Alkaline PF Resins Linear Extension by Urea Condensation with Hydroxybenzylalcohol Groups

A. PIZZI,* A. STEPHANOU, I. ANTUNES, and G. DE BEER

Department of Chemistry, University of the Witwatersrand, Johannesburg, South Africa

SYNOPSIS

The linear increase of phenol–formaldehyde (PF) resins by reaction under alkaline conditions of the ortho- and para-hydroxybenzylalcohol groups of the PF resin with small molar percentages of urea was followed by model compounds reactions. Apparent rate constants of the reactions of urea with o- and p-hydroxybenzylalcohols were obtained. Both the ortho- and para-isomerides appeared to react faster with urea than for their autocondensation. The ortho-isomeride appears to react faster with urea than the para-isomeride, under alkaline conditions. Autocondensation under alkaline conditions instead appears to be faster in the case of p-hydroxybenzylalcohol. The properties of PF resins prepared with the addition of small amounts of urea appear to be consistent with what is observed in the model compounds reactions: Their gel times become faster and viscosity increases with increasing amounts of urea addition. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Recently, considerable interest has been shown in phenol–urea–formaldehyde (PUF) resins[1-3] for the preparation of thermosetting wood adhesives presenting acceptable exterior or semiexterior performance and of lower cost.[2,3] For these reasons the kinetics of condensation of hydroxybenzylalcohols with urea under acid reaction conditions have been studied in depth.[1] Under acid conditions gelling and curing of the PUF resin can be carried out through methylol groups on the urea to obtain curing times of an exterior resin, under mild acid conditions, as fast as for urea–formaldehyde resins.[2,3] For this reason the possibility of carrying out the reaction under alkaline conditions was not investigated. Alkaline reaction conditions are, however, of interest because as recently shown[4] the presence of small amounts of urea increase rapidly, considerably, and mostly linearly the degree of polymerization of phenolic resins. This occurs without the resin precipitating out of water solution, indicating a much greater tolerance to water of the phenolic resin at the higher

molecular mass reached.[4] In this manner acceleration of the phenolic resin curing, while still maintaining full exterior grade performance, could be achieved, although not at a greatly lower cost due to the low amount of urea used.

This work describes the kinetics and effects obtained by the reaction of urea with the methylol groups of phenolic resins and of their simple model compounds o-hydroxy-benzylalcohol (saligenin) and p-hydroxybenzylalcohol.

EXPERIMENTAL

Condensation of Hydroxybenzylalcohols with Urea

A mixture of 2.25 g of hydroxybenzylalcohol, 15 g distilled water, 3 g sodium hydroxide (30% mass/mass), and 1.10 g urea was mechanically stirred and heated at 93, 85, and 75°C in a round bottom flask equipped with reflux condenser for 6 h. Samples were removed at 15, 30, 60, 90, and 120 min and 6 h, and immediately freeze dried in a Chriss Alpha I-5 freeze drier. Autocondensation of the two hydroxybenzylalcohols was carried out under identical conditions but without any urea addition. The freeze-dried samples were analyzed by IR spectroscopy (Fig. 1)

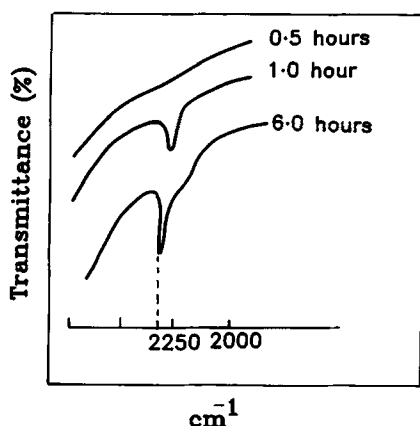* To whom correspondence should be addressed.

