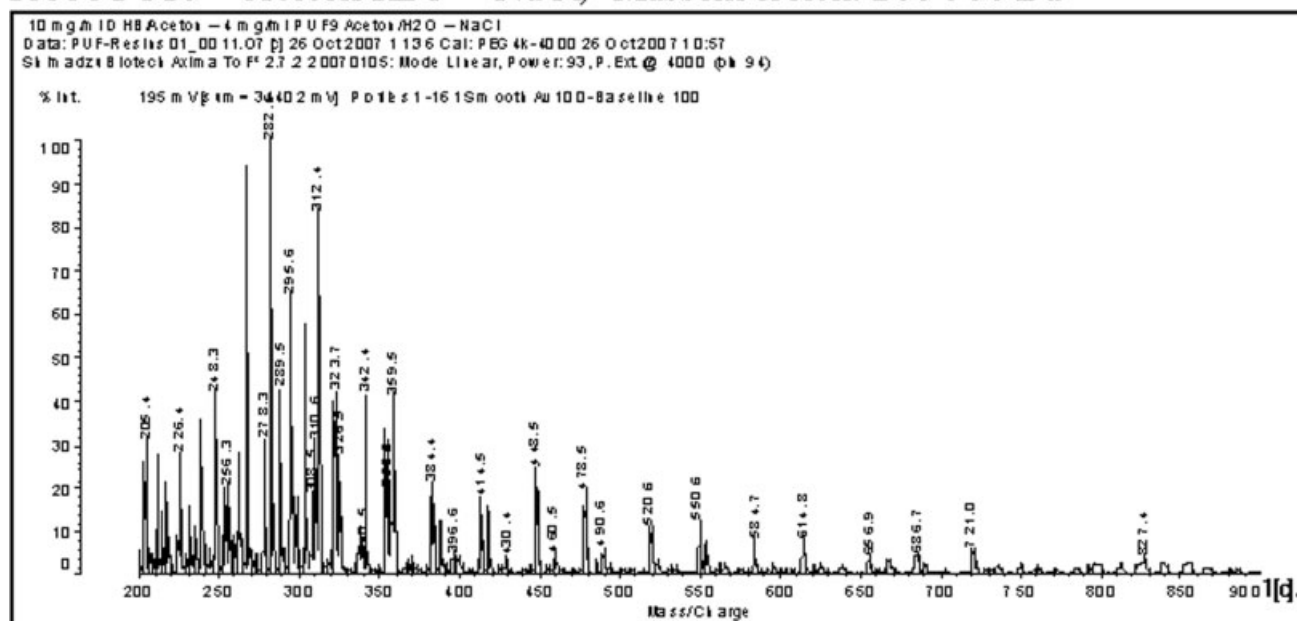
Probe PUF9 – Aceton/H₂O -- NaCl; Massenbereich: 200-900 Da

Figure 5 MALDI-ToF fragmentation peaks of finished PUF9 resin.

TABLE II
Description of Resin Synthesis and Sample Collection for NMR

Resin serial	Main characterizing description compare with control	Sample collection
PUF1 control	F : P : U : NaOH = 2.1 : 1 : 0.48 : 0.35, charge phenol, urea, and sodium hydroxide once at the beginning, <i>charge formaldehyde twice</i>	Collected samples each every 20 min after temperature reached 90°C. (PUF1A, PUF1B, PUF1C, and PUF1D)
PUF2 similar with Kim	F : P : U : NaOH = 2.1 : 1 : 0.48 : 0.53, <i>higher sodium hydroxide charge everything at once</i>	Collected samples each every 20 min after temperature reached 90°C. (KPUF2A, KPUF2B, KPUF2C, and KPUF2D)
PUF3	F : P : U : NaOH = 2.1 : 1 : 0.48 : 0.70, <i>More higher sodium hydroxide. Charge similar with PUF1</i>	Collected samples each every 20 min after temperature reached 90°C. (PUF3A, PUF3B, PUF3C, and PUF3D)
PUF4	F : P : U : NaOH = 2.1 : 1 : 0.48 : 0.35, <i>charge urea twice</i>	Collected samples just before second formaldehyde charge and after 20 min of second formaldehyde charge. (PUF4C and PUF4D)
PUF5	F : P : U : NaOH = 2.1 : 1 : 0.48 : 0.35, <i>charge phenol twice</i>	Collected samples each every 20 min after temperature reached 90°C. (PUF5A, PUF5B, PUF5C and PUF5E)
PUF9	F : P : U : NaOH = 2.1 : 1 : 0.48 : 0.35, <i>charge formaldehyde by drop wise</i>	Collected samples each every 20 min after temperature reached 90°C. (PUF9A, PUF9B, PUF9C and PUF9D)
PUF10	F : P : U : NaOH = 2.1 : 1 : 0.48 : 0.35, charge similar with PUF1 pH = 10 for 20 min, pH = 4.5 for 20 min, <i>then charge second formaldehyde and sodium hydroxide</i>	Collected samples each every 20 min after temperature reached 90°C. (PUF10A, PUF10B, PUF10C, and PUF10D)

