

# On the Networking Mechanisms of Additives-Accelerated Phenol–Formaldehyde Polycondensates

A. PIZZI, R. GARCIA, S. WANG

ENSTIB, University of Nancy 1, Epinal, France

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**ABSTRACT:** Determination by thermomechanical analysis (TMA) of the average number of degrees of freedom of polymer segments between crosslinking nodes of phenol-formaldehyde (PF) resin-hardened networks indicate that additive-accelerated PF resin polycondensations and hardening presented several different acceleration mechanisms. Some additives such as sodium carbonate appear to present purely an acceleration effect on the polycondensation reaction. Other additives such as propylene carbonate appear to present an acceleration effect by also inducing an increase in the average functionality of the system, due to alternate crosslinking reactions to which the accelerator itself does participate, leading to a tighter final network. These alternate crosslinking reactions can be of a different nature. In the propylene carbonate case, the reaction is related to a Kolbe–Schmitt reaction. In formamide, instead, it is related to its hydrolysis to formic acid and ammonia with the subsequent rapid reaction of the latter with two or more hydroxybenzyl alcohol groups of PF resols. The rapid reaction of the  $-\text{NH}_2$  group of formamide with two hydroxybenzyl alcohol groups of PF resols, a reaction which is also characteristic of urea and methylamine, also appears likely to occur. Both liquid- and solid-phase  $^{13}\text{C}$ -NMR supporting evidence of the mechanisms proposed is also presented. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 255–266, 1997

## INTRODUCTION

Alkaline phenol–formaldehyde (PF) resins have been used successfully for many decades as exterior wood adhesives for bonded wood products.<sup>1</sup> While the influence of many additives on their hardening has been studied for a long time, the mechanisms of hardening acceleration induced by these additives, especially in the presence of the wood substrate, has only started to be studied in recent years.<sup>2–5</sup> Thus, mechanisms of PF hardening acceleration by catalytic surface activation by lignocellulosic materials have been reported,<sup>6</sup> as well as a variety of mechanisms based on PF hardening acceleration induced by carboxylic acid

esters,<sup>2–5</sup> anhydrides,<sup>7</sup> amides,<sup>4,8,9</sup> and others. Some of the mechanisms which have been proposed are based on circumstantial, indirect evidence rather than on direct evidence, mainly because the chemistry of phenolic resins which is characterized by the presence of an almost infinite variety of oligomeric positional isomerides produced with the progressing of the reaction is particularly difficult and tedious to unravel.<sup>10</sup> Some of these mechanisms are not supported by any direct evidence<sup>5</sup> and are often only assumptions based on unacceptable interpretations of the organic chemistry involved.

Recently,<sup>11–13</sup> a method was presented which allows one to determine the average number of degrees of freedom of the polymer segments between crosslinking nodes both during hardening of and of hardened polycondensation networks as a function of the relative deflection of thermomechanical analysis (TMA) measurements in bending. The

Correspondence to: A. Pizzi.

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method has proved applicable with good results to melamine–formaldehyde,<sup>12</sup> melamine–urea–formaldehyde,<sup>14</sup> phenol–formaldehyde,<sup>12</sup> resorcinol–formaldehyde,<sup>12</sup> and tannin–formaldehyde<sup>12,15</sup> polycondensates and also to radical crosslinking polymers such as unsaturated polyesters and complex vinyls.<sup>11–13</sup>

In this article, the mechanisms of accelerated hardening and networking induced by several of these additives such as esters, carboxylic acid anhydrides, amides, amines, sodium carbonate, and propylene carbonate are examined by this technique on the basis of the type of hardened network and its density of crosslinking that they yield as well as on the basis of <sup>13</sup>C-NMR results as supporting evidence.

## EXPERIMENTAL

### Phenol–Formaldehyde (PF) Resin Preparation

Ninety-four parts by mass of phenol were mixed with 40 parts (20/80) of a methanol/water solution and 55 parts by mass of a 96% paraformaldehyde powder. After stirring for 30 min at 40°C, the temperature was increased over a period of 30 min to reflux (94°C). A total of 20 parts by mass of a 33% sodium hydroxide solution was added in four equal parts at 15 min intervals over the previous total of 60 min. The mixture was kept at reflux for 30 min and was then cooled. The resin solids content was 58%; viscosity, 300 centipoises at 25°C; and final pH, 10.8. In the case of the variation which to the above resin formamide, 60 g, was added, the reaction was continued at reflux for 15 min after addition of the formamide, while the rest of the procedure was left the same.

### Reactions of Different Phenols and of Phenolic Resins with Propylene Carbonate and Formamide in Absence or Presence of Formaldehyde

1. Four grams resorcinol in 4 g water at pH 12 was reacted with 3.7 g propylene carbonate for 2 h at 60°C. After separation by centrifugation of the sodium hydrogen carbonate solids formed, the liquid sample was analyzed by <sup>13</sup>C-NMR.
2. Four grams resorcinol in 6 g water at pH 12 was reacted with 1.7 g formamide for 2

h at 60°C. The liquid sample was analyzed by <sup>13</sup>C-NMR.

3. Fifty grams of the liquid PF resin prepared above was reacted and gelled with 4.5 g formamide at 90°C for 15 min. The air-dried gelled resin was analyzed by solid-phase CP-MAS <sup>13</sup>C-NMR.
4. Fifty grams of the commercial liquid PRF resin of pH 8.3 was cured at ambient temperature (i) by addition of 5 g paraformaldehyde (the resin gelled in about 5 h) and (ii) by addition of 5 g paraformaldehyde followed by 5 g of 30% ammonia solution (the resin gelled in a few seconds).