Figure 1 Variation of percent transmission 2250 cm^{-1} IR band indicating reaction of o-hydroxybenzylalcohol with urea as a function of reaction time at 93°C (0.5 h; 1.0 h; 6.0 h).

and by ^{13}C-NMR (Fig. 2), the latter using D$_2$O as solvent on a Bruker AC200. The results obtained follow. Reaction rates with urea were followed by the appearance of the IR band at 2250 cm^{-1} (Fig 1.) and in particular by the variation of the ratio of the percent transmittance of this band, with the invariable band at 3420 cm^{-1}, for the ortho-isomeride; for the para-isomeride by the ratio of the 2250 cm^{-1} band with the 1090 cm^{-1} band. Results are shown in Tables I and II and Figures 3–5. Autocondensation was followed by the ratio of the 1420 cm^{-1} band

(— CH$_2$OH scissoring) with the same fixed bands used above to follow the condensation of the hydroxybenzylalcohols with urea.

^{13}C-NMR ppm (Intensity in Parenthesis)

Saligenin 167.27 ppm (5.21), 131.98 (24.0), 131.78 (5.9), 131.27 (18.7), 121.88 (23.0), 116.93 (21.5), 63.81 (20.7).

p-Hydroxybenzylalcohol 168.79 ppm (5.0), 132.66 (26.6), 128.60 (7.1), 121.45 (23.4), 66.80 (15.3).

Saligenin/Urea Condensate 165.40 ppm (0.6), 164.6 (2.7), 161.17 (0.5), 133.16 (1.0), 132.80 (0.7), 132.30 (1.0), 132.02 (13.3), 131.54 (12.9), 131.08 (4.0), 130.42 (0.8), 130.25 (1.2), 120.97 (12.7), 120.32 (1.4), 119.82 (1.0), 118.46 (12.6), 63.45 (12.6), 37.12 (0.9).

p-Hydroxylbenzylalcohol/Urea Condensate 167.90 ppm (29.3), 165.41 (9.5), 164.80 (5.3), 133.70 (6.0), 132.65 (224.8), 132.47 (45.1), 129.97 (3.4), 129.11 (43.9), 122.56 (5.3), 121.22 (214.1), 120.86 (27.9), 66.77 (109.5), 42.07 (6.0), 37.14 (4.0).

60 min PF Resin, No Urea 160.00 ppm (4.4), 159.47 (6.3), 158.67 (5.6), 158.20 (4.2), 156.94 (3.1), 155.75, 155.65 (4.2), 155.14, 155.03 (6.3), 153.31
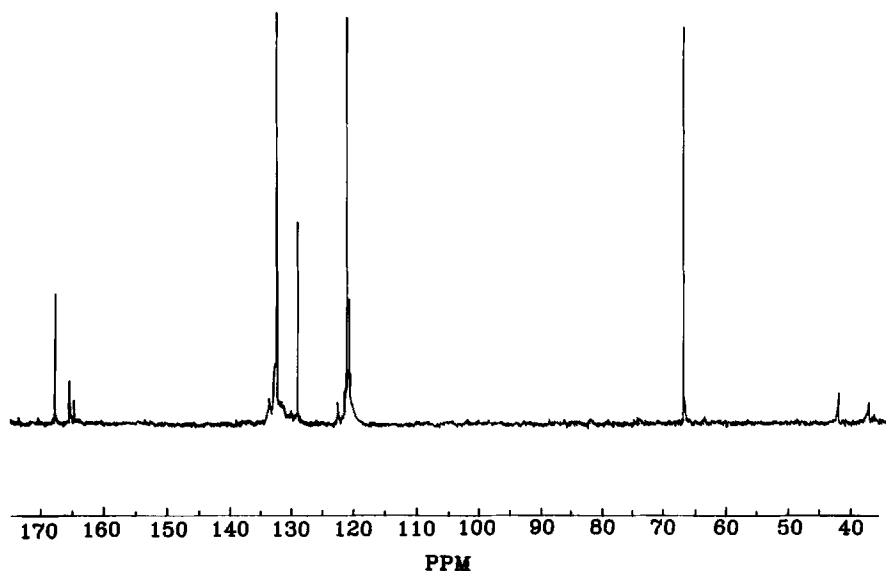