TABLE III
MALDI Fragmentation Peaks for PUF1 Resin

M + Na ⁺ (exp.) Da	M + Na ⁺ (calc.)	Relative intensity	Unit type			
			A	B	C	
			106	136	72	
239.8	240	15	–	–	3	[U–CH ₂] ₃
267.8	269	34	–	–	3	HOCH ₂ –[U–CH ₂] ₃ or U–CH ₂ OCH ₂ –U–CH ₂ –U–CH ₂
296.7	298	26	–	–	3	HOCH ₂ –[U(–CH ₂ OH)–CH ₂] ₂ [U–CH ₂] ₂
248.6 ^a	248	40	–	1	1	HOCH ₂ –P–CH ₂ –U
312.7 ^a	313	100	–	2	–	HOCH ₂ –P–CH ₂ –P–(CH ₂ OH) ₂
	or		–	–	4	[U–CH ₂] ₄
	or		–	1	3	HOCH ₂ –U–CH ₂ –U–CH ₂ –P–(CH ₂ OH) ₂
326.7	329	34	–	–	3	HOCH ₂ –[U(–CH ₂ OH)–CH ₂] ₂ [U–CH ₂]
	or		–	1	1	
342.9	343		–	2	–	(HOCH ₂) ₂ –P–CH ₂ –P–(CH ₂ OH) ₂
356.8	359	70	–	–	3	HOCH ₂ –[U(–CH ₂ OH)–CH ₂] ₃
384.8 ^a	385	18	–	2	1	HOCH ₂ –U–CH ₂ –P–CH ₂ –P–(CH ₂ OH) ₂
414.8 ^a	415	13	–	2	1	HOCH ₂ –U–CH ₂ –P(CH ₂ OH)–CH ₂ –P–(CH ₂ OH) ₂
448.8 ^a	449	19	–	3	–	HOCH ₂ –P–CH ₂ –P(–CH ₂ OH)–CH ₂ –P–(CH ₂ OH) ₂
	and/or		–	2	2	HOCH ₂ –[U–CH ₂] ₂ –P–CH ₂ –P–(CH ₂ OH) ₂
	or		–	2	2	[U–CH ₂] ₂ –P(–CH ₂ OH)–CH ₂ –P–(CH ₂ OH) ₂
478.8 ^a	479	15	–	3	–	HOCH ₂ –P–CH ₂ –P(–CH ₂ OH)–CH ₂ –P–(CH ₂ OH) ₂
	and/or		–	2	2	HOCH ₂ –[U–CH ₂] ₂ –P–CH ₂ –P–(CH ₂ OH) ₂
	or		–	2	2	[U–CH ₂] ₂ –P(–CH ₂ OH)–CH ₂ –P–(CH ₂ OH) ₂
521.0 ^a	521	9	–	2	3	HOCH ₂ –[U–CH ₂] ₃ –P–CH ₂ –P–(CH ₂ OH) ₂
551.0 ^a	551	18	2	2	–	(HOCH ₂) ₂ –P–CH ₂ –P–CH ₂ –P–CH ₂ –P–(CH ₂ OH) ₂
	or		1	3	–	HOCH ₂ –P–CH ₂ –P(–CH ₂ OH)–CH ₂ –P–CH ₂ –P–(CH ₂ OH) ₂
585.0 ^a	585	9	–	4	–	HOCH ₂ –P–CH ₂ –[P(–CH ₂ OH)] ₂ –CH ₂ –P–(CH ₂ OH) ₂
	and/or		–	3	2	HOCH ₂ –[U–CH ₂] ₂ –P–CH ₂ –P(–CH ₂ OH)–CH ₂ –P–(CH ₂ OH) ₂
	or		–	3	2	[U–CH ₂] ₂ –[P(–CH ₂ OH)] ₂ –CH ₂ –P–(CH ₂ OH) ₂
615.1 ^a	615	6	–	4	–	(HOCH ₂) ₂ –P–CH ₂ –[P(–CH ₂ OH)–CH ₂ –] ₃ –OH
	and/or		–	3	2	HOCH ₂ –[U–CH ₂] ₂ –[P(–CH ₂ OH)–CH ₂] ₂ –P–(CH ₂ OH) ₂
	or		–	3	2	[U–CH ₂] ₂ –[P(–CH ₂ OH)] ₂ –CH ₂ –P–(CH ₂ OH) ₂
667.3 ^a	665	5	–	2	5	HOCH ₂ –[U–CH ₂] ₅ –P–CH ₂ –P–(CH ₂ OH) ₂
721.6	721.6	7	–	5	–	HOCH ₂ –P–CH ₂ –[P(–CH ₂ OH)–CH ₂ –] ₄ –OH
827.7	827.6	5	–	6	–	HOCH ₂ –[P–CH ₂ –] ₂ [P(–CH ₂ OH)–CH ₂ –] ₄ –OH

Note that the predominant repeating units are 136 and 72 Da.

