

On the Chemistry, Behavior, and Cure Acceleration of Phenol–Formaldehyde Resins Under Very Alkaline Conditions

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SYNOPSIS

The curing acceleration by organic esters of alkaline phenol–formaldehyde (PF) resins can be explained by two different mechanisms. In the course of the work, the unexpected curing behavior of PF resins alone, under very alkaline conditions, was observed, which diverged from past assumptions. PF resins curing, which is supposed to be accelerated by the formation of phenate ions, is instead markedly slowed down by increasingly alkaline pHs and accelerates in the presence of esters. The mechanism of ester acceleration of PF resins curing was clarified and the effect of different esters was quantified and was related to the pK_a and quantity of the acid forming the ester. A second mechanism, which appeared also to explain the peculiar slowing down at increasing pH of PF resin curing, could not be confirmed; some evidence appeared to point to this second mechanism's existence, while other evidence appeared clearly to deny it. The impossibility of isolating an Na^+ phenol ring complex, theorized by other authors and other evidence, indicates that this second mechanism is unlikely to occur. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Phenol–formaldehyde (PF) resins are considered to be the first true synthetic polymers ever developed.^{1,2} Their chemistry and behavior, however, has not yet been completely elucidated. A considerable amount is known, and has been published on the fundamental and applied aspects of these polymers, yet new fundamental aspects can still be discovered. The work presented in this article addresses two such cases.

The so-called α - and β -sets acceleration of the cure of very alkaline PF resins for foundry core binders was pioneered in the early 1970s.^{3–5} In this application, the addition of considerable amounts of esters, such as propylene carbonate, methyl formate, and triacetin (glycerol triacetate), were found to accelerate the curing of the resin to extremely short curing times. This process is now used extensively, around the world, for foundry core PF bind-

ers. The mechanism of acceleration of the resin appears to have never been reported. In applying this concept to alkaline PF resins for thermosetting wood adhesives, and in clarifying the esters' acceleration mechanism, peculiar behavior (by known standards) was observed for all the PF resins used.

The effect of pH on the rate of curing and polymerization of phenolic resins is well known^{6,7} (Fig. 1). It is also widely accepted that at very alkaline pH, the rate of curing of phenolic resins accelerates.^{6,7} This occurs as the function of phenolic nuclei as nucleophiles is strengthened, by the ionization of the phenol, to form phenate ions.^{6,7} The literature, however, contains little information regarding the slope of the gel times (hence reactivity) curves, as a function of the pH, over a pH of 9.^{1,6,7} This is an unusual gap, considering that a great proportion of the total world output of PF resins is used as thermosetting wood adhesives, an application for which only PF resins of very high alkalinity, generally at pHs of between 10 and 13, are used to avoid acid hydrolysis of the lignocellulose substrate.

The work presented here is aimed: (i) at showing that at very alkaline pHs, the reaction and curing

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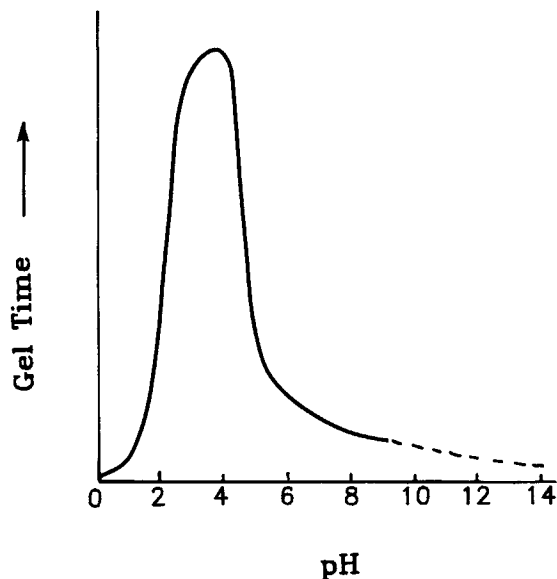


Figure 1 Gel time vs. pH curve of PF resin. Broken line indicates extrapolated assumption.

behavior of PF resins is unexpectedly different from that theorized or assumed, (ii) at discussing which is the possible mechanism underlying such a behavior, and (iii) at clarifying the mechanisms of cure-acceleration of PF resins by esters.

EXPERIMENTAL

Phenol-Formaldehyde (PF) Resin Preparation and Determination of Gel Times

Ninety-four parts by mass of phenol were mixed with 40 parts (20/80) methanol/water solution 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 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 60 min and was then cooled. The resin solids content was 60%, viscosity 3100 centipoises at 25°C, and final pH = 10.80.

The gel time dependence on pH at 94°C was determined over the entire pH range at a constant solids content of 50%, using the following method. Gelation is defined as the point at which the resin ceases to be a viscous liquid and becomes a soft, elastic, rubbery solid. Ten g of liquid resin was weighed in a glass test tube. When ester accelerator was needed, the ester was then weighed in the same

test tube. A wire spring was placed in the resin within the test tube and the resin (and accelerator) was mixed gently for a few seconds at ambient temperature. The test tube was then placed in a boiling water bath (94°C), the wire spring was manually moved rapidly upward and downward, and the time for gelation was measured using a stopwatch. The test was done twice. The elevated temperature caused gelling to accelerate. The gel time measurement was related to the speed of gelling of the resin under actual application conditions. Accelerated gel time tests at higher temperatures can be related to gel times at lower temperatures. There is then a measure, not only of resin curing at elevated temperature, similar to actual application conditions, but also a measure of the catalyzed working life of the resin and its uncatalysed storage stability.⁷ In addition to the gel times for the unaltered resins, gel times of the PF resins after the addition of 2.5%, 5%, 7.5%, and 10% by mass (on PF resin solids) of propylene carbonate, methyl formate, glycerol triacetate (triacetin), phenyl acetate, methyl salicylate, and ethyl butyrate, at the pHs indicated in Figures 2 to 4, were also determined. Reproducible results are shown in Table I.

Gel times of mixtures (not resinified in advance) of resorcinol 35% solution in water with 96% paraformaldehyde powder, at a resorcinol : formaldehyde molar ratio of 1 : 1.2, were also determined at 94°C

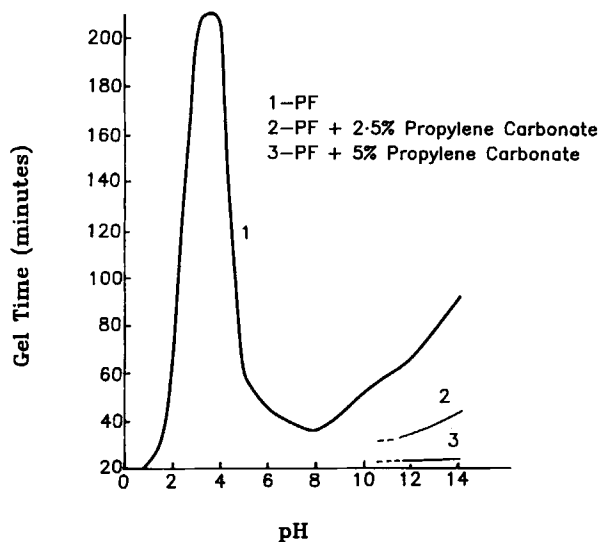


Figure 2 Actual experimental gel time vs. pH curves of a PF resin (1) alone, (2) with 2.5% propylene carbonate added, and (3) with 5% propylene carbonate added, showing the upward trend of the gel time curve, the acceleration effect of the ester, and the dependence of the acceleration effect from the quantity of the ester.