Figure 2 ^{13}C-NMR spectra details indicating presence of substituted urea after 2 h reaction of p-hydroxybenzylalcohol with urea: C — O p-hydroxybenzylalcohol = 167.90 ppm (relative intensity = 29.284); C=O unsubstituted urea = 165.41 ppm (relative intensity = 9.472); C=O substituted urea = 164.8 ppm (relative intensity = 5.285).

Table I   Data Obtained from the Reaction of
Condensation of Ortho-Hydroxybenzylalcohol
with Urea

Temp. (°C)	Time (s)	Peak Height Ratio	C_{sal}/mol/l	$1/C_{sal}$/l/mol/l
75	900	0.000	0.902	1.109
	1800	0.008	0.892	1.121
	3600	0.097	0.788	1.269
	5400	0.105	0.779	1.284
	7200	0.129	0.751	1.332
85	900	0.080	0.858	1.166
	1800	0.134	0.830	1.205
	3600	0.261	0.760	1.316
	5400	0.343	0.713	1.403
	7200	0.442	0.661	1.513
93	900	0.250	0.800	1.250
	1800	0.407	0.737	1.357
	3600	0.515	0.592	1.445
	5400	0.900	0.536	1.866
	7200	1.029	0.484	2.066

Table II   Data Obtained from the Reaction of
Para-Hydroxybenzylalcohol with Urea

Temp. (°C)	Time (s)	Peak Height Ratio	$C_{p \cdot sal}$/mol/l	$1/C_{p \cdot sal}$/l/mol/l
75	0	0.000	0.902	1.109
	900	0.011	0.892	1.120
	1800	0.021	0.884	1.131
	3600	0.040	0.867	1.153
	7200	0.077	0.835	1.197
85	900	0.062	0.848	1.179
	1800	0.114	0.803	1.245
	3600	0.117	0.800	1.25
	7200	0.206	0.723	1.383
93	900	0.171	0.824	1.214
	1800	0.333	0.753	1.328
	3600	0.357	0.740	1.351
	5400	0.435	0.706	1.416

(3.3), 135.79 (3.5), 135.36 (4.5), 135.26, 135.06
(4.7), 134.94 (6.7), 134.07 (3.4), 133.78 (4.3), 132.92
(7.3), 132.66 (7.3), 132.01 (13.5), 131.70, 131.58
(12.8), 131.12 (13.9), 130.38 (5.8), 129.93 (7.0),
129.39 (12.8), 121.82 (5.6), 121.62 (4.1), 116.74
(4.7), 116.46 (9.8), 116.18 (12.7), 66.23 (7.2
p— CH$_2$OH), 63.40 (22.1 o—CH$_2$OH), 62.73 (8.3),
51.46 (16.4), 41.97 (3.7), 36.93 (2.9).