^a species that are surely or most probably cocondensation products of urea, phenol, and formaldehyde.

TABLE IV
MALDI Fragmentation Peaks and Relative Proportions for PUF1, PUF1A, PUF5, PUF9, and PUF10 Resins

M + Na ⁺ (exp.) Da	M + Na ⁺ (calc.)	Relative intensity					
		PUF1	PUF1A	PUF5	PUF9	PUF10	
218.5	216	–	–	32	27	17	HOCH ₂ –[U–CH ₂] ₂ –OH [U–CH ₂] ₂ –U
226.4	227	39	13	74	28	86	
239.8	240	15	27	27	35	47	
248.5 ^a	248	39	36	53	41	–	
267.8	269	34	66	82	94	33	
282.5			82	66	100	34	HOCH ₂ –U–CH ₂ –U–CH ₂ –U–CH ₂ OH
296.7–298.6	298	26	42	36	65	100	
312.7 ^a	313	100	100	100	86	99	
326.7	329	34	26	53	28	–	
342.5	343	20	21	27	42	50	
356.8	359	70	42	36	34	–	
384.8 ^a	385	18	23	20	22	72	
414.8 ^a	415	13	15	15	17	–	
430.5			3	–	3	–	
448.8 ^a	449	19	18	19	25	–	
478.8 ^a	479	15	8	20	20	23	
521.0 ^a	521	9	9	10	12	–	
551.0	551	18	6	20	13	20	
585.0 ^a	585	9	6	9	9	10	
615.1 ^a	615	6	–	7	9	–	
667.3 ^a	665	5	–	–	5	–	
691.1	691	–	–	5	–	–	P–CH ₂ –[P(–CH ₂ OH)–CH ₂ –] ₄ –OH
721.6	721.6	7	5	12	6	–	
737.4		–	5	–	–	4	
751.0	751	–	–	6	–	–	HOCH ₂ –[P(–CH ₂ OH)–CH ₂ –] ₅ –OH
827.7	827.6	5	–	6	4	–	
857.6	857.6	–	–	4	–	–	HOCH ₂ –P–CH ₂ –[P(–CH ₂ OH)–CH ₂ –] ₅ –OH

^a Species that are surely or most probably cocondensation products of urea, phenol, and formaldehyde.