### <sup>13</sup>C-NMR Spectra

Liquid <sup>13</sup>C-NMR spectra were obtained on a Brüker MSL 300 FT-NMR spectrometer. Chemical shifts were calculated relative to (CH<sub>3</sub>)<sub>3</sub>Si-(CH<sub>2</sub>)<sub>3</sub>SO<sub>3</sub>Na dissolved in D<sub>2</sub>O for NMR shifts' control.<sup>16</sup> The spectra were done at 62.90 MHz for a number of transients of approximately 1000. All spectra were run with a relaxation delay of 5 s and chemical shifts were accurate to 1 ppm.

Solid-state CP-MAS (cross-polarization magic angle spinning) <sup>13</sup>C-NMR spectra of each sample were obtained on a Brüker MSL300 FT-NMR spectrometer at a frequency of 75.47 MHz. Chemical shifts were calculated relative to TMS for NMR control. Acquisition time was 0.026 s with the number of transients about 1200. All spectra were run with a relaxation delay of 5 s and were accurate to 1 ppm with a CP time of 1 ms and spectral width of 20,000 Hz. Spinning rates were 3.5 kHz.

### Thermomechanical Analysis (TMA) Determination of Average Number of Degrees Freedom of Accelerated PF Resin-cured Networks

Recently work on the formation of polymer networks by photopolymerizable and polyester surface finishes on wood and of polycondensation resins used as wood adhesives has yielded a mathematical relationship<sup>11–13</sup> among the energy of interaction ( $E$ ) at the synthetic polymer/wood interface calculated by molecular mechanics (work of adhesion), the number of degrees of freedom ( $m$ ) of the segment of the synthetic polymer between two crosslinking nodes, the coefficient of branching  $\alpha$ , hence, the functionality of the starting monomer, and the relative deflection ( $f$ ) obtained by thermomechanical analysis (TMA) of

**Table I Thermomechanical Analysis (TMA) Results for the Determination of the Density of Crosslinking of Different PF Resin + Accelerator-Hardened Networks**

	Deflection ( $\mu\text{m}$ )	$\alpha$	$m$	$t_{\text{gel}}$ ( $^{\circ}\text{C}$ )	$t_{\text{vitrif.}}$ ( $^{\circ}\text{C}$ )	$\alpha$	$m$
PF alone	16.1	0.5	6.8	142	158	0.5	6.8
+5% $\text{Na}_2\text{CO}_3$	14.2	0.5	5.9	132	154	—	—
+4.8% propylene carbonate	9.9	0.5	4.0	143	161	0.33	2.4
+7.1% glycerol triacetate	12.4	0.5	5.1	138	160	0.33	3.2
+5% acetic anhydride	11.4	0.5	4.7	140	169	—	—
+2.2% formamide	11.0	0.5	4.5	136	157	0.33	2.8
+1.5% methylamine	11.5	0.5	4.7	133	153	0.5	4.7

The amounts of accelerators added are expressed in percentages by weight on PF resin to achieve equal molar percentages of active component.

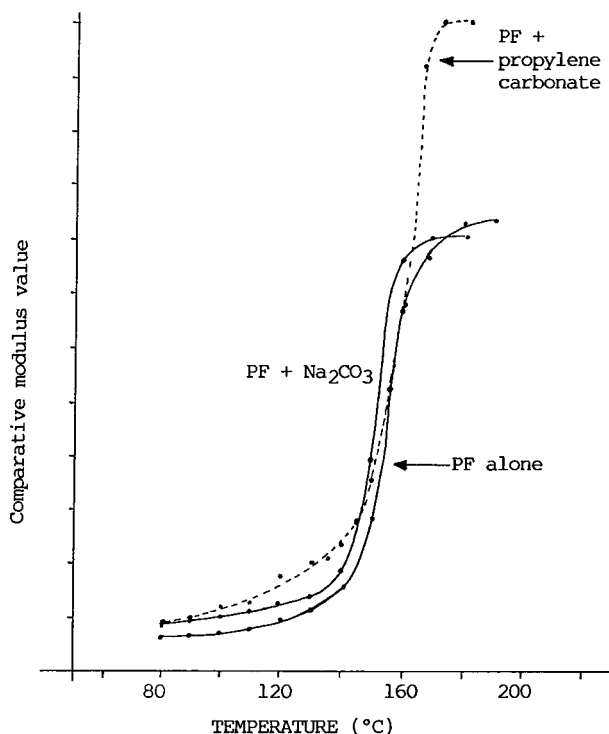
wood specimens coated or bonded with the adhesive through the expression  $f = km/\alpha E$ , where  $k$  is a constant.<sup>11–13</sup> Regression equations<sup>12</sup> correlating directly  $m$  with  $E$  and  $m$  with  $f$  have been derived for hardened phenol–formaldehyde (PF), resorcinol–formaldehyde (RF), melamine–formaldehyde (MF), and tannin–formaldehyde (TF) resins. These relationships will then be used to correlate the number-average degree of polymerization ( $\text{DP}_n$ ) and  $p_{\text{gel}}$  with  $m$  for the same PF resin hardened alone and in the presence of the different hardening accelerators used.