60 min PF Resin, 13.3% Molar Urea Added 164.60
ppm (3.7), 163.08 (3.1), 161.80 (2.3), 160.82 (4.2),
159.48 (5.7), 158.79 (4.1), 158.23 (3.9), 156.61 (3.2),
155.84 (4.2), 155.18 (4.7), 154.30 (5.1), 153.22 (3.4),
135.1 (5.2), 134.7 (6.0), 133.6 (4.3), 132.72 (7.1),
132.41 (13.8), 131.98 (12.6), 131.6 (11.8), 131.0
(4.6), 130.0 (5.3), 129.3 (10.7), 128.85 (6.7), 121.82
(5.2), 121.62 (3.4), 118.74 (4.3), 118.46 (8.9), 118.18
(11.8), 66.23 (6.4), 63.40 (14.2), 62.73 (8.3), 51.33
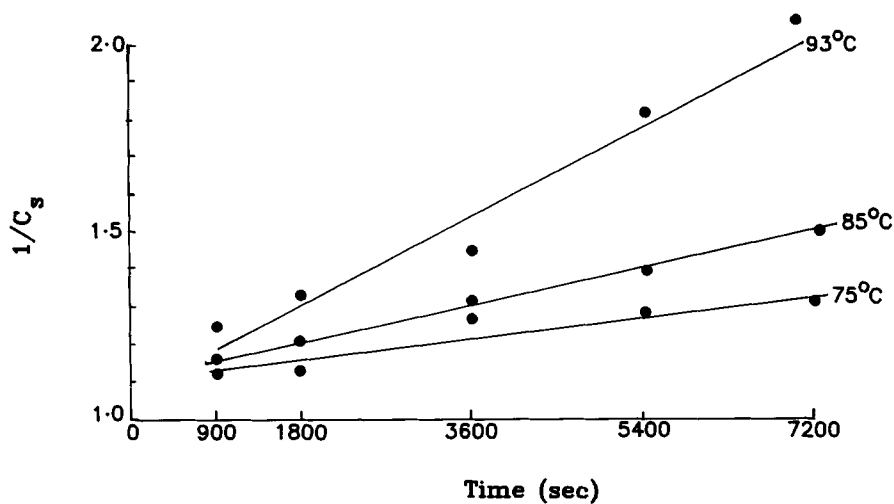(13.2), 41.69 (3.6), 36.30 (2.8).

Figure 3   Graphic representation of $1/C$ in function of reaction time at three different
temperatures (75, 85, 93°C) for appearance of —CH$_2$—NH— bond in o-hydroxyben-
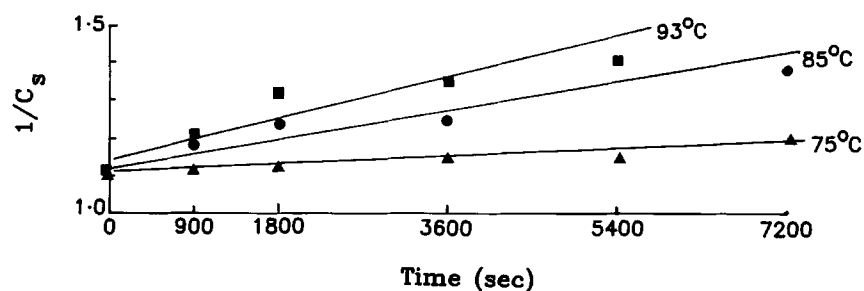zylalcohol/urea reaction (Table I).

Figure 4 Graphic representation of $1/C$ in function of reaction time at three different temperatures (75, 85, 93°C) for appearance of $-CH_2-NH-$ bond in p-hydroxybenzylalcohol/urea reaction (Table II).

IR Spectra (KBr) in cm^{-1} (% Transmittance in Parenthesis)

Saligenin 3439 cm^{-1} (21.5), 3200 (21.5), 3000 (32), 1620 (41), 1600 (40), 1490 (42), 1465 (27), 1420 (40), 1400 (39.5), 1330 (47), 1300 (42), 1270 (32), 1220 (46), 1200 (41), 1165 (50), 995 (25), 940 (43.5), 870 (49.5), 855 (50), 780 (47), 750 (25), 735 (37), 710 (46).

Saligenin + Urea, Time = 0 3550 cm^{-1} (23), 3430 (23.5), 3340 (28), 3050 (35), 3000 (35), 2910 (36),

2640 (33), 2000 (50), 1660 (24), 1600 (25), 1580 (21), 1560 (35), 1465 (17), 1435 (17), 1350 (52), 1300 (50), 1270 (19), 1210 (54), 1180 (55), 1140 (47), 1100 (55), 1030 (60), 980 (35), 945 (54), 920 (60), 860 (36), 770 (61), 750 (31), 725 (41), 620 (48), 600 (48).

