Ester Acceleration Mechanisms in Phenol–Formaldehyde Resin Adhesives

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ABSTRACT: An analysis of phenol–formaldehyde (PF) resins obtained by the addition of 0.5–5% glycerol triacetate (triacetin) as an accelerator during resin preparation showed the presence of intermediates involved in the acceleration mechanism. ^{13}C-NMR spectroscopy, matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectroscopy (MS), and gel permeation chromatography allowed us to identify some of the intermediates left over in the PF resin itself. The permanence in the resin of these labile intermediates, not easily observed otherwise, appeared to be due to the reaching of the diffusion-controlled phase of the reaction. The mechanism involved appeared considerably more complex and different from any of the mechanisms presented previously. As a consequence of the evident complexity of the mechanism, it was not really possible to advance a complete mechanism of the reaction nor determine the real cause of the increase in the strength of the final network. The mechanism involved the phenate ion of the resin to apparently give a carbonyl or carboxyl group attached to the aromatic ring. Either directly or by subsequent rapid rearrangement after the initial attack, these C═O groups were found on sites different from the ortho position. The appearance gathered from NMR shift calculation indicated preferential positioning or repositioning to the para site and, surprisingly, to the meta sites of the phenolic ring. The shifts of these C═O groups correspond to those of an anhydride and to no other intermediate structures previously thought of. Anhydride-like bridges were clearly shown by MALDI-TOF MS to contribute to oligomer structures in which linkages between phenol rings were mixed methylene bridges and anhydride bridges. These structures appeared to be temporary, possibly due to the instability of the anhydride bridges; hence, they were in small proportions at any given moment of the reaction. MALDI-TOF analysis clearly indicated that these structures were at some moment an integral part of the structure of the liquid resin and that they existed parallel to the methylene bridges pertaining to a normal PF resin structure. Previous spectra showed that similar but not identical intermediates were present also in organic and inorganic catalyzed PF resins.
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Key words: MALDI; NMR; resins; PF; mechanisms; acceleration; Kolbe-Schmitt

INTRODUCTION

Phenol–formaldehyde (PF) resins are among the most used thermosetting resins and have been used successfully for many years as exterior wood adhesives for exterior wood products.[1] Their characteristic use is mainly as binders for weatherproof and waterproof wood panels. Although extensively used, PF resins cure more slowly in a hot wood panel press than aminoplastic resins.[2,3] Recently, several different systems for the acceleration of PF resins curing have been developed.[3–9] Among these, an interesting one is the use of esters accelerators for alkaline PF resins. Although no doubt exists on the strong cure acceleration effect of esters, the mechanisms by which these cause such an acceleration has been cause of controversy during the last 10 years. To better appreciate why this is so, what different theories have been advanced, and what ground they have to stand on, it is necessary to explain in more depth the background of this subject.

BACKGROUND

The discovery of the ester acceleration of the curing of PF resin goes back to 1957.[10–12] The industrial application of such a discovery, exclusively for foundry core binders, was, however, only pioneered starting in the early 1970s.[13,14]

It must be pointed out that this PF hardening technology referred to the use of a very high proportion of ester on the phenolic resin. To illustrate the case, in the relevant literature, methyl formate and other esters have been used in proportions of up to 50:50 ester/PF resin solid.[15] This point must be made clear, first, to put some of the findings, which are discussed later, in perspective and, second, because claims that such a technology was used industrially for wood applications are incorrect.[12]

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Routine references in patents to wood and other applications were indeed mentioned at the same time as to foundry core binders[16–18]. However, this technology was never used at that time for wood adhesive application, as the proportions of esters needed were uneconomically high for such an application. The technology also presented considerable technical drawbacks for wood application, such as a resin dilution too excessive to yield any good wood panel adhesive performance. Furthermore, some of the favorite esters for foundry core applications,[15] such as methyl and ethyl formate, and most others have been proven to be unsuitable for wood adhesive applications,[19–22] simply because the gels obtained were far too soft and not strong enough.