To this purpose, the PF resin above was tested dynamically by thermomechanical analysis (TMA) on a Mettler apparatus. Samples of beechwood alone and of two beechwood plies bonded with each system of liquid polycondensate resins + accelerator (comparable molar amount as indicated in Table I) in a layer of 350  $\mu\text{m}$ , for a total sample dimensions of 21  $\times$  6  $\times$  1.1 mm, were tested in a nonisothermal mode between 40 and 220 $^{\circ}\text{C}$  at a heating rate of 10 $^{\circ}\text{C}/\text{min}$  with a Mettler 40 TMA apparatus in three-point bending on a span of 18 mm, exercising a force cycle of 0.1/0.5N on the specimens with each force cycle of 12 s (6 s/6 s). The classical mechanics relation between force and deflection  $E = [L^3/(4bh^3)][\Delta F/(\Delta f_{\text{wood}} - \Delta f_{\text{adhesive}})]$  allows the calculation of the Young's modulus  $E$  for each of the cases tested. As the deflections  $\Delta f$  obtained were proven to be constant and reproducible<sup>12,13</sup> and as they are proportional to the flexibility of the assembly, the relative flexibility as expressed by the Young's modulus of the two primers can be calculated for the

two finishes through the relationship  $E_1/E_2 = \Delta f_2/\Delta f_1$ . The values of  $m$ ,  $E$ , and  $\alpha$  for the resins presented in Table I were then calculated according to already reported methods according to the phenomenological equation  $f = km/\alpha E$  and connected regression equations which have already been reported.<sup>11–13</sup> In Table I are reported the values of  $m$  obtained from this analysis for systems in which further reactions on the phenolic ring other than the formaldehyde and methylol group attack have been demonstrated, or are suspected. They present a value of Flory's  $\alpha$  both of 0.5 (phenol trifunctional) and of 0.33 (phenol nuclei tetrafunctional), while systems, such the control PF resin alone, for which further attack on the ring does not appear to occur, are reported for only values of  $\alpha = 0.5$ .

## DISCUSSION

The results in Table I indicate that equimolar amounts of different additives added to the same phenolic resin give a different average number of degrees of freedom  $m$  of the hardened network of the PF resin. This means that the average densities of crosslinking of the final networks produced are different for different accelerating additives, indicating that different mechanisms of hardening acceleration of the PF resin appear to be at work. The first important difference is the difference between the value of  $m$  of the PF resin to which additives have not been added in relation to the values of  $m$  of all the additive added resins.



**Figure 1** Comparative increase of relative moduli as a function of temperature of TMA joints bonded with the same PF resin alone and accelerated with equivalent molar percentages of sodium carbonate and propylene carbonate.

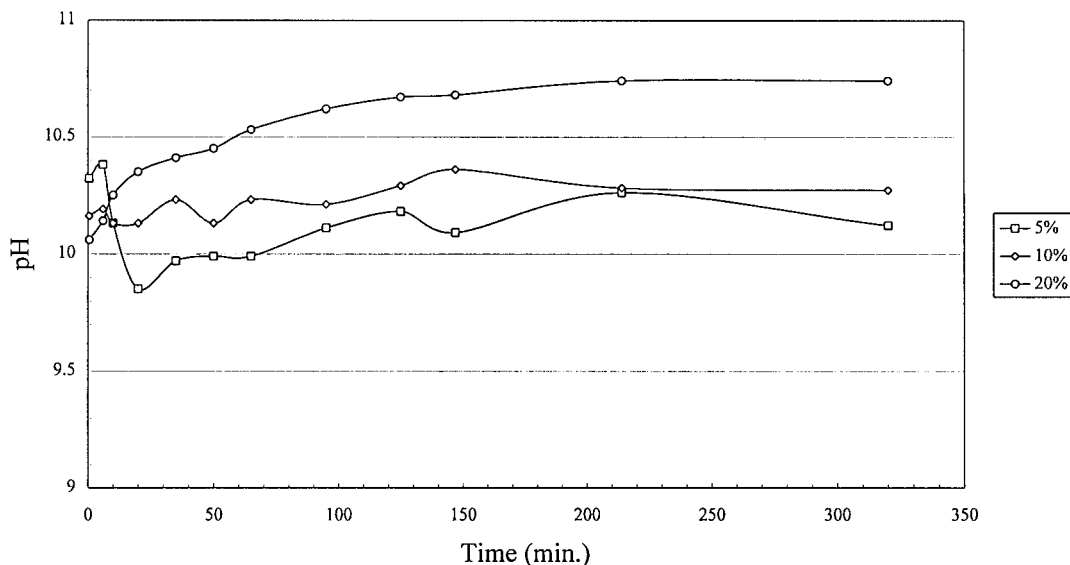
It is not the advancement of the resin or the rate of its curing in nonisothermal experiments which determines its density of crosslinking: Whatever variation of the pH was introduced in the control resin, better crosslinking and a lower variation of  $m$  than what is presented in Table I could not be achieved; the value presented in Table I is the lowest achieved. This is an indication that most of the additives do not just accelerate the hardening of the resin but participate in some way in the crosslinking of it.

The second difference of interest is that sodium carbonate and propylene carbonate present a very different behavior. While sodium carbonate behaves mostly as a pure accelerator, this is not the case for propylene carbonate. Thus, in Figure 1, the trend in the elastic modulus curves of the PF resin alone and of the PF resin added of equivalent carbonic acid amounts by the addition of sodium and propylene carbonate is shown. Sodium carbonate imparts to the PF elastic modulus curve exactly the same trend as does the PF control case (the two curves are parallel) but with the acceler-

ator-added curve shifted to lower temperatures—hence, earlier reaction times and a lower gel time temperature. Thus, sodium carbonate behaves as a true accelerator of PF hardening.