Probe PUF10 – Aceton/H₂O -- NaCl; Massenbereich: 200-900 Da

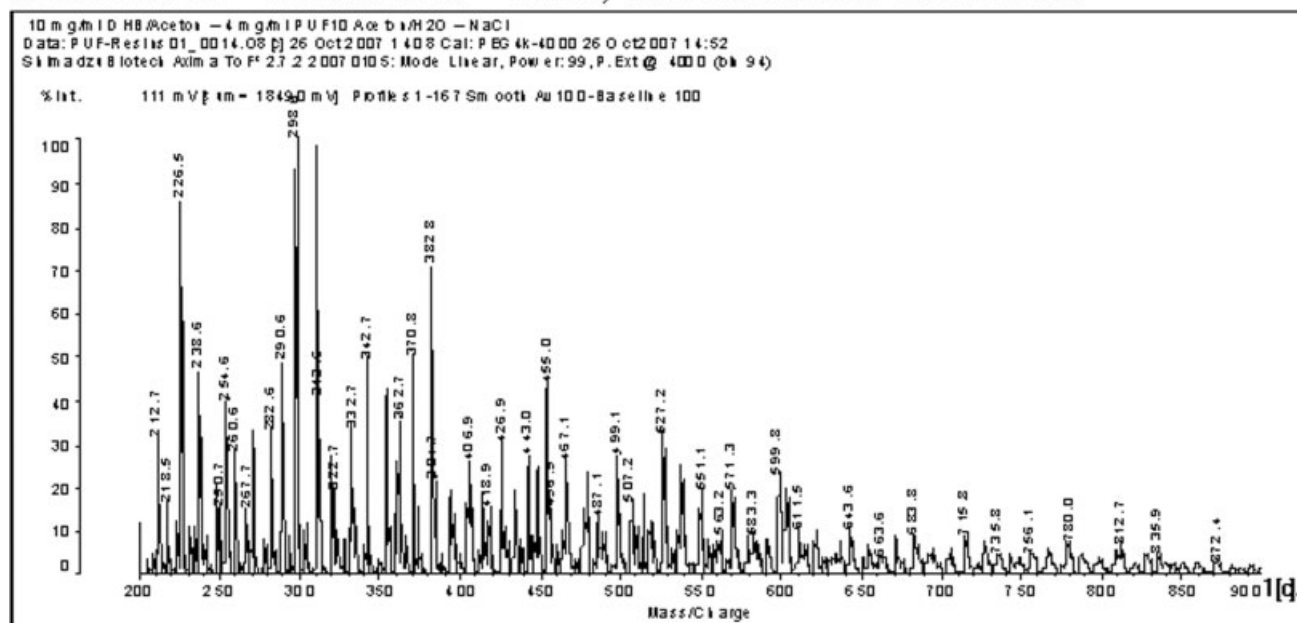


Figure 6 MALDI-ToF fragmentation peaks of finished PUF10 resin.

KPUF 2D, Na-Adducts; mass area: 270-900 Da

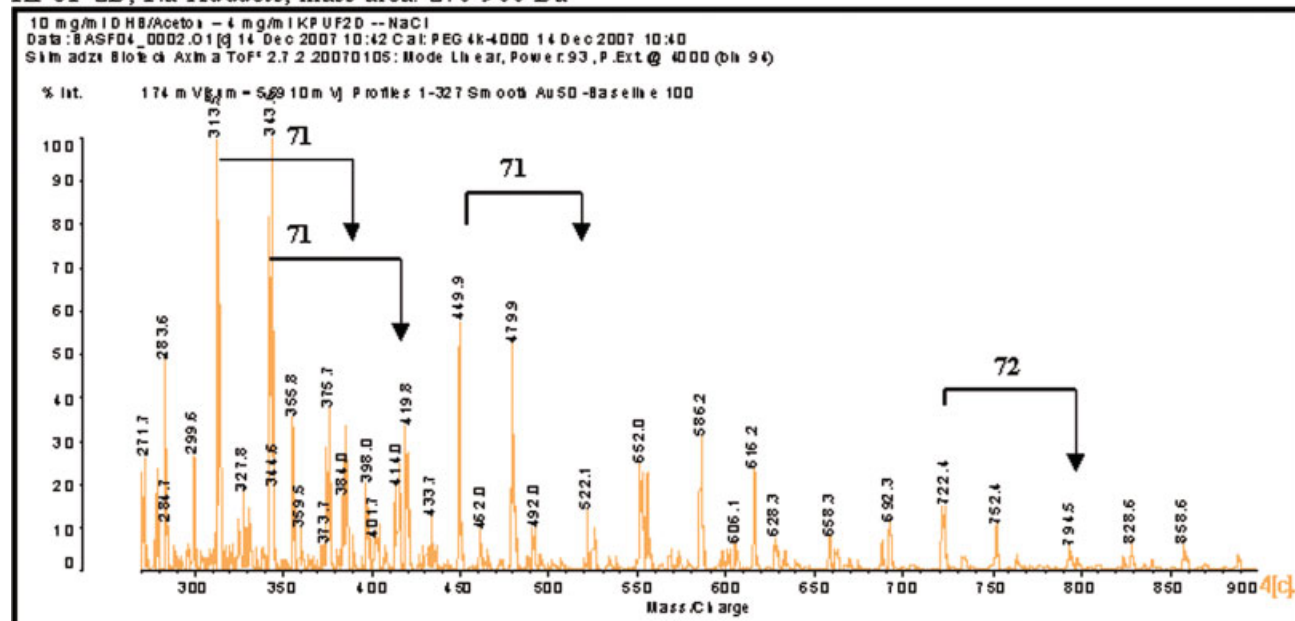


Figure 7 MALDI-ToF fragmentation peaks of finished PUF2 resin. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

formaldehyde that is added in two equal amounts at the beginning and in the middle of the reaction. PUF5 is prepared by adding phenol twice (at the beginning and in the middle of resin preparation). PUF9 is prepared as PUF1 but by adding formaldehyde continuously drop wise throughout the whole resin preparation reaction. The main differences

comparing Figures 3–5 appears to be (i) the greater regularity and evenness in peak intensity decrease in the growth of oligomers of progressively higher molecular weight seen in the right side of the spectrum for PUF9 in relation to PUF1 (cf. Figs. 3 and 5). (ii) The greater percentage proportions of lower molecular weight UF-based oligomers in PUF5, in