This remained the situation until 1994, with the process virtually unknown outside foundry core resins. In 1993 and 1994, a series of publications on the use of esters as accelerators of PF resin wood adhesives appeared.[5,6,19–23] In these, PF resins for wood panel products were accelerated to industrially meaningful hardening times by the use of esters. Some fundamental differences from the previous technology were introduced to achieve this result. These follow:

1. Only two organic esters were found to satisfy the requirements for wood panel adhesive application, namely, glycerol triacetate (triacetin) and propylene carbonate (PC). The others listed in previous literature[15] were mostly of no use in this field. Furthermore, PC had considerable disadvantages, such as yielding too short a pot-life for the resin to be used; hence, it was not favored and was dropped.
2. Most importantly, the proportion of ester on PF resin solids was much lower than in the original technology, with only a maximum of 17% triacetin ester added to the resin.[22] This was still too high, but the idea was then too use a very low condensation PF resin (and, hence, much cheaper) coupled with the ester to obtain good results. In this, the resin succeeded well. Later work[3] indicated that the amount of ester needed for wood panel adhesives with standard PF resins for wood was as low as 2.5 wt % ester in PF resin solids. This is, then, a rather different technology from that used in foundry core binders, with up to 50% esters.

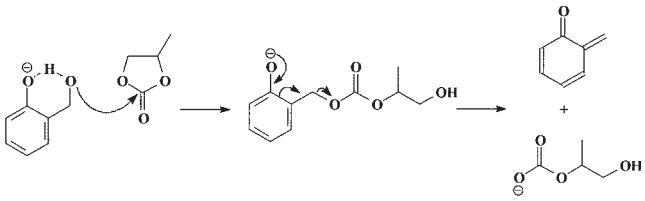
No mechanism was ever published or hinted at up to that time on the old ester acceleration technology by any of the initial authors, a lapse that is not unusual in industrial research.

PC also presents, in relation to other esters, an anomalous behavior as an accelerator.[19–22] Notwithstanding this, it was retained in the study undertaken on the ester acceleration mechanism. This was done with the belief that because it imparts very fast resin hardening, a more complete reaction, clearer results could be gathered. The mechanism proved particularly troublesome to determine. Reactions of PC with PF resins and with hydroxybenzyl alcohol model compounds did not yield any resin, on analysis, different from that obtained without ester acceleration.[20] This needs to be stated to put into perspective that the later research by other authors who found the same did not add anything new to the subject but just took the easy way out.

Thus, all that could be gathered was that the resin was faster and much stronger. However, the reaction of PC with a very fast reacting phenol, namely, resorcinol, in the absence of PC and only in this fortuitous case under standard PF resol conditions, indicated that something different might well occur. The published ^{13}C-NMR spectrum of the reaction of resorcinol and PC showed a secondary pattern of a reaction product.[20,22] The NMR shifts of this reaction product were identified in later work as being those of an aromatic ester attached to the aromatic ring of the phenol or even more closely to an interphenols anhydride.[24] This was indeed the first indication that the ester became, probably just temporarily, part of the structure of the resin.

A mechanism was then proposed on the basis of an alternative crosslinking reaction yielding temporary ketone bridges[20] and hence increasing the functionality of the aromatic ring and eventually the labile temporary organic anhydride bridges.[24] These were supposed to supplement the standard PF methylene bridge crosslinking. In short, the temporary participation in the network formation of the ester or one of the compounds derived from it was proposed. This proposal was based on the NMR-observed presence of –C═O groups on (1) the aromatic ring in the case of the resorcinol experiment described previously;[20,24] (2) the considerable increase in strength of the hardened PF network observed, which indicated a higher level of crosslinking;[24] and (3) finally, the similarity of the reaction of PC, after both PC and CO_2 gave hydrogen carbonate ions in water, with the Kolbe–Schmitt reaction for the preparation of salycilic acid from phenol and CO_2.[20,25] As faulty as this mechanism might have been, there was at least some tangible, positive proof according to the three previous points that something different may occur in PF resin hardening.