The trend in the propylene carbonate elastic modulus curve obtained by thermomechanical analysis (TMA) instead shows (i) at first a faster increase followed by a slower increase than that the sodium carbonate case (Fig. 1), while still presenting a value of the gel temperature more similar to that of the PF resin alone than what was obtained with sodium carbonate, a gel point which might then be obtained in a different manner. (ii) Second, after the initial part of the curve, a second stage of the modulus increase curve appears to lead to a much tighter crosslinked network than in the case of sodium carbonate. This indicates that some important difference between the type of action of the two accelerators exists: Sodium carbonate, in the main, does not appear to increase the crosslinking of the resin but just accelerates it, while propylene carbonate might well present both a similar accelerating mechanism, although clearly to a different extent, as well as being an active part of the process of crosslinking. If this was really due only to the accelerating influence of the  $\text{HCO}_3^-$  ion as has been advocated<sup>4,5</sup> (a mechanism for which no evidence has been presented), then the curves of the two materials would be coincident, and they are not. In this regard, it is interesting to note that even when it was tried to demonstrate that exclusively  $\text{HCO}_3^-$  induced acceleration exists, it was found otherwise, and as a consequence,<sup>5</sup> the experimental data had to be overcorrected based on unrealistic pH effects (see Fig. 2). What was observed for the modulus curves is confirmed by macroscopic gel time tests at 100°C shown in Table II, from which it is clear that sodium carbonate is a better accelerator at lower proportions of addition, but that at a higher proportion of additions where a structural rather than a catalysis effect is likely to be predominant, propylene carbonate becomes by far the better accelerator.

Further proof of complex reactions between propylene carbonate and phenolic nuclei leading to compounds in which the carbonic acid has attacked the phenolic is shown in Figure 3(a) and (b). In Figure 3(a) is shown the  $^{13}\text{C}$ -NMR spectrum of the product of the reaction of resorcinol (a stronger nucleophile than phenol for which such a reaction would be more easily observed) with propylene carbonate, in the absence of formalde-



**Figure 2** Variation of pH as a function of time at 50°C of a PF resin to which were added different percentages of sodium carbonate.

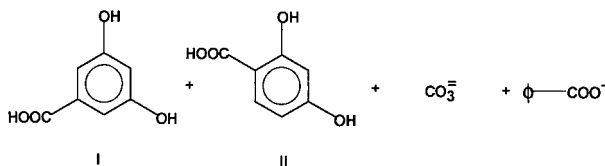
hyde. The NMR spectrum of resorcinol alone before the reaction is shown in Figure 3(b). In Figure 3(a), the major peaks of the pattern shown are those of resorcinol unreacted, namely, its C1 and C3 at 160.70 ppm, C5 at 133 ppm, C4 and C6 at 109.91 ppm, and C2 at 106 ppm and of the propylene glycol, namely,  $-\text{CH}_2-\text{OH}$  at 70.54

ppm, of of  $\text{CH}-\text{OH}$  at 69.22 ppm, and of  $-\text{CH}_3$

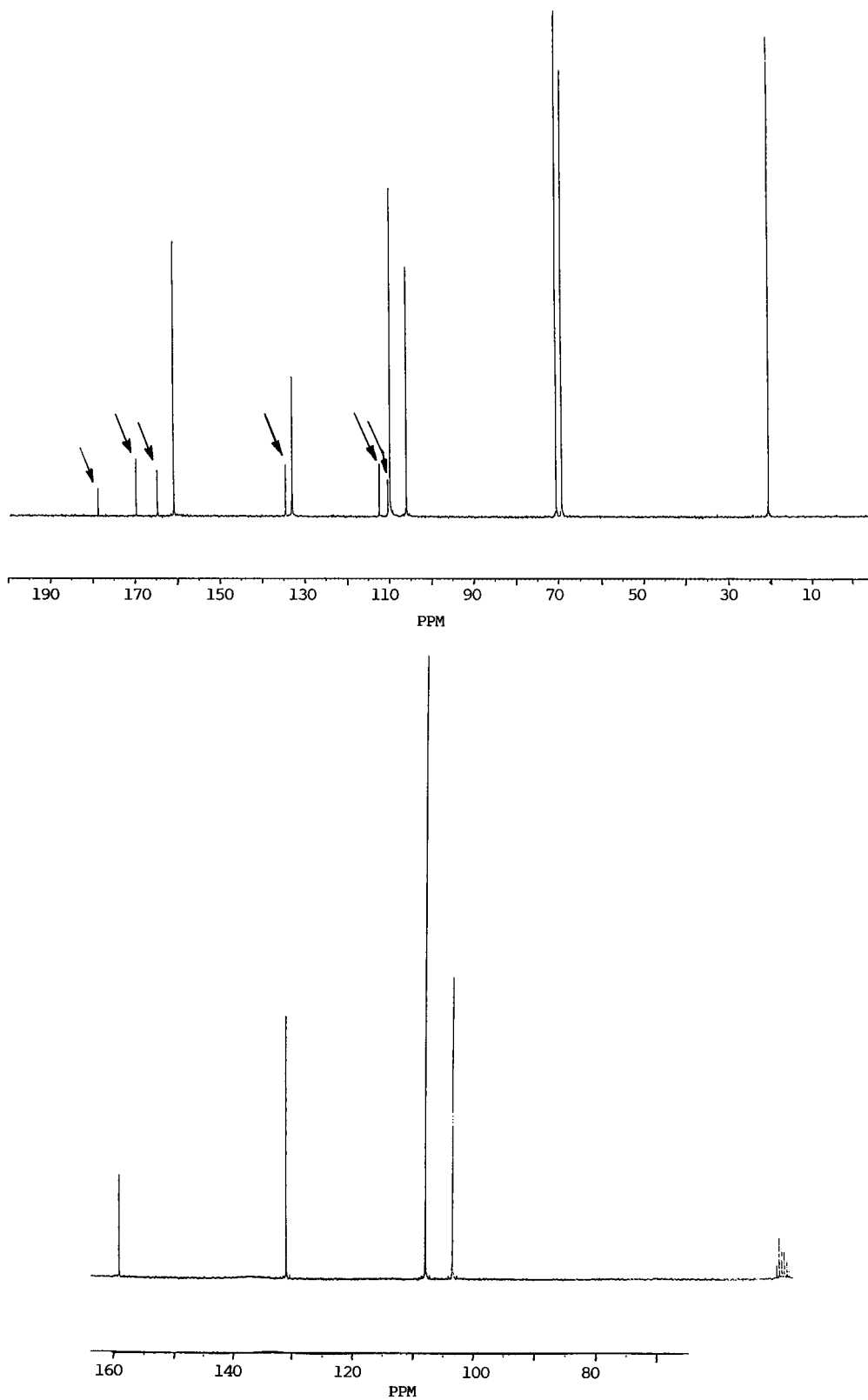
at 20.60 ppm. On this major, expected pattern, the very clear second pattern of peaks of the reaction product is clearly visible: Hence, peaks at 178.61, 169.54, 164.55, 134.49, 112.40, and 110.36 ppm. In Table III are given the assignments expected and found for the two best-fitting and, hence, most probable compounds formed and represented by this pattern of peaks. From Table III, it is clear that the reaction products are the following:

**Table II Gel Times in Minutes of PF Resin Alone and Accelerated by  $\text{Na}_2\text{CO}_3$  and by Propylene Carbonate**

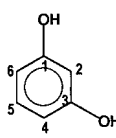
	Additive on PF Resin Solids			
	0%	5%	10%	20%
PF alone	40.33	—	—	—
PF + $\text{Na}_2\text{CO}_3$	40.33	13.55	12.35	12.63
PF + propylene carbonate	40.33	24.22	22.70	6.63



More interesting still is that while  $\text{CO}_3^{2-}$  might exist superimposed on the 169.54 ppm peak of the  $-\text{COOH}$ , although the relative intensities of the signals at 169.54 ppm and at 178.61 ppm ( $-\text{COO}^-$ ) in relation to the two signals at 110.36 and 112.48 ppm indicate that even  $\text{CO}_3^{2-}$  might be completely absent, there is no trace of either  $\text{HCO}_3^-$  (which has obviously precipitated out of solution as  $\text{NaHCO}_3$  [Ref. 5]) or of any other carbonic acid and carbon dioxide (which should appear at  $\pm 128$  ppm [Ref. 17]) species. The possibility of the product peaks' pattern belonging to a dicarboxylic acid species, thus a resorcinol nuclei carrying two vicinal carboxylic acid groups, namely, on C5 and C6, was also considered. However, only two of the six expected shifts of the six carbon atoms of the resorcinol ring match the shifts which could be expected with this species, and, thus, this species is clearly not present. The idea that a dicarboxylic species might be present was derived by the fact that the carboxyl carbons of an aromatic anhydride would give a signal between 163 and 165 ppm (Ref. 17) (i.e., phthalic anhydride carboxyls appear at 163.1 ppm) and

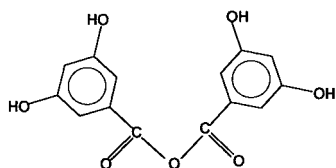


**Figure 3** Liquid-phase  $^{13}\text{C}$ -NMR of (a) the reaction mix of resorcinol and propylene carbonate in the absence of formaldehyde and (b) of resorcinol alone.

**Table III** Expected and Experimentally Found Deviations from Resorcinol Carbon Shifts in ppm for the Compound Obtained by Reaction of Resorcinol with Propylene Carbonate [Fig. 3(a)]


	Compound I		Compound II		Anhydride	
	Expected (ppm)	Found (ppm)	Expected (ppm)	Found (ppm)	Expected (ppm)	Found (ppm)
C1	-0.3	0.0	+1.6	+4.6	-0.3	0.0
C2	+5.2	+4.9	0.0	0.0	+5.2	+4.9
C3	-0.3	0.0	+5.2	+4.9	-0.3	0.0
C4	+1.6	+2.5	0.0	0.0	+1.6	+2.5
C5	+2.1	+1.9	+1.6	+1.7	+2.1	+1.9
C6	+1.6	+2.5	+2.1	+2.2	+1.6	+2.5
C=O (-COOH)	172.6	169.5	172.6	169.5	—	—
C=O (-COO <sup>-</sup> )	177.6	178.6	177.6	178.6	—	—
C=O (anhydride)	—	—	—	—	163-165	164.6

that a clear signal at 164.55 ppm exists, this signal having been interpreted above as the only clear nonmixed peak indicating the existence of compound II. An aromatic anhydride, however, does not need to be a cyclic anhydride. A perfect match of the shifts reported is attained for a compound of the type