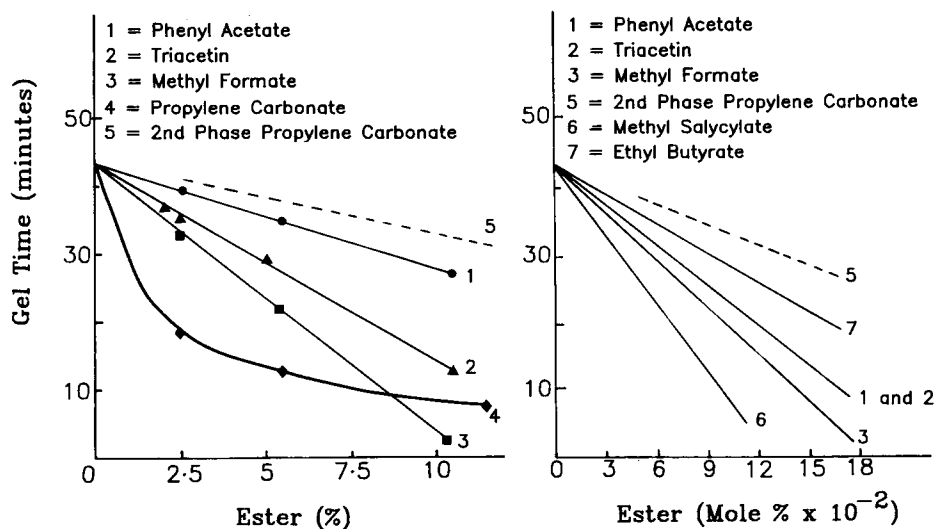


Figure 3 (a) Dependence of gel time of a PF resin, at pH = 11.26 from the percentage of ester added (percentage ester, by mass, on PF resin solids), and the type of ester added. (b) Dependence of gel time of a PF resin, at pH = 11.26, from the molar percentage of ester added on the mass of PF resin solids, illustrating the dependence on quantity of ester, pK_a , of the type of acid in the ester, and effect of diprotic acid (from propylene carbonate).

with and without propylene carbonate, according to the methods described above, and as shown in Figure 8.

UV Absorbance Curves and UV Extinction Curves as a Function of pH³⁸⁻⁴

0.100 g ortho/para-hydroxybenzyl alcohol were dissolved in 20 mL of water, after adjusting the pH to 10 and 12 correspondingly, by using NaOH (0.02 M). The solution was diluted to a final concentration of 3.22×10^{-4} M. The pH of 200 mL hydroxybenzyl alcohol solution was adjusted by adding small amounts of acetic acid/NaOH, thus maintaining the concentration constant, and UV absorption spectra were obtained using a Varian-Series 634 spectrophotometer. The absorbance at a fixed wavelength was also recorded and was plotted as a function of pH.

IR Investigation of Phenol with Propylene Carbonate in the Absence of Formaldehyde

- 4.023 g resorcinol in 4 mL water at pH = 11.95 was reacted with 3.733 g propylene carbonate (3.10 mL) for 2 h, once at ambient temperature, and once at 60°C. The IR spectra, at 15 min intervals, were taken throughout the reaction. ¹³C NMR spectra in D₂O were performed.
- 4.00 g phenol in 2.662 g water and 4.314 g propylene carbonate, at pH 13.01 (adjusted with

KOH), were reacted at ambient temperature, 60°C and 87°C, for 2 h. IR spectra were taken at 15 min intervals throughout the reaction. IR of the isolated crystals were also obtained (by KBR pill).

- 1.948 g saligenin (*o*-hydroxybenzyl alcohol), in 2 mL water at pH 13.37, were reacted with 1.644 g propylene carbonate for 2 h at both ambient temperature and 60°C. IR spectra were taken at 15 min intervals throughout the reaction.

IR Spectra (% Transmittance in Parentheses)

- *Phenol/propylene carbonate reaction (pH 13, ambient temperature)*: 3430 cm⁻¹ (33), 3100 (23), 2975 (17), 2650 (17), 1880 (36), 1650 (0.5), 1440 (0.8), 1390 (5), 1060 (36), 1020 (14), 990 (20), 880 (37.5), 840 (8.5), 715 (26.5), 680 (39), 620 (53.5).
- *Phenol*: 3400 (31), 1605 (29), 1510 (36), 1485 (33), 1380 (47), 1240 (33), 1180 (45), 1160 (49.5), 1060 (43.5), 1020 (54), 990 (58), 880 (56), 800 (41), 747 (31.5), 680 (31).
- *Propylene carbonate*: 3559 (63), 2975 (52.5), 2900 (57), 1780 (37), 1545 (68), 1480 (61), 1440 (64), 1385 (52), 1340 (54), 1220 (62.5), 1170 (48), 1115 (50.5), 1040 (47.5), 950 (71), 910 (76), 840 (75), 770 (57), 700 (62).
- *Saligenin (o-hydroxybenzyl alcohol)*: 3425 (37.5), 3120 (40), 1600 (59.5), 1580 (58), 1470

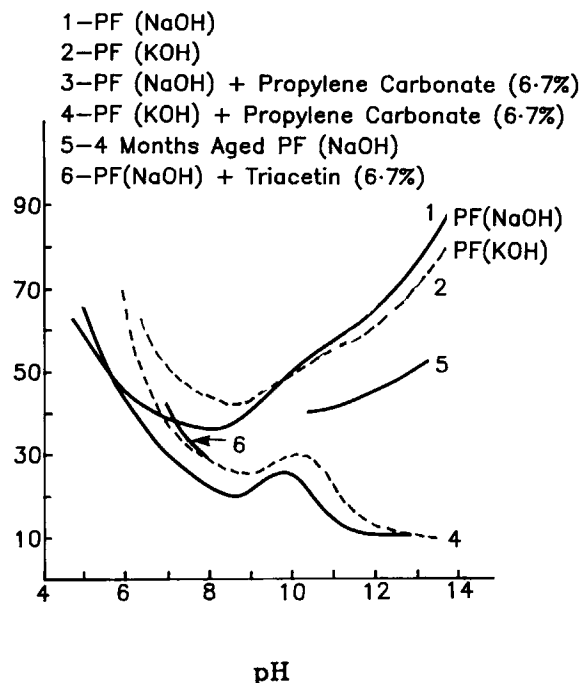


Figure 4 Cure retarding at high pH and ester acceleration effect of NaOH- and KOH-prepared PF resins (ester = propylene carbonate). Note "bumps" caused by methylene ether's formation and decomposition, at pH 8-11. Curve 5, the effect of 4 months' aging of PF resin of curve 1 on the extent and starting pH of retardation effect, should be noted. The start of acceleration for curves 4 and 6, showing the difference between propylene carbonate and triacetin and the starting point of acceleration at pH 5.5 and 7.1, can be compared.

(62), 1450 (46), 1410 (62), 1380 (60), 1280 (63), 1260 (50), 1180 (62), 1105 (62), 1040 (71), 990 (46), 930 (67), 860 (72), 840 (73), 765 (71), 745 (46), 720 (63), 700 (72).

- *Saligenin/propylene carbonate reaction*: 3425 (32), 2925 (41), 1580 (55), 1495 (46), 1450 (40), 1240 (43), 1085 (57), 1040 (59), 980 (68), 910 (68), 820 (67), 745 (57.5).