Subsequent work was done by Higuchi et al.[26] on PF resin acceleration caused by PC, Na, and K inorganic carbonates and a number of other materials, such as formamide. They did not find any difference between the structure of the PF resin with and without the accelerators, which was exactly what we had found.[20] Their experience with inorganic carbonates led them to conclude that the effect was only a catalytic effect and that there was no difference among the



Scheme 1

actions of PC, the inorganic Na and K carbonates, and formamide (and other amides). They proposed a catalytic mechanism of action for the carbonate ion (and exactly the same for the amides) as shown in Scheme 1 for PC.[26,27]

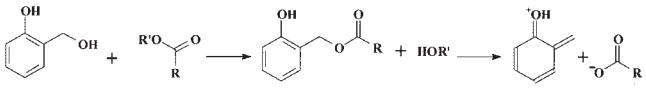
It must be clearly pointed out that no proof whatsoever has ever been offered to support this mechanism. It is pure assumption. It was only advanced as the researchers involved could not find any difference in the structure of the PF resins with the different additives. Furthermore, it is a convenient mechanism to propose because it is not demonstrable. The subsequent work of Pizzi et al.[24] pointed out the incorrectness of these claims by proving, instead, (1) that PC not only accelerates the resin but increases considerably the strength of the hardened resin network, (2) the inorganic carbonates only accelerate resin curing but do not increase its hardened network strength at all, and (3) the mechanism of resin acceleration by formamide and other amides is totally different from that of the esters and of the carbonates. It became evident too and was clearly argued[24] that in the case of PC, two mechanisms of acceleration appear to be at play. The first mechanism is of pure acceleration due to the carbonate ion, whatever its origin: inorganic or organic. For this the mechanism of Higuchi and coworkers might well be still acceptable, although there is no proof to support it (there are other mechanisms proposed on this, equally undemonstrated[24]). The second mechanism occurs only for PC, and it is proper to esters. On this basis, the mechanism proposed by Higuchi's group, undemonstrated and indemonstrable, proved wrong for the amides and clearly indicated that such a doubtful hypothesis could be considered, at best, only for the mechanism of acceleration proper to all inorganic carbonates. For the second mechanism, proper to the esters, Higuchi's proposal has no significance.

Further work on this controversial mechanism was then presented by Riedl's research group in a series of three articles.[28–30] These compared the relative effects of PC and the inorganic Na and K carbonates on PF resin curing. In the first of these articles[28] in 1999, this research group, with differential scanning calorimetry, also showed that carbonates had a cure acceleration effect on PF alkaline resols. However, they found that the reaction of PC with PF resins followed autocatalytic behavior, whereas Na and K inorganic carbonates did not but rather followed *n*th-order reaction kinetics. First, this was confirmed by a different technique, the difference in behavior between PC and inorganic carbonates. Second, it indicated again that PC might well be involved in the reactivity of the PF resin, leading to increasing functionality,[28] and that this is definitely not the case for the inorganic carbonates. This again negated the mechanism originally proposed by Higuchi for PC. Work that followed,[29] on liquid-phase ^{13}C-NMR results, showed again that the three carbonates acted differently. Furthermore, for liquid-phase ^{13}C-NMR of the PC-accelerated PF resin, a new peak appeared at 150 ppm. This was interpreted[29] as possibly due to an acyl group linked to the PF resin or to one of the intermediate carbonyl compounds proposed earlier;[20] this seemed to be involved in the increasing reactivity of the phenolic rings.

A further publication from another research group appeared in 2002[31] and tried to reconcile all the different data mentioned previously. This article returned to the use of a simple model compound, hydroxymethyl phenols such as saligenin, as already used for experiments earlier,[5,20] and as with the earlier groups, with this approach, little difference was found between the reaction products of hydroxybenzyl alcohols with and without a PC accelerator. Some differences were found, however.

First, by rate-limiting experiments and calculation, they found that the PC cure accelerator did not act as a true catalyst, as suggested in the mechanism proposed by Higuchi's group, but was instead consumed during the reaction. This confirmed the results of Riedl's group, who found that PC did not seem to act as a standard catalyst because its performance was concentration- and temperature-dependent.[28] It also confirmed the existence of two different mechanisms for PC acceleration, as proposed in 1997 by Pizzi et al.[24]

Second, they found by high pressure liquid chromatography (HPLC) that the relative proportions of the individual reaction products obtained varied, which suggested that the cure accelerator was not incorporated into the reaction products, as suggested by Pizzi and coworkers.[5,20] Permanent incorporation of the PC into the final network is, then, apparently, not possible, but temporary incorporation, as later proposed by Pizzi et al.,[24] is still possible. However, in this regard, Conner et al.[31] also noted that the ^{13}C-NMR data of PF resins cured in the presence of PC contained peaks that might be interpreted as consistent with an incorporation mechanism,[5,20,24] as shown by Riedl and coworkers.[28–30] Their own NMR analysis of the model compounds reaction products, however, did not show anything different from the standard PF oligomers, as in earlier investigations. This could be also explained