PUF 3D, Na-Adducts; mass area: 270-900 Da

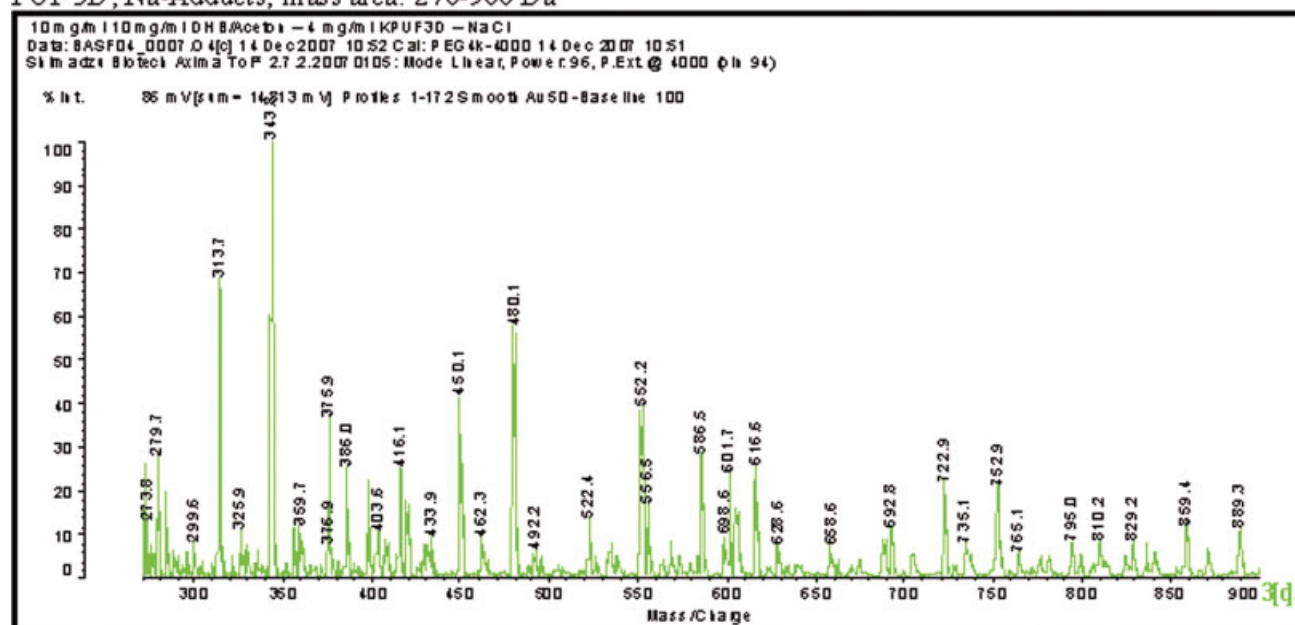


Figure 8 MALDI-ToF fragmentation peaks of finished PUF3 resin. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

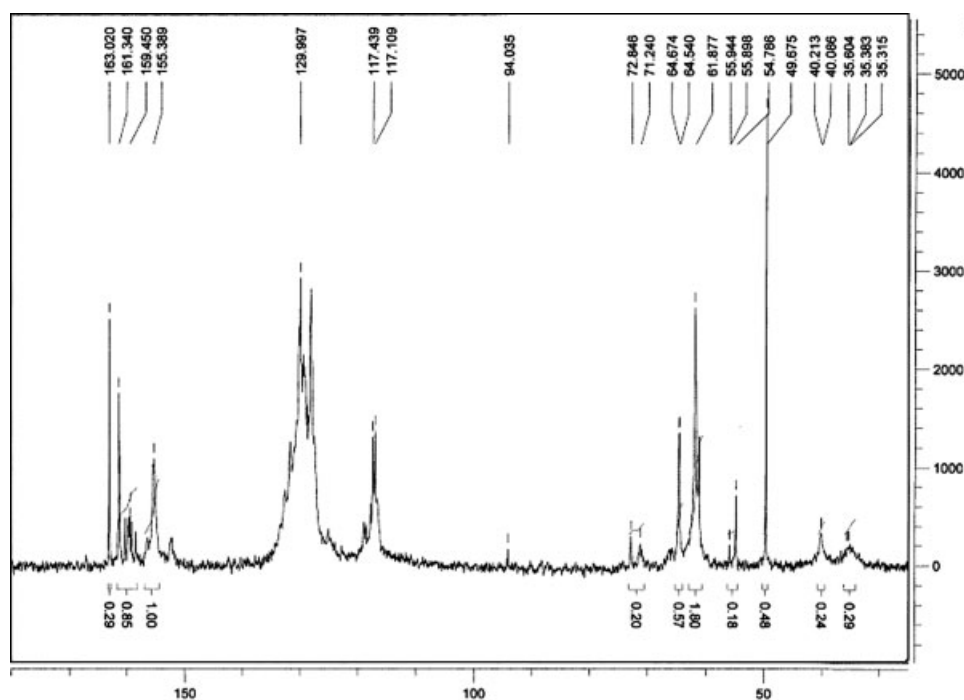


Figure 9 ^{13}C NMR spectrum of PUF1 resin showing the mixed methylene bridge signal at 54.8 ppm.