C^{13} NMR Spectra

- *Resorcinol* (intensity in parenthesis): 166.9 (16.7), 132.9 (6.8), 132.8 (11.5), 132.7 (6.6), 109.5 (12.6), 109.2 (21.0).
- *Propylene carbonate*: 155.9 (1.3), 74.6 (10.6), 71.4 (15.0), 19.2 (17.0).
- *Resorcinol/propylene carbonate reaction*: 178.6 (1.1), 169.5 (2.2), 164.5 (1.8), 160.7 (10.9), 134.5 (2.1), 133.0 (5.6), 132.9 (3.9), 132.8 (0.8), 112.4 (2.1), 110.4 (1.5), 109.9 (13.1), 106.03

(9.9), 105.97 (3.3), 70.5 (20.6), 69.2 (18.7), 20.6 (19.4).

Paper Chromatography and Molecular Mechanics of PF Oligomers

The PF oligomers, listed in Table II, were obtained as follows: the three dihydroxy-diphenylmethanes were prepared and were treated according to the method of Pizzi and de Sousa.⁸ Two of the hydroxybenzyl alcohols were prepared according to Freeman,^{9,10} while the *o*-hydroxybenzyl alcohol (saligenin) and *p*-hydroxybenzyl alcohol were bought as pure AR grade. The dihydroxydiphenylmethanes and hydroxybenzyl alcohols *R_f* values were obtained on Watman No. 1 chromatography paper, according to the method of Freeman^{9,10} and Pizzi and de Sousa.⁸ The experimental *R_f* values are shown in Table II.

The values of the secondary interactions (sum of van der Waals, H-bonds, electrostatic and torsional contributions), between each of the PF oligomers and the surface of a schematic model of the surface of a crystallite of Cellulose II, have already been reported^{8,11,12} and were obtained according to established molecular mechanics methods.¹³⁻¹⁵ The computational methods and constrained and noncon-

Table I Gel Times Values and Standard Deviation of the NaOH Catalyzed PF Resin Without and with 6.7% by Mass of Propylene Carbonate

pH	Gel Time and Standard Deviation (sec)	
	PF Alone	PF + Propylene Carbonate
6	2668 ± 21	2541 ± 26
6.5	2414 ± 28	2096 ± 23
7	2287 ± 29	1747 ± 22
7.5	2160 ± 17	1493 ± 28
8	2128 ± 22	1270 ± 25
8.5	2223 ± 26	1175 ± 22
9	2446 ± 31	1334 ± 26
9.5	2732 ± 23	1490 ± 21
10	2986 ± 22	1461 ± 19
10.5	3240 ± 27	1111 ± 24
11	3431 ± 24	826 ± 25
11.5	3653 ± 30	667 ± 23
12	3875 ± 18	623 ± 24
12.5	4193 ± 22	604 ± 16
13	4510 ± 11	604 ± 24
13.5	4955 ± 16	559 ± 22

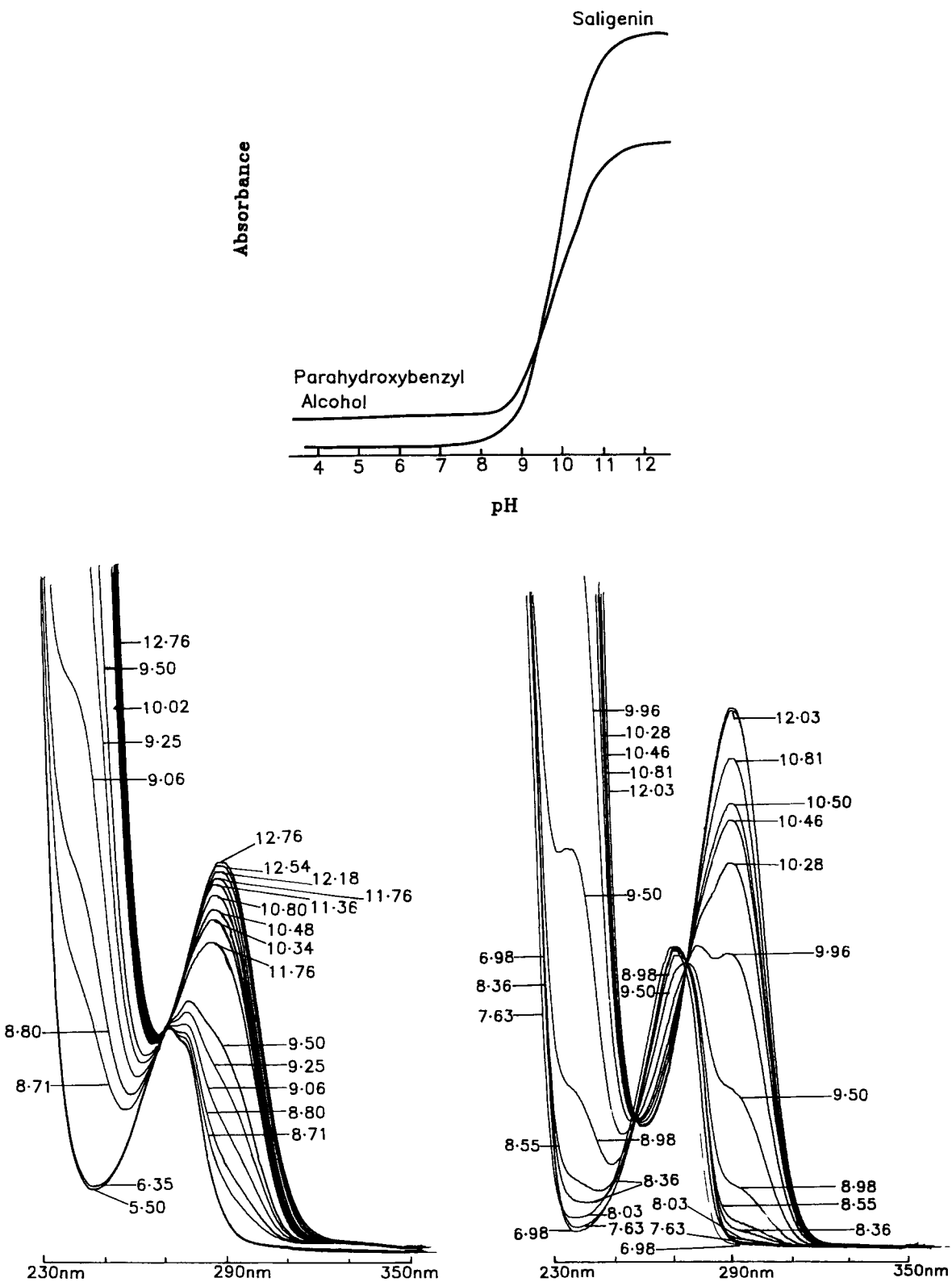


Figure 5 (a) UV extinction curves in function of pH of saligenin and ortho-cresol (coincide), and *p*-hydroxybenzyl alcohol and para-cresol (coincide), (b) UV absorbance vs. frequency of saligenin and ortho-cresol (coincide), and (c) UV absorbance vs. frequency of *o*-hydroxybenzyl alcohol and para-cresol (coincide).