Scheme 2

by the extraction with chloroform of the reaction products from the water solution. All the standard PF oligomers would migrate into the more polar chloroform, but a less polar compound, such as the fleeting esters or acyls or anhydride structures observed by Pizzi and Riedl, would migrate much less or not at all. Only the chloroform fractions were analyzed. This might well have played a role in the type of reaction products found.

Conner advanced the hypothesis that the acceleration proceeded through a transient transesterification mechanism of the PF hydroxybenzyl group with the acid residue of the ester. He did not present any proof for this. Such a mechanism was not demonstrated, and again, it is a very difficult one, almost impossible, to demonstrate.

The concept of a transesterification mechanism is older than the article from Conner. Detlefsen[12,32] advanced this mechanism in 1999 from even older work (from 1993)[33] but in a more detailed manner. In this mechanism, the ester is used to increase the reactivity of the hydroxymethyl group of the PF resol. Two steps occur. First, transesterification occurs, with the acyl group of the ester being transferred to the hydroxymethyl group of the PF resol. The hydroxymethyl group is converted to a carboxylate. The second step entails the first-order decomposition of the new ester so formed to a quinone methide and a carboxylate, with the carboxylate being a more stable leaving group than the hydroxyl (Scheme 2).

This mechanism is definitely more acceptable and has the advantage of perhaps explaining some of the carbonyl groups observed by NMR by Pizzi and especially by Riedl. Detlefsen proposed this mechanism with no proof for it other than the indirect proof of the unpublished work of Lemon[12] and the unpublished work of Murray,[33] which showed that quinone methides form from *o*-hydroxymethyl and not *p*-hydroxymethyl groups in the presence of esters. However, the intermediate species were not isolated, there was no proof for the mechanism, and it would be again a difficult one to prove. It is clear enough from Detlefsen articles that this mechanism was only an intelligent proposal.

From a theoretical point of view, the main criticism that can be advanced for this mechanism is that transesterification is not really likely to any great extent when the alcohol, here, the hydroxybenzyl group of a PF resin, is far more acid than the alcohol in the starting esters. Furthermore, such a mechanism does not allow differentiation among the accelerating effect of inorganic Na and K carbonates and organic carbonates and esters. Thus, it might address some aspects of the acceleration but not the whole story. Some doubts, then, must unfortunately be expressed on the feasibility of such a mechanism.

Both Conner et al.[31] and Park and Riedl[29] found that the presence of PC alters the relative proportions of reacting ortho and para sites, with the accelerator dramatically increasing the reactions of ortho sites with methylol groups. The involvement of the phenolic —OH in the mechanism appears then certain, which vindicates the similarities invoked earlier to a Kolbe–Schmitt reaction,[20] where the phenolic hydroxyl involvement is fundamental in yielding almost exclusively ortho attack. The final conclusion of Conner was that the types and amount of methylene crosslinks differ when PC is present versus when it is not. Namely, the crosslink density per unit volume would be different, as suggested by ^{13}C-NMR relaxation time studies.[29] A more recent publication in 2004 by Higuchi et al.,[27] again with model compounds, confirmed this concept of the different distribution of ortho–para to para–para linkages. The belated hypothesis in this same article of a double mechanism for PC acceleration was rather late in recognizing this fact in relation to when this concept was first advanced.[24] In short, the pure catalysis mechanism proposed by Higuchi was proven to have no significance, as no proof was presented for it and none could be brought for it, and it should be considered as definitely put to rest. As mentioned previously, the only possibility for it to be valid might be for the purely catalytic action of inorganic carbonates.