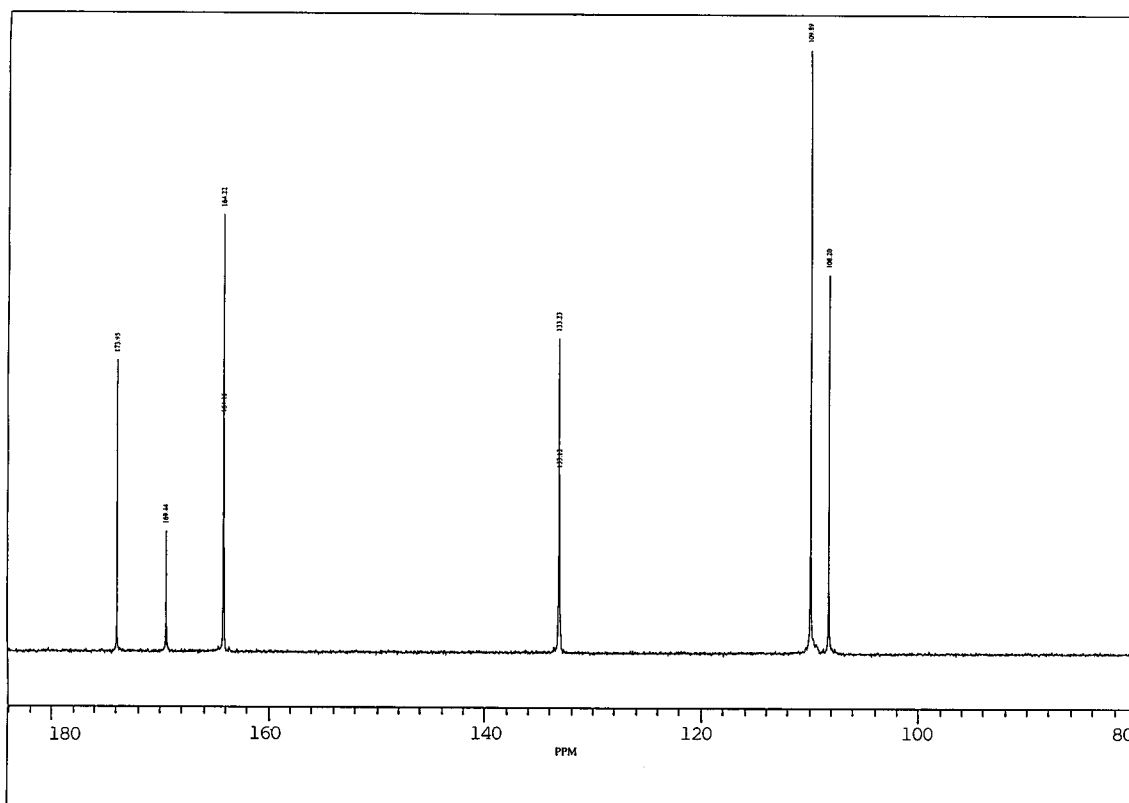
thus, an aromatic noncyclic anhydride. Hence, what appears to be present in the supernatant solution, and not in the mostly sodium hydrogen carbonate precipitate,<sup>5</sup> is a mixture of compounds I and II as already indicated above or a mixture of compound I of its carboxylate ion and of the above anhydride. The second possibility appears to be the most likely due to the better fit between expected and found peak shifts and patterns as shown in Table III. This also means that a link between phenolic nuclei, other than a methylene bridge, can be formed. Just a few of these addi-

tional crosslinks in a polymeric resin, even for a short, transient period of time if they are unstable, and even in lower proportion than for resorcinol (as is likely to be the case for phenol which is less reactive), are enough to increase the average functionality<sup>18,19</sup> of a polymeric PF resin system. Formaldehyde should not be in such an excess, so that a considerable amount of *ortho* and *para* sites is still available (for steric reasons, the more crowded a resin is on these sites, the more hindrance would exist to limit reaction on a *meta* site, too). The characteristic and very unusual aspect of an attack on the *meta* site has been remarked on and reported before.<sup>2</sup> It is also clear that if the anhydride exists it might decompose at a higher temperature curing, with what type of further reactions it is not possible to say with the data available.

The same accelerating mechanism based on the hydrogen-bonding-based intermediate activated complexes ascribed to hydrogen carbonate ions was also ascribed to formamide.<sup>4</sup> Weaker acid carboxylic amides do not show any accelerating effect.<sup>4</sup> However, at least one amide which does not really present the structure advocated for the same intermediate to be formed, namely, urea, the diamide of carbonic acid, is well known to ac-

celerate PF hardening under an alkaline environment<sup>8,9</sup> and well known to accelerate it by a completely different mechanism<sup>8,9</sup> than the one proposed.<sup>4</sup> The amidic groups of urea react readily under an alkaline environment with two and three methylol groups of PF resins<sup>8,9</sup> to form urea-to-phenol methylene bridges. In Table I are then presented the values of  $m$  for a formamide-accelerated PF resin and for a PF resin to which methylamine has been added. Methylamine has a completely different structure than that of formamide and cannot form the intermediate activated complexes advocated for the proposed acceleration mechanism by formamide. It has, however, a reactive  $-\text{NH}_2$  group which could accelerate the hardening of a PF resin by simultaneously reacting with two methylol groups of the PF resin, a mechanism similar to that of urea. It was chosen instead of urea to avoid any controversy which could arise in the case of the latter due to the presence of two reactive amidic groups. If the hydrogen-bond-induced intermediate activated complex mechanism<sup>4</sup> is valid, the value of

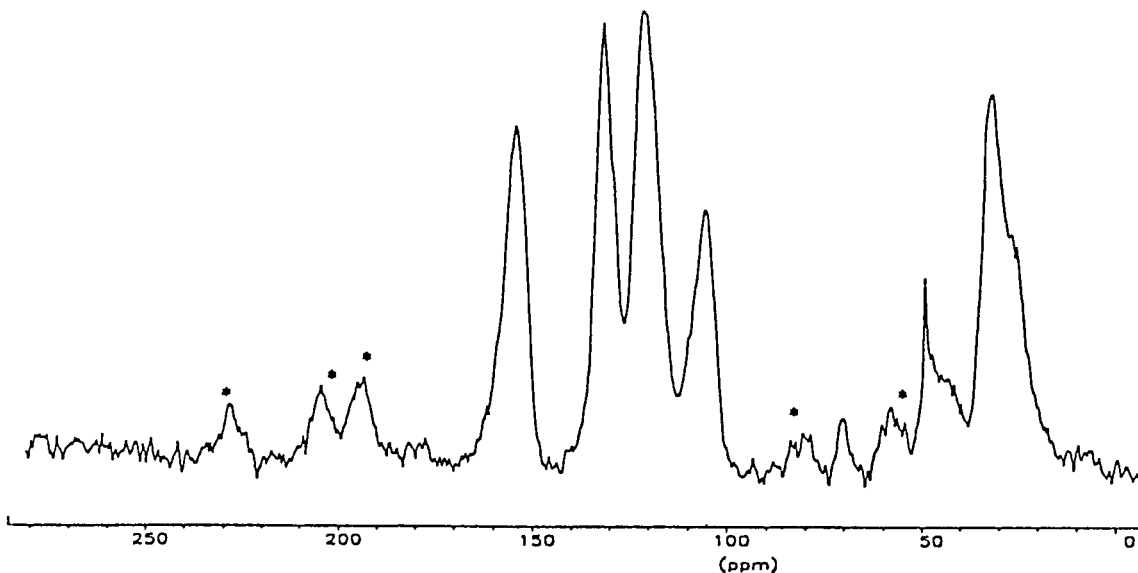
$m$  for formamide should be, at most, identical to that of the PF resin alone and not in anyway lower. If the mechanism by  $-\text{NH}_2$  group reaction with the PF resin hydroxybenzyl alcohol groups is instead valid,<sup>8,9</sup> then formamide should give a much lower value of  $m$ —hence, a much tighter hardened network than that of the phenolic resin alone, and methylamine which can only present this latter mechanism should give a result of  $m$  comparable to that obtained with formamide. The results in Table I for the PF resin alone, formamide, and methyl urea show clearly that it is the latter mechanism which causes the hardening acceleration. Confirmation of the difference in the mechanism can be gathered by the liquid  $^{13}\text{C}$ -NMR of the reaction of a solution of resorcinol with formamide at  $60^\circ\text{C}$  for 2 h (Fig. 4) and the solid-phase CP-MAS  $^{13}\text{C}$ -NMR of the reaction product of a PF resin with formamide (Fig. 5). In the first one, superimposed on the formamide (169.44 ppm) and resorcinol (164.22, 164.16, 133.23, 133.12, 109.89, and 108.20 ppm) patterns is also a peak at 173.95 ppm that appears to repre-