Table II Comparison of Computational Energy Results^{8,11} with Experimental Paper Chromatography *Rf* Values⁸⁻¹⁰ for Oligomers Formed by Reaction of Phenol with Formaldehyde, Showing a Lack of Comparison for the Relative Position of *o*-Hydroxybenzyl Alcohol (Saligenin) and a Good Comparison for the Na⁺/Hydroxybenzyl Alcohol Complex

Species	Minimum ^{8,11} Interaction Energy (kcal/mole)	Experimental ⁸⁻¹⁰ <i>Rf</i>
Trihydroxybenzyl alcohol	-50.0	0.34
<i>o,o</i> -dihydroxydiphenylmethane	-20.8	0.55
<i>o</i> -hydroxybenzyl alcohol	-19.7	0.84
<i>o,p</i> -dihydroxydiphenylmethane	-17.9	0.55
<i>o,p</i> -dihydroxybenzyl alcohol	-15.0	0.61
<i>p,p</i> -dihydroxydiphenylmethane	-14.7	0.65
<i>p</i> -hydroxybenzyl alcohol	-13.3	0.80
Na ⁺ / <i>o</i> -hydroxybenzyl alcohol complex	-12.2	0.84

strained force fields used have already been extensively reported.^{8,13-15} The results obtained are shown in Table II.

DISCUSSION

The curves of gel time vs. pH in Figure 2 illustrate the unexpected behavior of the Na⁺-catalyzed PF resins. Over a pH of approximately 10, the rate of curing of the PF resin slows down markedly, instead of accelerating, as has always been supposed. It continues to slow down markedly with increasing pH. As also can be seen in Figure 2, the increasing addition of an ester increasingly accelerates the reaction in the pH range under consideration. At the lower amounts of esters, the upward trend of the gel time curves in the graph is still in evidence. During the reaction, hydrolysis of the ester occurs (gel times are carried out at 100°C) as evident by following the reaction by IR spectroscopy. Thus, in the reaction of both phenol and orthohydroxybenzyl alcohol (saligenin) with propylene carbonate, the C=O carbonyl signal shifts from 1800 cm⁻¹, characteristic of the ester before the reaction occurs, to 1650 cm⁻¹ at the end of the reaction. An indication of this is that the ester has hydrolyzed to form another carbonylic or carboxylic compound, possibly the corresponding acid (the 1650 cm⁻¹ band is characteristic of the acid carboxylate ion¹⁶). The influence of dilution and pH variation was kept in check during all these experiments, especially because just dilution effects could have been the cause of the phenomena: the dilution of the resin introduced by

the addition of the NaOH solution renders, of course, the upward slant of the curves even more evident. The effect noticed is strong and persists also when the concentration and pH of the resin are maintained constant.

The effect of different esters and of different amounts of esters on the curing acceleration of the same PF resin are shown in Figure 3: the different esters used were propylene carbonate, methyl formate, triacetin (glycerol triacetate), phenyl acetate, ethyl butyrate, and methyl salicylate. Comparing the slope and relative positions to each other of these curves with the *K_a* and *pK_a* of the acids involved in these esters, shown in Table III, it becomes evident that the strength and dissociation of the acid involved in the ester determines the rate of curing acceleration of the resin, with one exception, propylene carbonate, which will be discussed in more detail later. This correspondence between rate of cure and *K_a* of the acid in the ester is the first clear indication that some sort of acid-base mechanism

Table III Acid Dissociation Constants³⁸ of Acids Involved in Some Cure-Accelerating Esters

	<i>K_a</i>	<i>pK_a</i>
Salicylic acid		
(<i>o</i> -hydroxybenzoic)	1.07×10^{-3}	2.97
Formic acid	1.77×10^{-4}	3.75
Acetic acid	1.76×10^{-5}	4.75
<i>n</i> -Butyric acid	1.54×10^{-5}	4.81
Carbonic acid	4.3×10^{-7}	6.37

might be involved in the cure-acceleration effect. In more detail, the curves in Figure 3(b), in which the dependence of gel-time on ester amount has been expressed as percentages of moles of acid generated by dissociation of the ester, indicate that at a constant amount of acid, there is no difference between triacetin and phenyl acetate, both esters of acetic acid. Furthermore, the relative positions of curves in Figure 3(b) are in the order of the relative pK_a values of the acids in the esters. The only exception is propylene carbonate, in which the correlation between amount of ester and gel time is not linear, and the curve of which can be divided into two well-defined reactions: first, up to approximately 2½% ester on PF resin solids, showing extremely fast curing-acceleration, and, second, from approximately 5% ester, responding to the relative pK_a of the first hydrogen of carbonic acid (Table III).

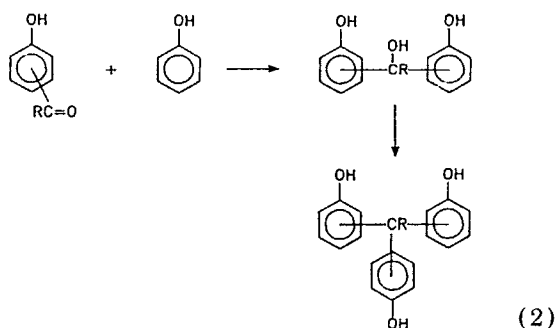
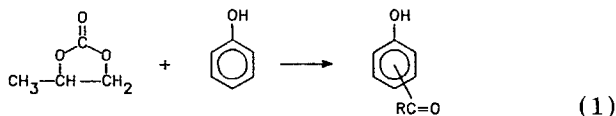
Other interesting features are noted in Figure 4, namely the "bumps" evident in the 8.5–11 pH range, observed in the curves of the ester-accelerated PF resins. At first, it was thought that these might be caused by the time delay required for propylene carbonate dissociation at different pHs. While this might well contribute to the intensity of the "bumps," it is not the main, nor the only, cause. Because in the PF curves without ester in Figure 4, the same bumps, but less marked due to the upward trend of the curves, are also noticeable in the same pH range. The 8 to 9.5 pH range is known to be a range in which the methylol groups of a phenolic resin readily react to form metastable methylene ether crosslinks.¹⁷ Cleavage of methylene ethers crosslinkages occurs readily, especially outside this pH range, with consequent rearrangement to methylene linkages and liberation of formaldehyde.^{7,17} It is this mechanism that best accounts for the presence of these "bumps" in the curves: they are more noticeable with the downward trend of the ester-catalyzed curves than with the marked upward trend of the plain PF curves.

Of all the ester accelerators, only propylene carbonate appeared to deviate from the established trend. Even taking into consideration both protons of carbonic acid, the fast gel times observed up to 2½% to 3% [Fig. 3(a)] could be best reported in Figure 3(b), only near, but not quite up to the slope of formic acid. First, phenol was reacted with propylene carbonate, in the complete absence of formaldehyde, to determine if a crosslinking mechanism other than the usual methylene crosslinking of PF resins could be detected. The reaction was followed at pH 13 and at ambient and higher temperatures.