There is an important difference between all of the works presented up to this point. Conner used extremely high amounts of ester in resins solids, namely, between 22 and 32 wt %, according to the old original technology. He also used some esters that could not be used for wood adhesives and a formaldehyde/phenol molar ratio of 1, which is very low and very far from that used for industrial PF resins. Pizzi (with the exception of the resorcinol reaction) and Riedl instead used small amounts of accelerators, between 2.5 and 7.5% and 4%, respectively, and molar ratios of 1.8 and 2.2, respectively, which were consistent with industrial PF molar ratios. These differences might perhaps be determinant in the production of different results. Higuchi instead never reported the amounts of PC in resin solids; hence, his results up to this point are really impossible to check.

Now that the general background has been exposed, one last remark is essential: perhaps the choice of PC as the test ester was a mistake, as it led to several problems. First, inorganic Na and K carbonates are and have been used for a considerable time as PF resin accelerators. This has led to the suspicion that the ester mechanism has to be the same. Second, the existence

of carbonic acid led to the thought that the reaction could be nothing other than a CO_2 Kolbe–Schmitt reaction or the equivalent. Third, PC is not used or usable in industrial practice for wood adhesives because of a number of serious technical problems. The only one advisable accelerator for wood application is glycerol triacetate (triacetin),[22] a different ester. With the exception of Conner, who also used ethyl formate (also unsuitable for wood[19]) on top of PC and triacetin, but at extremely high percentages, all the studies on the mechanism were done with PC. This has slanted the field but has been so for a number of mistaken reasons: for example, (1) because it was the faster accelerator, and hence, a more complete reaction and better insight into the mechanism was sought[5,20] and (2) because the mechanism was thought to be the same as the inorganic carbonates with which some groups were already familiar.[26] This has probably been a mistake for two reasons. First, PC has an anomalous behavior as an accelerator,[20] possibly due to the fact that carbonic acid is a diprotic rather than a monoprotic acid such as that used for the common esters.[20] Second, carbonic acid is volatile, which enhances the now quite apparent impermanence of the accelerating intermediates and which renders it particularly difficult to find or isolate any intermediate.

In this study, we dealt with revisiting the accelerating mechanism of PF resol resins for wood by esters, with the appropriate ester for this use, namely, triacetin, and in the small proportions used for this application.

EXPERIMENTAL

The PF resin, with a total molar ratio of formaldehyde/phenol (F/P) of 1.81, was prepared as follows.[6] To 10.2 g of phenol were added 0.8 g of methanol, 6 g of a 98% paraformadehyde fine powder, and 3.4 g of water. The temperature was increased from 40 to 90°C under continuous mechanical stirring over a period of 30 min. Three amounts of 0.17 g each of a 33% NaOH water solution were added to the reaction mixture over this period. When the temperature reached 90°C, the pH was adjusted to 11 with the 33% NaOH water solution. Triacetin (0.5 wt % of phenol) was then added, and the mix was reacted for 60 min, with this time starting when the temperature reached 90°C. Resins with 1 and 1.5% triacetin were also used, and these were reacted for 30 min. The resin was then cooled and stored. A resin of very high viscosity at ambient temperature was obtained. Notwithstanding the high viscosity, the resin remained stable for a few days. The resin preparation was repeated several times, and all of the samples were subjected to NMR to test the consistency of what is reported here.

The resin was tested by gel permeation chromatography (GPC), ^{13}C-NMR, and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry (MS).

GPC

A Waters 515 HPLC pump and GPC system was used, and the PF resins were analyzed through a Styragel HR1 column [for determination of weight-average molecular weights (M_w's) between 100 and 5000] at an elution rate of 1 mL/min after the poly(ethylene glycol) calibration of the column. The poly(ethylene glycol) samples used for calibration had M_w's of 200, 300, 400, 600, 1000, 2000, 3400, 8000, and 10,000. Each resin sample was tested without filtration to observe the colloidal aggregates obtained. A Waters 410 refractometer was used as the detector.

MALDI-TOF MS

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

MALDI-TOF sample preparation

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

NMR

The liquid ^{13}C-NMR spectrum of the PF resin used were obtained on a Brüker MSL 300 Fourier transform NMR spectrometer (Brüker France, Wissembourg, France). Chemical shifts were calculated relative to $(CH_3)_3Si(CH_2)_3SO_3Na$ dissolved in D_2O for NMR shift control.[34] The spectra were done at 62.90 MHz for a number of transients of approximately 1000. All the spectra were run with a relaxation delay of 5 s, and chemical shifts were accurate to 1 ppm.