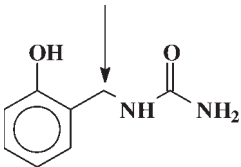
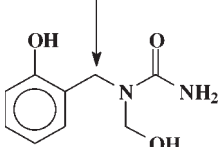
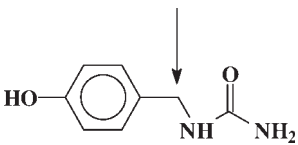
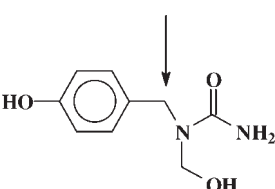
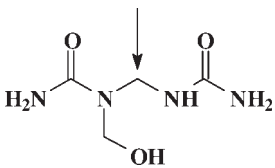
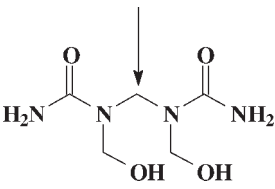
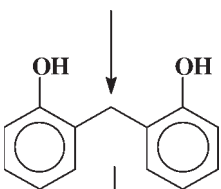
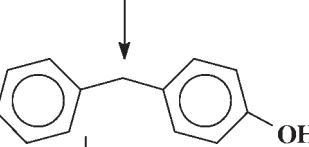
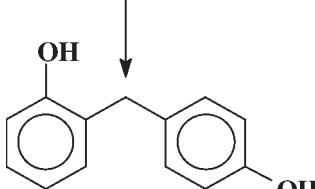
line with the greater opportunity urea has had to react with formaldehyde due to halving the proportion of the initial phenol in this formulation (cf. left hand side of Fig. 4 with Figs. 3 and 5). This more pronounced proportion of lower molecular weight UF-based oligomers, and respectively, lower proportion of higher molecular weight PF oligomers, is also observed in PUF1A when compared to PUF1. This is expected, as PUF1A is a resin sample just taken at the beginning of the PUF1 reaction where higher F oligomers participation is more likely. Although some trends in isolated peaks are also noticeable these trends are not regular and thus not many conclusions can be drawn more than what said earlier.

The results of PUF10 show some differences from those of the other PUF resins (Fig. 6, Table IV). The MALDI-ToF spectrum of this resin still presents the series 312.8, 382.8, 455.0, 527.2, 599.6, and 671 Da separated by the repeating 72 Da motive, corresponding to a PF dimer as in Table II, and to the oligomers linking to this, respectively, 1, 2, 3, 4, and 5 $-\text{U}-\text{CH}_2-$ repeating units, hence up to even longer UF segments linked to a PF dimer. However, in this resin, the peak at 298.8 becomes the dominant one, whereas it is rather small or even absent in the case of the other resins in Figures 2–5. The difference then between the 298.8 and 312.8 Da peaks can then just be ascribed to a $-\text{CH}_2-$ with the consequence that a series 226.5 Da (this peak too having acquired much greater intensity), 298.8, 312.8, 382.8, 455.0,

527.2, 599.6, and 671 Da can be ascribed to a series of UF oligomers of formula $[\text{U}-\text{CH}_2]_2-\text{U}$, $[\text{U}-\text{CH}_2]_3-\text{U}$ (298.8 Da), $[\text{U}-\text{CH}_2]_4$ (312.8 Da), $[\text{U}-\text{CH}_2]_5$, $[\text{U}-\text{CH}_2]_6$, $[\text{U}-\text{CH}_2]_7$, $[\text{U}-\text{CH}_2]_8$, and $[\text{U}-\text{CH}_2]_9$. This sequence explanation, not possible for the other resins, is very possible and likely for PUF10. The usual, pure PF oligomers sequence 312.8 Da, 448.8 Da, and 584.8 Da is also still present. Furthermore, a sequence 298.8 Da, + 72 Da = 370.8 Da, + 136 Da = 507.2 Da is present confirming that also for resin PUF10 cocondensed PUF species exist although they appear to be in much lower proportion in relation to the relative proportions of pure UF and pure PF oligomers than for the other PUF resins. This resin was in effect prepared according to a rather different synthesis sequence than the other resins. Formaldehyde was added in two steps as for resin PUF1, but, after a first 20 min reaction period at pH 10, an acid step was introduced. Thus, the reaction was brought down to pH 4.5 for 20 min at 90°C, the acid pH thus markedly favoring and enhancing UF condensation whereas simultaneously slowing down and inhibiting phenol-formaldehyde condensation.²⁹ The MALDI-ToF spectrum then just confirms that pure UF oligomers predominate, as indeed the preparation parameters used would lead to predict. Even in this very unfavorable situation though, even if in great minority, mixed cocondensed species are still present.