Saligenin + Urea, 85°C, Time = 6 h 3550 cm^{-1} (13), 3440 (15.5), 3350 (18), 3050 (21), 3000 (21), 2910 (23), 2640 (20), 2250 (30) ($-CH_2-NH-$), 2000 (37), 1660 (12), 1620 (14), 1590 (11), 1560 (23), 1470 (9), 1440 (9.5), 1350 (40), 1300 (36), 1270 (9.5), 1210 (40.5), 1180 (43), 1140 (37), 1100 (43), 1035 (48), 980 (21), 955 (41), 920 (47), 860 (24), 770 (46), 750 (19), 725 (29), 620 (31), 600 (37).
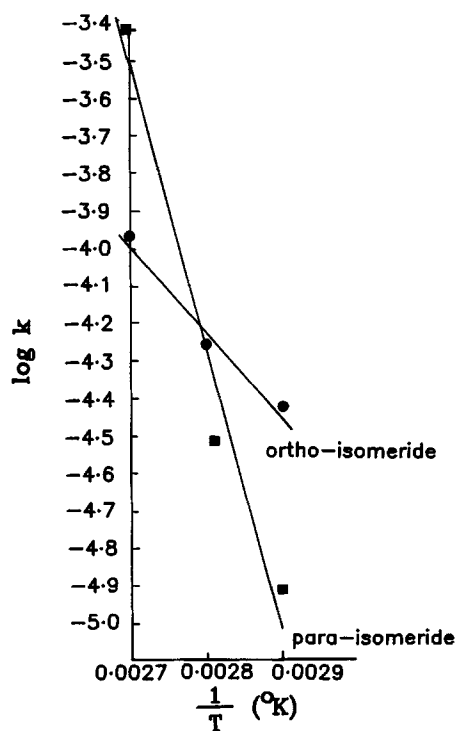
Preparation of PF Resin

Ninety-four parts by mass of phenol were mixed with 40 parts (20/80 m/m) methanol/water and 55 parts by mass of 96% paraformaldehyde powder. After stirring for 30 min at 40°C the temperature was slowly, over a period of 30 min, increased to reflux (94°C). A total of 20 parts by mass of 33% sodium hydroxide water solution was added in four equal parts at 15-min interval over the previous total of 60 min. The mixture was kept at reflux for 60 min and then cooled. The resin solids content was of 59% and final pH = 10.8. Total refluxing time for each resin was of 60 min. In the variations combining urea, urea was added in amounts of 2, 3, 5, and 8 g. For each amount a variation of the resin was made in which the urea was added at 15 or 30 or 45 min during the total refluxing period (of 60 min). After 60 min refluxing, each resin was cooled on ice. After the initial set of resins were prepared a further set was made, using 0, 2, 4, and 8 g urea, added at time zero but refluxing for only 30 min. Viscosity of all
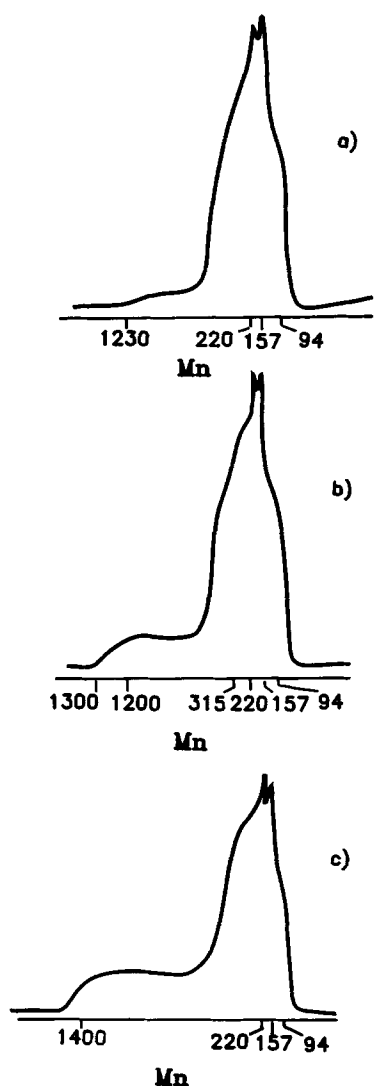

Figure 5 Log_{10} k vs. $1/T$ (T in K) for the reaction of ortho- and para-hydroxybenzylalcohol with urea (Table III).