**Figure 4** Liquid-phase  $^{13}\text{C}$ -NMR of the reaction mix of resorcinol and formamide in the absence of formaldehyde.



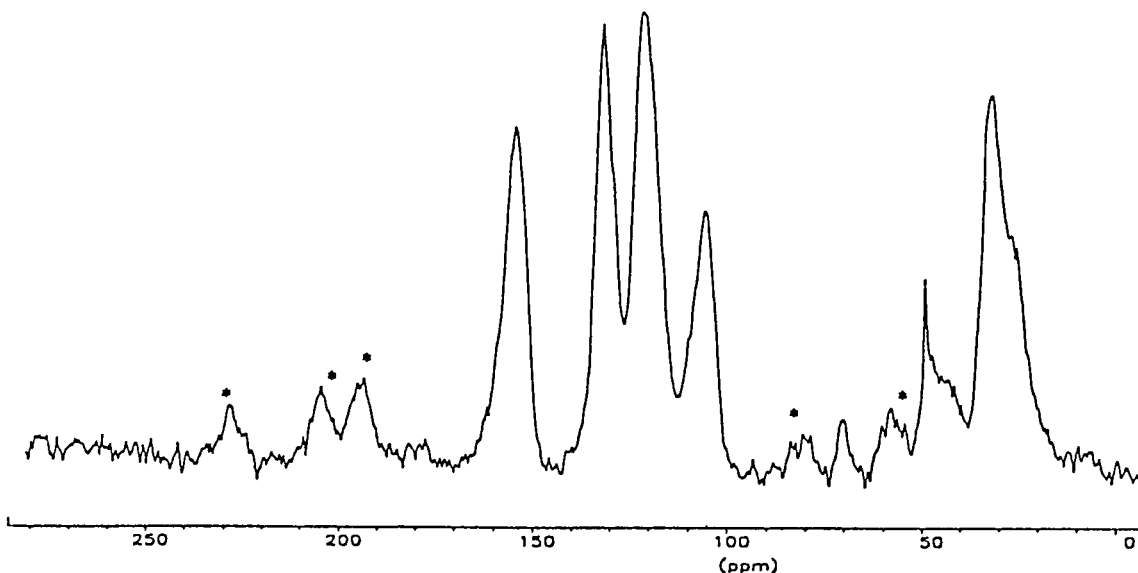




**Figure 6** Solid-state CP-MAS  $^{13}\text{C}$ -NMR of a PRF resin hardened at ambient temperature by addition of 10% paraformaldehyde and accelerated by addition of 10% by weight 30% ammonia solution in water (\* = spinning side bands).

(PRF) resin hardened by addition of formaldehyde only and by addition of formaldehyde + a high amount of ammonia (Figs. 6 and 7) show the appearance in Figure 6 of the strong band at 105 ppm (characteristic of aromatic carbons linked to benzylamine bridges, but in Figure 5 obscured by a spinning side band due to the small amount of formamide used) and also the presence

of the 71 ppm band ( $-\text{CH}_2-\text{NH}-\text{CH}_2-$ ) which does not appear in the resin hardened without ammonia, confirming the above mechanism of acceleration pertaining to formamide. Gel times of PF and RF resins accelerated with formamide and with ammonia also show that ammonia gives faster gel times but of the same order of magnitude as formamide.<sup>21</sup>



**Figure 7** Solid-state CP-MAS  $^{13}\text{C}$ -NMR of a PRF resin hardened at ambient temperature by addition of 10% paraformaldehyde (\* = spinning side bands).