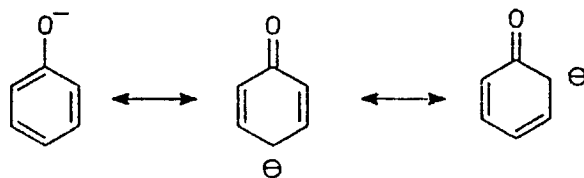
The carbonyl band of the ester at 1780–1800 cm^{-1} disappeared and a strong carbonyl signal at 1650 cm^{-1} appeared (Fig. 7). New peaks at 3100 cm^{-1} and 2675 cm^{-1} appeared, the first small, the second marked. Significantly, disubstituted aromatic nuclei bands at 840 cm^{-1} and 715 cm^{-1} and a clear 880 cm^{-1} band of trisubstituted aromatic nuclei appeared, while the monosubstituted benzene ring band at 800 cm^{-1} disappeared. This appears to indicate the reaction of some species on the aromatic nuclei of the phenol. The 715 cm^{-1} band is characteristic of 1,2-disubstituted aromatics, while the 840 cm^{-1} band is characteristic of both 1,4-disubstituted and 1,2,4-trisubstituted aromatic nuclei. Both 1,4 and 1,2,4 substitution are present, because the 840 cm^{-1} band is particularly strong, indicating the sum of two bands, while the 880 cm^{-1} band, which is weaker, is only characteristic of the 1,2,4-trisubstituted aromatics (Fig. 7). Most of the IR bands tended to broaden, indicating that a certain extent of polymerization had also begun. The broad band, at 1650 cm^{-1} , is characteristic of $-\text{COO}^-$, but too broad to be caused only by this, while the 1420–1440 cm^{-1} broad band appears to be a combination of a medium/strong $-\text{COO}^-$ resonance band and of a medium 1,4-disubstituted aromatic resonance band. The particularly noticeable broadening of these two bands appears also to indicate that if some sort of crosslinking and polymerization has occurred, the disubstituted aromatic nuclei and the >C=O are somehow involved. The IR spectra of the reaction of phenol with propylene carbonate, in the absence of formaldehyde, at ambient temperature, is shown in Figure 7. Saligenin (*o*-hydroxybenzyl alcohol) was also reacted with propylene carbonate and showed the same trends, although less marked, due to the normal polymerization mechanism, resulting in crosslinking from methylene groups being superimposed onto the new reaction. Furthermore, C^{13} NMR of the products of the reaction of resorcinol with propylene carbonate, also in absence of formaldehyde, indicate clearly that a >C=O chemical species has become attached to the aromatic nuclei of resorcinol: This is noticeable by the shift and splitting of the 109 ppm bands of the two ArC-O- in resorcinol into two bands of much lower intensity at 109 and 105 ppm, indicating the introduction of asymmetry at the C_4 , C_6 , or C_2 of resorcinol. Equally, four C-O (or C=O) bonds, at 179, 169, 165, and 161 ppm, in place of the single resorcinol one at 167 ppm, indicate, respectively, the

presence of a carboxylic acid, two $\text{Ac}-\text{C}-\text{O}$ from resorcinol (now split and separate, indicating asymmetry), and one from the new carbonyl species reacted with the aromatic nuclei.

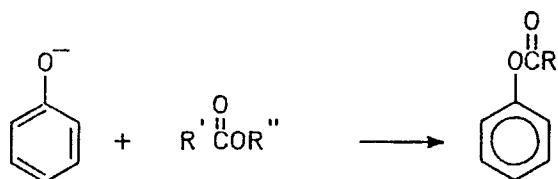
Thus, it appears that at first some chemical species reacts on the phenolic aromatic ring, giving rise to disubstituted and even trisubstituted nuclei. Second, the small new band, at 3100 cm^{-1} , is characteristic of hydroxybenzyl alcohols (for instance, saligenin by itself presents clearly this band). The presence of some type of hydroxybenzyl alcohol group, when there was none at the start of the reaction, gives already some idea of what is happening. The most indicative strong new band is the one at 2675 cm^{-1} , which is large when using phenol and is smaller when using saligenin. This band is characteristic of an aromatic keto group and, particularly, of aromatic aldehyde groups when a strong carbonyl band at $1600\text{--}1700\text{ cm}^{-1}$ is also present, which it is. An hypothesis of the mechanism of acceleration involved could then be advanced. At first a chemical species, most likely formed by the dissociation of propylene carbonate, attacks and reacts with the aromatic nuclei of phenol. This new group presents a carbonyl moiety, from C^{13} NMR and the IR bands pattern most likely an aromatic aldehyde or keto group. This then generates hydroxybenzyl alcohol-like groups on further condensation with other aromatic phenolic nuclei, leading to polymerization: all this in the absence of initial formaldehyde. As the keto or aldehyde group formed by the initial attack on the phenolic ring is aromatic, this might imply dissociation at first of only one of the propylene carbonate ester bonds, followed by some complex internal rearrangements. It is clear that both an aromatic aldehyde or keto group would present a three sites crosslinking capability, explaining the apparent fast acceleration effect.



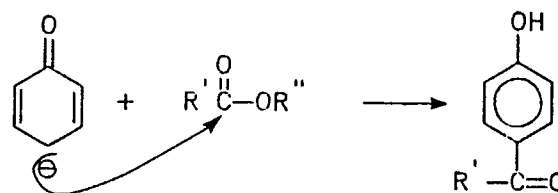
Thus, $R = H$ or possibly an alkylic group. The above appears clearly by following the reaction by IR spectroscopy. It is not immediately clear, however, how a carbonylic group finds itself attached to the aromatic nuclei of phenol. Potentially, any ester should have this capability in alkaline solutions, thus it is well known^{1,7} that:



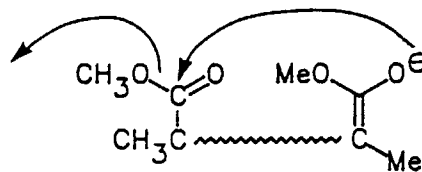
with eq. (1)



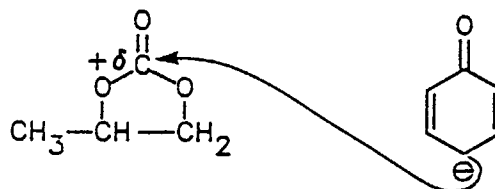
occurring, but also eq. (2),



Reactions similar to that shown in eq. (2) above are known. For instance, in group transfer polymerization,^{18,19} a strong base is capable of producing:

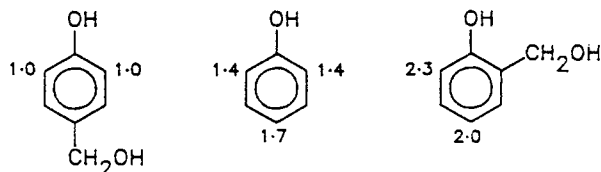


In the concentrated NaOH environment, prevalent at high pH in a PF resin, with a reactive metastable compound, such as propylene carbonate, a similar carbanion attack may be considered.



Freeman²⁰ and Freeman and Lewis²¹ determined the relative reactivities of individual nuclear positions

in phenol and methylol phenols under alkaline reaction conditions as:

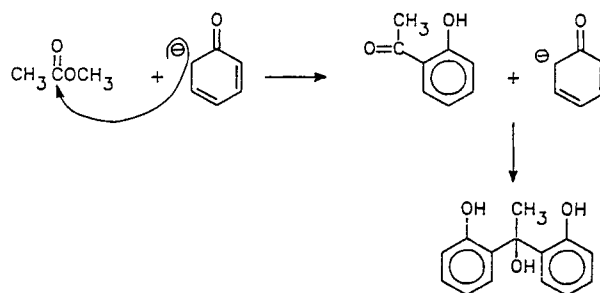


It is clear that phenolic carbanions, formed by ortho-methylol moieties in the PF resin, will be the ones reacting first. The reaction of propylene carbonate with phenol, hydroxybenzyl alcohols, and PF resins then appears to be nothing else than a variant of the Kolbe-Schmitt²² synthesis (in which salicylic acid is obtained from phenol and carbon dioxide). The existence, under very alkaline conditions, of both OH^- and phenolic carbanions will lead to competitive reactions determining the relative proportions of products obtained. An hypothesis for the mechanism of reaction can then be advanced (Fig. 6).