DISCUSSION

The reaction of hydroxybenzylalcohol groups of phenol–formaldehyde (PF) resols with urea was at first investigated by following the reactions of model compounds. Thus, o-hydroxybenzylalcohol (saligenin) and p-hydroxybenzylalcohol were reacted with urea under alkaline conditions. The reaction was followed by IR spectrometry.

In the infrared spectrum of the reaction of condensation of ortho-hydroxybenzylalcohol (saligenin) with urea, the peak at 2250 cm^{-1} is due to the —CH_2NH— bond formation. Table I and Figure 3 show that the peak heights increase at a set temperature with time. In the special case where the two reactants are introduced in equal stoichiometric proportions, the integrated rate expression becomes indeterminate and this requires taking limits of quotients for evolution. Thus, for the second-order reaction in a polycondensation with equal initial concentration of two different reagents, in this case saligenin and urea, the second-order rate equation becomes

$$\frac{1}{C_s} - \frac{1}{C_{s_0}} = kt$$

where C_s and C_{s_0} are the molar concentrations of any one of the two reagents (in this case saligenin) at time = 0 (C_{s_0}) and at time $t = t(C_s)$. Plotting the variation of the inverse of the saligenin concentration $(1/C_s)$ as a function of time provides a test for the above rate expression: a linear relationship confirms that the reaction follows a bimolecular, second-order kinetic law. The trend shown in Figure 3 (from the data in Table I) for the reaction of saligenin with urea is clearly linear, confirming a second-order rate law for these two reactions. The same applies for the reaction of p-hydroxybenzylalcohol with urea shown in Figure 4. This indicates the appearance of the —CH_2NH— bond suggesting that the hydroxybenzylalcohol is reacting with urea. The ratio of two peak heights was used to calculate the apparent rate constants for the reaction between hydroxybenzylalcohols and urea. In the case of the reaction of saligenin with urea, the two peaks used in the ratio were the following: (1) peak at 2250 cm^{-1} denoting formation of —$\underline{CH_2NH}$— bond[6] and (2) peak at 3420 cm^{-1} which is due to the phenol–OH. The latter peak does not increase or decrease in height with time as the phenolic hydroxy group does not participate in the reaction. The ratio of these two peaks was found to increase with time. Table I shows this trend.

Figure 6 GPC of (a) 60 min reflux PF resin with no urea addition, (b) 60 min reflux PF resin with 3.3% urea molar addition after $\frac{1}{2}$ reflux period (of 30 min), and (c) 60 min reflux PF resin with 13.3% urea molar addition after $\frac{1}{2}$ reflux period (30 min).

the resins at 25°C were measured and gel times[5] at 95°C also measured. The gel times tests were performed on triplicate samples of each resin by placing 10 g of the resin in a test tube after having adjusted the resin pH to 12 (obtained by adding 5–10 drops of 40% NaOH solution). The test tubes were placed in water at 95°C under continuous mechanical agitation and the time taken for the resin to gel measured. Average results are shown in Table IV.

Gel permeation chromatography of the resins was carried out on a Waters HPLC, on a column using tetrahydrofuran as the mobile phase. Some of the relevant results are shown in Figure 6.

Autocondensation of the o-hydroxybenzylalcohol must also be taken into account. For the autocondensation of o-hydroxybenzylalcohols the IR band of interest is at 1420 cm⁻¹ and is due to —CH₂OH scissoring. The IR spectra show that the peak heights decrease at a set temperature with time indicating that o-hydroxybenzylalcohol also undergoes self-condensation.