Recently, other researchers have denied the existence of cocondensation between phenol and urea

TABLE V
Methylene ($-\text{CH}_2-$) ^{13}C NMR Shifts in PUF, PF, and
UF Resin Segments

	47.5 ppm
	54.8 ppm
	43.3 ppm
	54.8 ppm
$\text{H}_2\text{NCONH}-\text{CH}_2-\text{NHCONH}_2$	50.04 ppm
	51.5 ppm
	63.7 ppm
	30.9 ppm
	39.8 ppm
	34.7 ppm

through aldehyde-generated methylene bridges, advancing the idea that PUF resins are only a mixture of PF and UF oligomers without cocondensation. The MALDI-ToF results above clearly show instead that noticeable proportions of cocondensates do indeed form, and this with a variety of formulations. First, it was noticed that the PUF formulations other researchers described as copied from our previous work^{10,11} were instead not the same contrary to what stated in their article.¹⁴ Second, we then investigated by MALDI-ToF and NMR PUF resins prepared (i) exactly according to our previously published formulations^{10,11} and variations on the theme, as well as (ii) according to the exact formulations used and reported instead by the other research group¹⁴ to see if a problem could exist and if so what such a problem could be. Figures 7 and 8 report the MALDI ToF results obtained with the resins prepared according to the procedures and proportions as defined by the other research group.¹⁴ It is clear that mixed PUF cocondensates clearly form, showing the same patterns observed for the resins in Figures 2–5. Thus, the peak species at 384, 414, 522, and 722 Da (Fig. 7) can exclusively be coreacted PUF oligomers. With one exception they are the same mixed, cocondensed PUF species shown in Tables III and IV, their relative proportions being also similar. Furthermore, the peak species at 313, 449.9, 479.9, 586.2, and 616.2 in Figure 7 are mixed species with a high probability of containing cocondensed PUF oligomers as shown in Table III. The same applies for the PUF3 resin in Figure 8 where the peaks at 386, 416, 522, and 795 can only be cocondensed PUF oligomers, and the peaks at 313.7, 450.1, 480.1, 586.5, and 616.6 Da have also a high probability of containing cocondensed PUF oligomers.

It is of interest to compare the species distribution observed by MALDI-ToF with the liquid phase ^{13}C NMR of the same resins. Comparison of the relative integrated peaks areas for different groups for all the finished resins showed correspondence with what observed by MALDI-ToF. It was then realized that the other research group¹⁴ had judged the presence or not of phenol to urea methylene bridges exclusively by the presence or absence of the small 44 ppm peak of the methylene bridge between phenol and urea identified in previous work under acid conditions by Tomita et al.^{30,31} and by no other means. Intense ^{13}C NMR work on liquid resins that presented by MALDI-ToF markedly high proportions of PUF cocondensates showed that this peak never appeared. An example of this is shown in Figure 9 showing the ^{13}C NMR of the finished PUF1 resin (sample PUF1D) where such peak does not appear notwithstanding that the MALDI-ToF spectra in Figures 2 and 3 show clearly and undeniably that phenol and urea cocondensates are present. It is