As for the Kolbe-Schmitt reaction, it is the ortho position of the phenol, thus the ortho carbanion, which will react preferentially, although the para-carbanion will also react. The final products I and II, in Figure 6, show the existence of an aromatic ketone (I), of a substituted hydroxybenzyl alcohol (II) and disubstituted aromatic nuclei, as shown by IR. The same reaction as for phenol alone would occur also with a linear phenol-formaldehyde resin. On this crosslinking mechanism, the usual methylol to methylene crosslinking of PF resins is superimposed. Thus, the second crosslinking mechanism, caused by propylene carbonate, is the likely cause of esters acceleration of PF resins. Acceleration is observed due (i) to the presence of the equivalent of another trifunctional reagent (compare to difunctionality of formaldehyde for instance), (ii) to a phenolic nuclei on which a methylol group is already present, becoming from a trifunctional at least a tetrafunctional reagent (or even more functional if more than one propylene carbonate reacts), (iii) by the higher concentration of reagents (the ester being a proper reagent and not a catalyst), and (iv) by carbonic acid being a diprotic acid. All four causes above will induce much earlier gelling and consequently the observed gelling acceleration. It is interesting to note that for propylene carbonate, this effect begins at around pH 7 (Fig. 4), a pH at which phenolic carbanions are known to exist in a higher proportion than OH^- .⁷

Examination of the behavior of the other esters indicates that this mechanism is also at work. Their

reactions are slower than that of propylene carbonate because they function as reagents of lower functionality. Thus



and because they are monoprotic acids rather than diprotic, as carbonic acid is. The dependence of the acceleration effect of the ester of monoprotic acids from the pK_a of the acid is not casual, but it is related to the intensity of the nominal $+\delta$ charge on the carbon of the carbonyl group, explaining the different intensity of acceleration.

Could another mechanism be responsible for the ester acceleration effect? Another explanation for the lengthening of gel times at higher pHs and the acceleration effect can be hypothesized, but the experimental evidence gathered is inconclusive, some appearing to indicate the mechanism's existence and some appearing to deny it. It is necessary to discuss this to put the previous mechanism into perspective.

In 1948, Caesar and Sachanen²³ postulated that the phenolic hydroxy group must be involved in the reaction of the methylol group to form methylene linkages in alkaline phenol-formaldehyde resins. They based their hypothesis on a comparison between the impossibility of reacting thiophene and formaldehyde in an alkaline environment with the ready reaction by phenol and formaldehyde under the same reaction conditions. Their hypothesis was only a postulate, without any proof, and was disregarded and criticized at the time. It was considered, however, interesting and unusual enough to be reported by Megson¹ and advanced again as a possible explanation for NaOH catalysis by Fraser et al.^{24,26} Caesar and Sachanen postulated the formation of an intramolecular chelate group, holding the Na^+ between the phenolic and the ortho-methylol hydroxyls of a PF resin. They carried their idea too far by again postulating the exchange of the Na^+ ion from the phenolic hydroxy group to the methylol group to form $\text{Na}^+ - \text{OCH}_2 -$ ions, which was an unlikely possibility. The criticism of their ideas stemmed mainly from this latter assumption. It is unlikely that an alcoholic group can behave as an acid when a more acid group, such as the phenolic

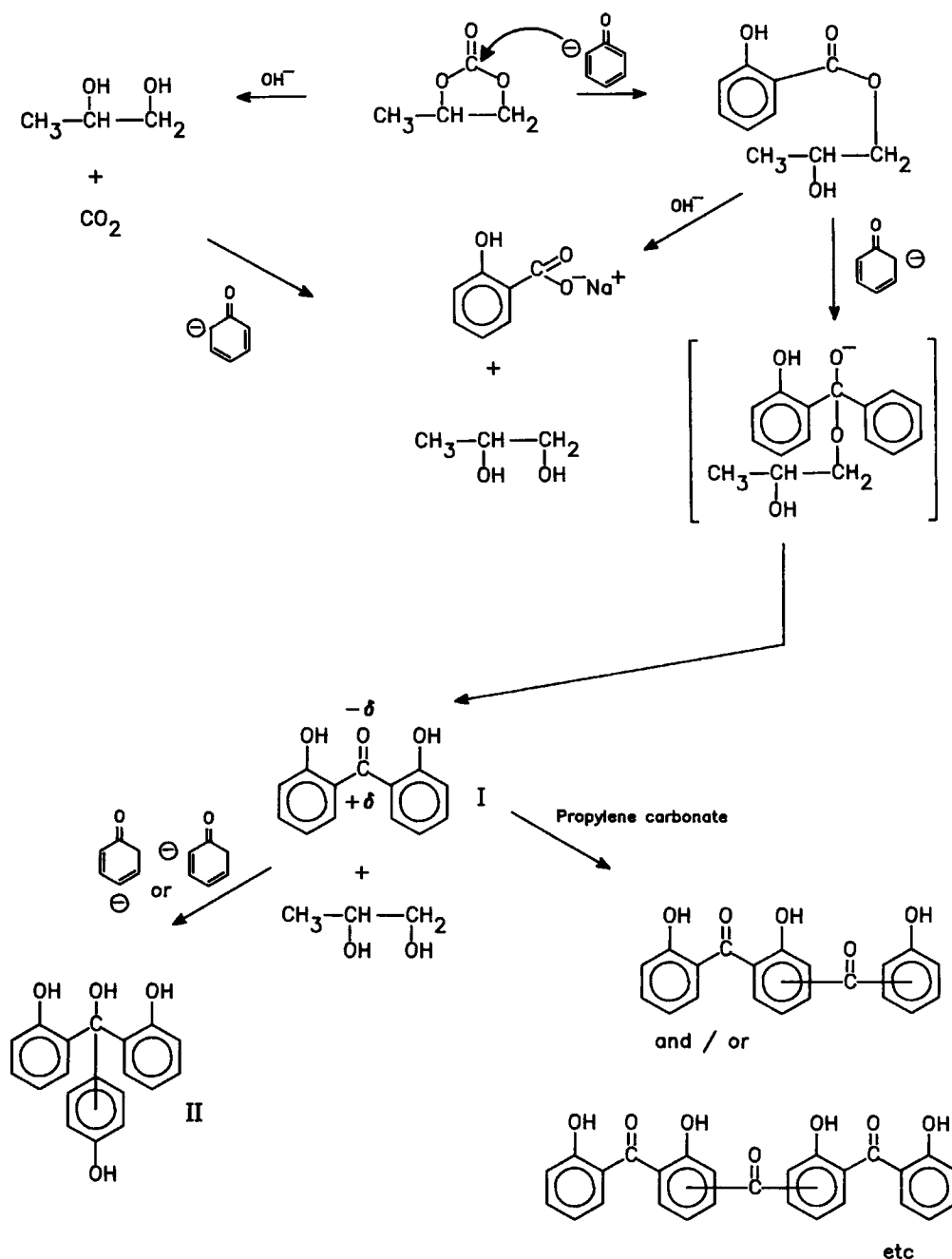
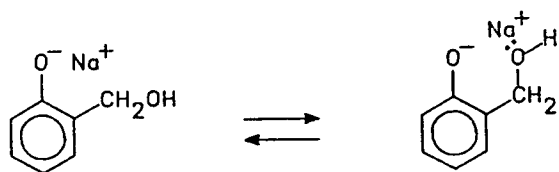