In the case of the reaction of the p-isomeride with urea, the two peaks used in the ratio were the peak at 2250 cm⁻¹ and at 1090 cm⁻¹, which is due to CH₂ absorption. The latter peak does not increase or decrease with time since the CH₂ does not participate in the reaction. The ratio of these two peaks was found to increase with time. Table II shows this trend. The 3420-cm⁻¹ peak was not used because this peak was weakly resolved in the infrared spectra.

Thus, as under alkaline conditions (pH ≈ 11.5) both autocondensation of ortho- and para-hydroxybenzyl alcohol and the condensation of the two hydroxybenzylalcohols with urea occurred, apparent rate constants representing the two competing reactions could be obtained. These are shown in Table III. A graphic representation of the variation of the apparent rate constants of the reactions of the two hydroxybenzylalcohols with urea as a function of the inverse of the reaction temperature are shown in Figure 5. These results indicate that while the autocondensation of the p-hydroxybenzylalcohol is faster than the autocondensation of the o-hydroxybenzylalcohol, confirming previous results in acid environment,[6] this is not the case with the condensation reactions with urea. First of all, the condensations with urea of both hydroxybenzylalcohols are

more rapid than both the autocondensation reactions. Second, at temperatures of 85°C or higher the p-hydroxybenzylalcohol appears to condense with urea more rapidly than the equivalent o-isomeride (Fig. 5). At temperatures lower than 85°C the o-isomeride reaction with urea is faster than that of the p-isomeride. At 85°C the two reaction rates are equivalent (Fig. 5). The Arrhenius equations of the dependence of the two isomerides condensations with urea from the temperature are shown in Table III.

The applied results of gel times and viscosities shown in Table IV appear also to confirm that the reaction of hydroxybenzylalcohol groups on a phenolic resin with urea is favored over the autocondensation with a phenolic nuclei, in the alkaline pH range. This can be seen in Table IV by comparing the gel time and viscosity of a PF resin not containing urea, reacted for 60 min in relation to the resins in which urea has been added. All the latter present faster gel times and higher viscosities.

The presence of the —CH₂—NH— bond in the reaction products was confirmed by ¹³C-NMR. For the p-isomeride of the —CH₂— bands at 42.06 and 37.08 ppm present in autocondensation the second band shifts to 37.15 ppm while in the o-isomeride the band at 37.12 ppm appears.[7] More important, carbonyl groups of —CH₂— substituted ureas[4,6] are visible at 165.4, 164.6, and 161.2 ppm for the saligenin/urea condensate and at 165.4 and 164.6 for the urea/p-hydroxybenzylalcohol condensate.

Variation of physical properties of PF resins prepared using small additions of urea also appear to confirm the results obtained by model compounds

Table III   Apparent Rate Constants of the Condensation Reaction of Ortho- and Para-Hydroxybenzylalcohols with Urea and of Their Autocondensation

| Temperature (°C) | Reaction with Urea (pH = 11.5) | | | Self-Condensation Reaction |
	Apparent Rate Constant $(1 \times mole^{-1} \times s^{-1})$ $(1 \times mole^{-1} \times s^{-1})$	ln A	E_a (kcal/mole)	Apparent Rate Constant
	Ortho-isomeride			
75	3.74×10^{-5}			—
85	5.52×10^{-5}	4.99	10.432	9.91×10^{-6}
93	1.07×10^{-4}			—
	Para-isomeride			
75	1.23×10^{-5}			—
85	2.98×10^{-5}	12.783	16.635	1.3×10^{-5}
93	3.88×10^{-4}			—

Table IV   Gel Times and Viscosities of Identical PF Resins with Different Additions of Urea