Compounds based on a reasonably strong carboxylic acid like formic acid, such as methyl formate and formamide, are very likely to give this type of reaction and additional crosslinking, too. Methyl formate is known to be the faster accelerator after propylene carbonate,<sup>2,3,22</sup> while the results for formamide in Table I clearly indicate that for formamide additional crosslinking is present. Thus, formamide participates in the reaction by both crosslinking with the methylol groups of the PF resin through its  $-\text{NH}_2$  groups. All the above is nothing that could not have been foreseen by classical organic chemistry knowledge: Nucleophilic acyl substitution reactions of carboxylic acid esters, amides, anhydrides, and chlorides are one of the most fundamental and well-known reactions of these compounds.<sup>23,24</sup>

Once the nature of the accelerating mechanism induced by increased crosslinking and its existence through the determination of the number of degrees of freedom  $m$  of the PF networks formed is defined, it would be necessary to address the nature of the first accelerating mechanism which appears to be common to both sodium carbonate and propylene carbonate. Only speculation is possible: The mechanism involved could be one of the two proposed up to now, namely, the hydrogen carbonate ion intermediate activated complex mechanism,<sup>4</sup> proposed without any evidence and for which direct evidence would be rather difficult to gather, and the mechanism<sup>25,26</sup> based on rapid transesterification reactions of the hydroxybenzyl alcohol group of a PF resol. This latter mechanism is based on the easily occurring transesterification of propylene carbonate with methanol through which dimethyl carbonate is rapidly obtained<sup>25,26</sup> and suggests that dibenzyl carbonate bridges are initially formed between phenolic nuclei which are eventually transformed to dimethylene ether bridges by the loss of  $\text{CO}_2$ . In this regard, other reactive materials which will readily undergo transesterification analogous to that of propylene carbonate with methanol are trialkyl borates, tetraalkyl titanates, and trialkyl phosphites in an alkaline environment: Gas injection of methyl borate (and carbon dioxide) has been found to enhance as well the results of wood composites bonded with formaldehyde-based resins,<sup>27</sup> just as the addition of propylene carbonate and glycerol triacetate have been shown to do in wood composites bonded with phenolic resins.<sup>3</sup> With the data presented in this article, it is not possible to distinguish which one of the two mechanisms is the

one which is valid or even if other mechanisms could be possible.

In conclusion, additive accelerated PF resin polycondensations appear to present several different acceleration mechanisms. Some additives such as sodium carbonate appear to present purely an accelerating effect on the polycondensation reaction. Other additives such as propylene carbonate present both an acceleration effect as well as inducing an increase in the average functionality of the system, due to alternate crosslinking reactions to which the accelerator itself does participate, leading to a tighter final network. These alternate crosslinking reactions can be of a different nature, such as in the propylene carbonate case, in which the reaction is related to a Kolbe-Schmitt reaction, and the rapid reaction of  $-\text{NH}_2$  groups of formamide and of the ammonia obtained by its alkaline hydrolysis with two, or more (for ammonia) hydroxybenzyl alcohol groups of PF resols, which is also characteristic of urea and methylamine.

## REFERENCES

1. A. Pizzi, *Wood Adhesives Chemistry and Technology*, Marcel Dekker, New York, 1983, Vol. 1.
2. A. Pizzi and A. Stephanou, *J. Appl. Polym. Sci.*, **49**, 2157 (1993).
3. A. Pizzi and A. Stephanou, *Holzforschung*, **48**(2), 150 (1994).
4. M. Higuchi, S. Tohmura, and I. Sakata, *Mokuzai Gakkaishi*, **40**(6), 604 (1994).
5. S. Tohmura and M. Higuchi, *Mokuzai Gakkaishi*, **41**(12), 1109 (1995).
6. A. Pizzi, B. Mtsweni, and W. Parsons, *J. Appl. Polym. Sci.*, **52**, 1847 (1994).
7. A. Pizzi and A. Stephanou, *J. Appl. Polym. Sci.*, **51**, 1351 (1994).
8. A. Pizzi, A. Stephanou, I. Antunes, and G. De Beer, *J. Appl. Polym. Sci.*, **50**, 2201 (1993).
9. M. Ohyama, B. Tomita, and C.-Y. Hse, *Holzforschung*, **49**, 87 (1995).
10. N. J. L. Megson, *Phenolic Resin Chemistry*, Butterworth, London, 1958.
11. F. Probst, M.-P. Laborie, A. Pizzi, A. Merlin, and X. Deglise, *Holzforschung*, to appear.
12. A. Pizzi, *J. Appl. Polym. Sci.*, **63**, 603 (1997).
13. A. Pizzi, F. Probst, and X. Deglise, *J. Adhes. Sci. Technol.*, **11**, 573 (1997).
14. C. Cremonini and A. Pizzi, *Holzforsch. Holzverwert.*, **49**, 11 (1997).
15. R. Garcia, PhD Thesis, University of Nancy 1, Nancy, France, 1997.

16. E. Breitmaier and W. Voelter, *Carbon-13 NMR Spectroscopy*, 3rd ed., VCH, Weinheim, 1987.
17. E. Pretsch, T. Clerc, J. Seibl, and W. Simon, *Tables of Spectral Data for Structure Determination of Organic Compounds*, 2nd ed., Springer-Verlag, Berlin, 1989.
18. W. H. Carrothers, *Collected Papers*, Wiley-Interscience, New York, 1940.
19. F. Rodriguez, *Principles of Polymer Systems*, 3rd ed., Hemisphere, New York, 1989.
20. J. McMurry, *Organic Chemistry*, 3rd ed., Brooks/Cole, Pacific Grove, CA, 1992, p. 822.
21. S. Wang, unpublished results, 1996.
22. P. H. R. B. Lemon, *Int. J. Mater. Prod. Technol.*, **5**(1), 25 (1990).
23. J. McMurry, *Organic Chemistry*, 3rd ed., Brooks/Cole, Pacific Grove, CA, 1992, pp. 701–702.
24. P. Sykes, *A Guidebook to Mechanism in Organic Chemistry*, Longmans, London, 1963, pp. 203–204.
25. A. Knop and L. A. Pilato, *Phenolic Resins*, Springer-Verlag, Berlin, 1985.
26. L. A. Pilato, private communication, 1994.
27. R. L. Geimer, A. Leao, D. Ambruster, and A. Pablo, in *Proceedings of the 28th International Particle-board Symposium*, Washington State University, Pullman, 1994, pp. 243–259.