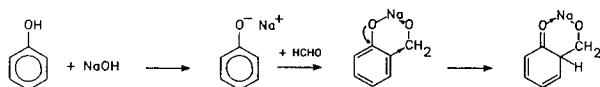
Figure 6 Proposed reaction scheme of phenol and propylene carbonate. In PF resins, traditional methylene crosslinking is superimposed and is parallel to this mechanism.

hydroxyl, is present. For instance, the acceleration or retardation of phenol-formaldehyde resins in an acid, neutral, and even mildly alkaline environment by bivalent or trivalent ions, such as Zn^{2+} , Ba^{2+} , Cr^{3+} , and others, was first reported by Fraser et al.,²⁴⁻²⁶ and was ascribed to ring mechanisms similar to those proposed for Na^+ . Their hypothesis was

demonstrated by the isolation and characterization of several of these ring complexes²⁷ and by the determination of their kinetics of acceleration and the retardation of PF resins.²⁸ The proposed mechanism for the progressive retardation of PF resins, which appear to be consistent with what is observed and all the rest of the evidence, is then:



The mechanism would be likely to occur both in an already formed PF resin, as shown above, in which the methylol group attached to the aromatic nuclei is already present, as well as in the reaction of phenol and formaldehyde in the presence of NaOH, as originally postulated by Caesar and Sachanen.²³



The presence of this mechanism and of the ring complex would explain the progressive retardation of PF resins curing at increasingly higher pHs. Freeman²⁰ and Freeman and Lewis²¹ determined the relative reactivities of individual nuclear positions in phenol and methylolphenols, under alkaline reaction conditions (see above). From these, it is clear that the rate of curing of a PF resin is mostly dependent on the ortho-hydroxybenzyl alcohol reactive sites present in the PF resin, with the *p*-hydroxybenzyl alcohol reaction sites being too slow to be the determining factor in the rate of cure of the resin. Thus, any structural rearrangements, even small

ones, that affect the electronic structure of *o*-hydroxybenzyl alcohols is likely to have a noticeable effect on the rate of curing of the resin. After the Na^+ ring complex is formed, two factors affect the reactivity of the *o*-hydroxybenzyl alcohol moieties in the resin: First, the methylol group is blocked, or its mobility is decreased, and its capacity to react to methylene linkages and crosslinkages is affected. Second, the inclusion of Na^+ in the complex decreases the electron density on the phenolic aromatic ring, markedly reducing the carbanion negative charge, which is the main force driving the PF condensation reaction under alkaline conditions. Thus, as the pH increases, a higher proportion of methylol groups are blocked (or, better, they would show a decrease in their collisional factor) and a higher proportion of carbanions present a less negative charge, slowing the reaction down, as observed in the gel-time curves presented (Figs. 2 and 4). The Na^+ complex ring can only be stable at higher pHs and is likely to be in equilibrium with free Na^+ ions present in the solution. At lower pHs, the amount of Na^+ in solution is insufficient to maintain the chemical equilibrium sufficiently shifted towards the ring complex to ensure its stability.

With the above mechanism, the main acceleration effect of the esters, used in the α - and β -set, its dependence from the dissociation of the acid, and their characteristic behavior already reported above, can

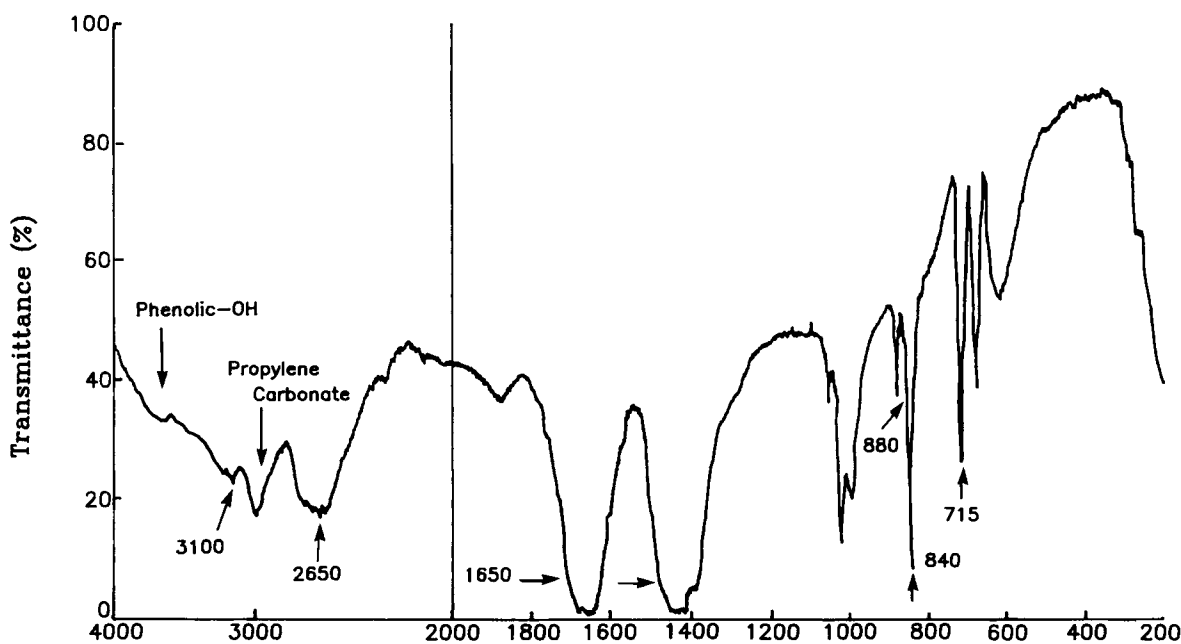


Figure 7 IR spectra of dried crystals of the product of the reaction of phenol and propylene carbonate at room temperature for 2 h. Relevant peaks for discussion are indicated by arrows.

easily be explained as an acid–base interaction. As the ester dissociates, the acid generated is able to disturb the Na^+ ring complex equilibrium in two ways: (i) by extracting Na^+ ions from the ring, regenerating reactive methylol groups and carbanions, which are then able to continue reacting to methylene crosslinkages, and (ii) by subtracting Na^+ ions from the ring complex in the equilibrium, shifting the equilibrium away from the ring complex and again regenerate reactive methylol groups and charged carbanions, again allowing the PF reaction to proceed faster. The effect would then be dependent, from the quantity and the acid strength of the acid, even at constant pH, as has been observed.

In practice, it is impossible to isolate the Na^+ complex or to confirm its existence, as it would be stable only in solutions of high Na^+ concentration. Direct and indirect proof for and against its existence has, however, been obtained. Paper chromatography of phenol-formaldehyde oligomers, in particular, of all the hydroxybenzyl alcohols, correlates with the molecular mechanics computational results of their interaction with the surface of crystalline cellulose.⁸ The *Rf* sequence of all the hydroxybenzyl alcohols on a paper chromatogram correlates with the sequence of their values, both of minimum and average energy of interaction, with the cellulose surface obtained by molecular mechanics computation.⁸ There is, however, one exception to this trend in all the paper chromatography results reported for hydroxybenzyl alcohols by Freeman,^{9,10} and other authors.^{29–34} The exception is saligenin (ortho-hydroxybenzyl alcohol), the surface interaction energy of which appears to be out of line with its experimental *Rf* value on paper chromatography. Saligenin has the highest experimental *Rf* of all the hydroxybenzyl alcohols, indicating that its energy of interaction with the substrate surface should be one of the lowest, while the molecular mechanics computational results indicate that it should be the second slowest-moving compound (Table II). However, saligenin is always in the presence of some sodium hydroxide, which is necessary to dissolve it in water. Molecular mechanics computations indicate that the Na^+ ring complex of saligenin would be stable. It also indicates that its secondary forces interactions with the cellulose surface are in line with the experimental *Rf* value observed for saligenin paper chromatography. This correspondence is illustrated in Table II. Again, an indication that saligenin in very alkaline pH might only be present in the form of the proposed Na^+ complex, intramolecular H-bonding of saligenin without Na^+ in-

creasing its computational *Rf*, but only by about half of what is needed, and thus its participation could be discarded.