Urea		Gel Time (100°C)					Viscosity (25°C)				
Molar % on Phenol	Mass %	Average (min)	15/45 (min)	30/30 (min)	45/15 (min)	30' (min)	Average (cps)	15/45 (cps)	30/30 (cps)	45/15 (cps)	30' (cps)
0	0	60	60	60	60	71	300	300	300	300	260
3.30	2.1	46	42	47	48	70	920	1000	840	920	260
5	3.2	35	31	41	32	—	1027	1060	960	1060	—
8.3	4.3	29	25	36	26	65	2300	3100	1000	2800	300
13.3	8.5	25	34	17	24	49	3480	1000	6500	2950	625

reactions, and are shown in Table IV. The trends shown in Table IV appear to infer that the average degree of polymerization of the resin increases when increasing amounts of urea are added, and that the polymer grows mostly linearly as indicated by the increase in viscosity, and by ^{13}C-NMR as reported in previous results.[4,8] These are only indications but are also supported by what is observed by gel permeation chromatography (GPC) of the PF resins in Figure 6. In Figure 6 the GPC traces of a PF resin of phenol–formaldehyde molar ratio 1 : 1.8 without urea addition, and after 3.4 and 13% molar urea addition are shown, all after 60 min reaction time. The proportion of the high molecular mass fraction increases from 23.7% at 0% urea to 32.1 and 48.9%, respectively, for 3.4 and 13% molar urea addition. It is also interesting to observe, by ^{13}C-NMR and by sodium sulfite titration method of the same resins, how the relative proportions of o-CH$_2$OH (63.40 ppm) and p-CH$_2$OH groups (66.23 ppm) on the resins vary with increasing urea amounts. The relative proportions of ortho : para groups vary from 3.07 : 1 for no urea content to 2.8 : 1 and 2.22 : 1 at 3.3 and 13.3% molar urea addition (see Experimental). The inference here is that o-methylol groups on the phenolic resin appear to favor reaction with urea more than p-methylol groups. This result supports the findings obtained by model compounds reactions. Furthermore in the resin containing 13.3% molar urea, in the carbonyl region, carbonyls belonging to the mono-, di, and trisubstituted urea, at, respectively, 164.8, 163.0, and 161.5 ppm, become clearly visible.

In conclusion, phenol–formaldehyde resins appear to increase linearly in degree of polymerization (DP) very rapidly by the addition of small amounts of urea to levels not easily achievable without urea.
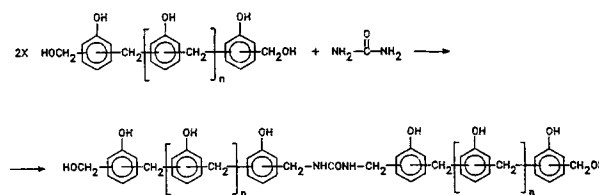
This is supported by both the increase in viscosity and faster gel times with increasing percent urea, as shown in Table IV.

REFERENCES

1. B. Tomita and C. Y. Hse, in *Proceedings of Symposium on Adhesive Technology for Tropical Woods*, May 1992, Taipei, Taiwan, 1992.
2. B. Tomita and C.-Y. Hse, *J. Poly. Sci.*, in press.
3. S. Oyama, B. Tomita, and C.-Y. Hse, Formulation and Performance of Phenol-Urea-Formaldehyde Resin Adhesives, Prep. 41st Annual meeting, Japn Wood Res. Soc., p. 200, 1991.
4. E. Scopelitis and A. Pizzi, *J. Appl. Polym. Sci.*, **488**, 2135 (1993).
5. A. Pizzi, *For. Prod. J.*, **28**, 12, 42 (1978).
6. R. Rammon, *J. Adhesion*, **19**, 115 (1986).
7. J. R. Havens and J. L. Koenig, *Appl. Spectroscopy*, **37**, 226 (1983).
8. L. Gollob, 1989, in *Wood Adhesives Chemistry and Technology*, Vol. 2, A. Pizzi, Ed., Dekker, New York, pp. 121–153.