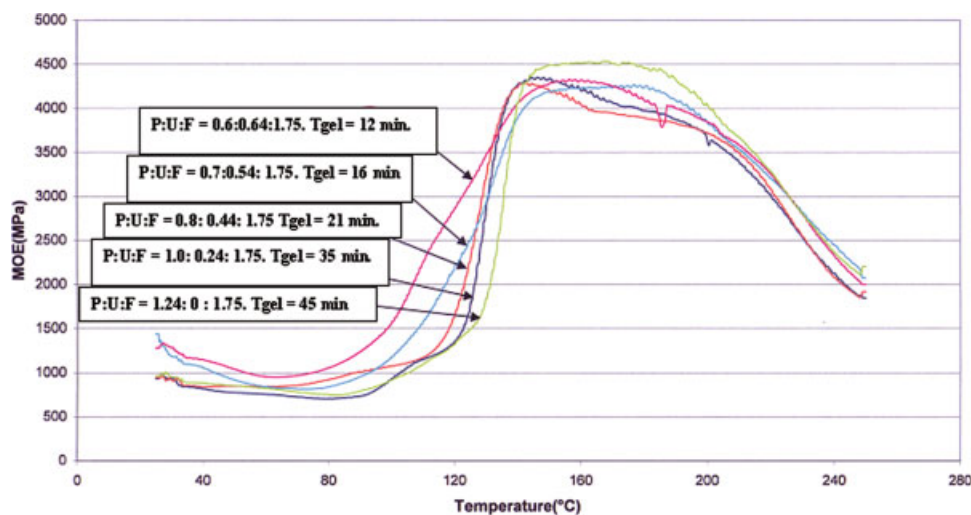


Figure 10 Thermomechanical analysis (TMA) comparing the curing rate results of a control PF resin (P : U : F molar ratio = 1.24 : 0 : 1.75) and of PUF resins of P : U : F molar ratios of (1.0 : 0.24 : 1.75), (0.8 : 0.44 : 1.75), (0.7 : 0.54 : 1.75), (0.6 : 0.64 : 1.75). Total molar ratio is the same for all the resins at (P + U) : F = 1 : 1.41. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

clear then that methylene bridges connecting phenolic oligomers to UF oligomers cannot present themselves only at 44 ppm. A study by ChemWindow of the possible shifts of such methylene bridges under a variety of environments is shown in Table V. These show that such methylene bridges are expected at 43.3 ppm, 47.5 ppm, and 54.8 ppm. A shift approaching 44 ppm can be expected only in the case of a methylene bridge linking a nonsubstituted phenol nuclei in para to an unsubstituted urea, and not in the case of substituted nuclei. It also understandable why Tomita et al.^{30,31} promoted this shift: he was working with model compounds and preparing just this type of unsubstituted mixed species under acid conditions, hence different from the alkaline ones under which PUF resins for wood are prepared. However, in the heavily substituted phenols environment of PF oligomers and resins and equally heavily substituted ureas environment of UF resins the shifts expected are clearly different, namely 47.5 ppm and 54.8 ppm as indicated in Table V. The NMR spectrum in Figure 9 shows quite clearly the peak at 54.8 ppm, this being just as noticeable as those of methylene bridges linking phenol to phenol and urea to urea. The relative integrals of PU, *p,p*PP, *o,p*PP, and UU methylene linkages are, respectively, of 0.18, 0.24, 0.29, and 0.48 in Figure 9. All the PUF resins prepared (Table II) present this pattern, and thus present to a greater or lesser extent methylene bridges linking phenolic species to urea species. It is interesting to point out that on the NMR of the group sustaining the lack of cocondensation¹⁴ this peak does indeed occur, but its area looks much smaller. This appears to indicate that phenol-to-urea cocondensation occurs even in

their resins, negating their hypothesis. Its lower proportion results probably from errors of synthesis and/or of its control.

As an example of the curing acceleration introduced by a PUF resin in relation to a PF resin, in Figure 10 are shown thermomechanical analysis of (TMA) curves of MOE as a function of temperature for PUF resins of different urea contents, whereas maintaining constant throughout the (P + U) : F molar ratio to 1.24 : 1.75. Thus Figure 10 reports the curing rate results of a PF resin (P : U : F molar ratio = 1.24 : 0 : 1.75) and of PUFs of P : U : F molar ratios of, respectively, (1.0 : 0.24 : 1.75), (0.8 : 0.44 : 1.75), (0.7 : 0.54 : 1.75), (0.6 : 0.64 : 1.75). The gel time of the resins in Figure 10 passes from 45 min for the pure PF resin to, respectively, 35, 21, 16, and 12 min for PUF resins of increasing urea molar content, fully confirming results reported previously with a number of different techniques.^{10,11}

CONCLUSIONS

MALDI-ToF mass spectrometry has consistently confirmed on a number of PUF resins that phenol-urea cocondensates exist. A noticeable proportion of methylene bridges connecting phenol to urea were detected alongside methylene bridges connecting phenol to phenol and urea to urea. Variations of the PUF preparation procedure did always yield a certain proportion of these mixed phenol to urea cocondensates. Their relative proportion depended in part by the preparation procedure used. Comparison of the MALDI-ToF results with a ¹³C NMR investigation showed that in a real PUF resin the methylene

bridge signal at 44 ppm, characteristic of phenol to urea unsubstituted model compounds, does not appear at all. Thus, this peak cannot be taken as an indication of the existence of phenol and urea condensation under actual resin preparation conditions. The peak indicating cocondensation in PUF resins in which the phenolic nuclei and urea are substituted appears instead at 54.7–55.0 ppm. Thermomechanical analysis has again confirmed that the resin gelling greatly accelerates with increasing urea molar content.

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