There is further, but not conclusive, proof that only the *o*-hydroxybenzyl alcohol moieties of PF resins are the ones involved in the retardation effect. First, at pH 13.5–14, the gel-time curves in Figure 2 indicate a gel-time, which is only, approximately, 45% of that obtained at the pH of minimum reactivity (pH 3.5–4), inferring that only some types of reactive groups and sites are involved in the retarding effect (but this would also be valid for the first mechanism presented). Second, gel-time curves of aged PF resins, hence resins of a higher degree of polymerization and lower methylol group content, show a shift in the onset of the retarding effect from pH 8.5–9 to pH 10–10.5 and a less marked upward trend of the gel-time curve (Fig. 4). Aging decreases the number and proportion of the more reactive carbanions sites and methylol groups, those of the *o*-hydroxybenzyl alcohol moieties: the retarding effect will then appear later and will be slightly less intense, as shown in Figure 4. This, unfortunately, would also be valid for the first mechanism presented, and thus it is nondetermining, indirect proof.

The first direct and negative proof, apparently denying the existence of this mechanism, is provided by UV spectrometry. If the Na^+ ring complex exists, possibly three species should be observed by UV at different pHs for *o*-hydroxybenzyl alcohol, namely the phenolic hydroxyl, the phenate ion, and the Na^+ ring complex. Only two species are instead observed, exactly that for *p*-hydroxybenzyl alcohol and exactly that for *o*-cresol (ortho-methylphenol, in which the ring complex cannot exist). These are shown in Figure 5. It could be argued that UV might not be able to distinguish between the alleged Na^+ ring complex and the noncyclical Na^+ phenate ion, but this evidence is damning nonetheless.

The second indirect evidence, also apparently denying the existence of the Na^+ ring complex mechanism at such high pHs, is the behavior of PF resins prepared and catalyzed exclusively with KOH, and with NaOH totally absent. The hypothesis of Bender,³⁵ was checked, which is that KOH catalyzed resins are faster due to the atomic radius of K^+ being greater than Na^+ and thus forming unstable, or not forming at all, K^+ ring complexes. In this respect, the original discoverers of the α -set ester acceleration effect recommended that only KOH-catalyzed PF resins be used.^{3,4} This was contradicted later by a Japanese researcher³⁶ that found the acceleration effect to be equally valid with purely NaOH cata-

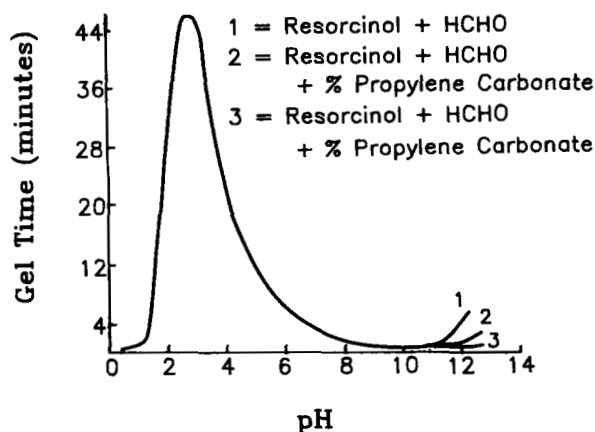
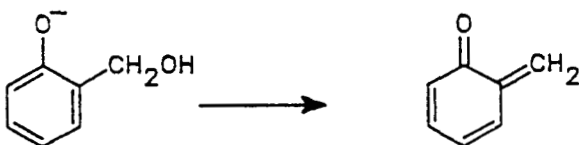


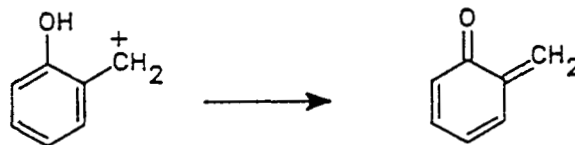
Figure 8 Shift of the start of retardation and the propylene carbonate acceleration effect for the resorcinol/formaldehyde reaction. Gel times vs. pH curve.

lyzed resins. KOH prepared and catalyzed PF resins, the results of which are shown in Figure 4, indicate clearly that the differences between KOH- and NaOH-catalyzed resins do not warrant Bender's assumptions regarding the existence of an Na^+ ring complex. The existence of the Na^+ ring complex remains elusive and the data presented in this article appear clearly to indicate that the ring complex is not formed. This is because the only two types of data appearing to indicate its existence are debatable. The *Rf* value of saligenin in paper chromatography could also be explained by intermolecular and not only intramolecular hydrogen bonding and perhaps by applying a more sophisticated molecular mechanics algorithm. Conversely, the difference in the onset of the ester accelerating effect in aged resins can be explained by the appearance of consistent amounts of quinone methides.

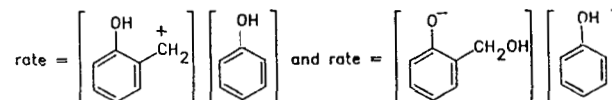
Any possible explanation for the newly observed strong cure-retarding effect, shown by NaOH- and KOH-catalyzed PF resins at higher pHs, is likely to lie in the formation of quinone methides. Megson¹ states that quinone methides yield dibenzyl ethers crosslinks with ease and methylene bridges with great difficulty. Thus, in the ionic environment present in a 50% solution of a PF resin, as the proportion of quinone methides increases, the crosslinking condensation is likely to slow down. Quinone methides form easily from ionic species, hence



where no negative charge is present, hence no carbanion-driven reaction occurs, equally



where there is no positive charge to drive the condensation reaction as the reaction is schematically driven by



The progressive rearrangement to quinone methides and their increasing proportion will progressively slow down the condensation step of the reaction, as is observed.

Finally, it is of interest to observe whether such an effect occurs only with phenol or applies also to reaction of other phenols with formaldehyde. The much more reactive resorcinol was used for this purpose. C^{13} NMR has already shown that it reacts with esters (see above). Figure 8 shows the effect to be present also with the faster reacting resorcinol, with the upward trend of the gel time curve, however, occurring at much higher pHs and being of much lower intensity. Ester acceleration also presents the same shifted trends (Fig. 8). This is in agreement with the results of Abe,³⁷ which reported that reactivity of a phenol towards formaldehyde appears to be inversely proportional to the acidity of its phenolic hydroxy groups. Resorcinol is less acid than phenol,³⁷ and it is more reactive towards formaldehyde. The less acid the phenol, the higher the pH at which a high proportion of carbanions is formed, which is consistent with the data shown in Figure 8. As a scale of increasing acidity³⁷ passes from resorcinol to *p*-cresol, phenol, and catechol, one could foresee at which approximate stage the slowing down of the phenolic resin crosslinking may occur when using other phenols.

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