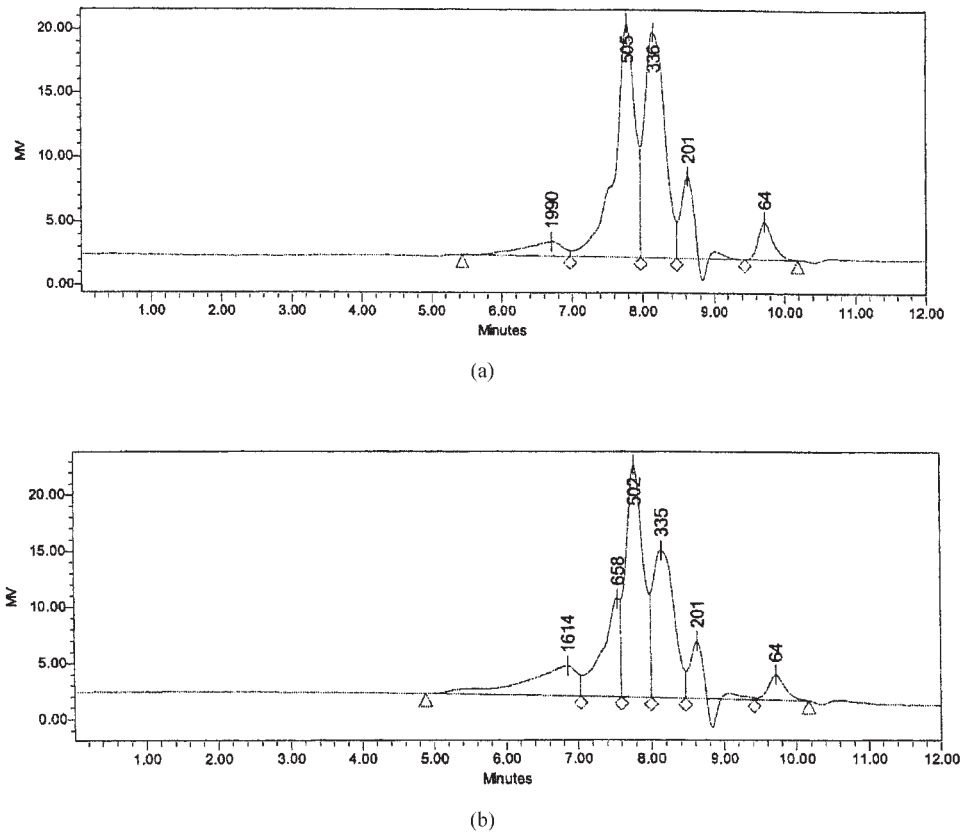


Figure 1 Gel permeation chromatogram of a control PF resin (a) after 25 min of reacting at pH 11 and 90°C and (b) after 40 min of reacting at pH 11 and 90°C. No accelerators were added.

RESULTS AND DISCUSSION

In Figure 1(a,b) and Figure 2(a,b) are shown the GPC chromatograms of the distribution of molecular masses obtained with a simple F/P molar ratio of 1.8. Figure 1(a,b) refers to the PF resin after 25 min of reaction and 40 min of reaction, respectively. The number-average molecular weights (M_n's) of the different peaks observed were 64, 201, 335, 502–505, 658, and a very small proportion of higher molar masses [e.g., 1990 in Fig. 1(a) and 1614 in Fig. 1(b)].

The peak at M_n = 64 included complex-free formaldehyde species such hemiformals of the type CH_3OCH_2OH (M_n = 62) obtained by the reaction of free PC with the methanol initially added to the reaction mixture. The peak at M_n = 201 was centered on a nonhydroxymethylated PF dimer of the type $HOC_6H_4—CH_2—C_6H_4OH$ (M_n = 200). The average peak of M_n = 332 was the first presenting PF oligomers, such as hydroxymethylated and nonhydroxymethylated PF dimers and trimers such as $HOC_6H_2(—CH_2OH)_2—CH_2—C_6H_2(—OH)(—CH_2OH)_2$ (M_n = 322), $HOC_6H_4—CH_2—C_6H_4(—OH)—CH_2—C_6H_4OH$($M_n$ = 310), and $HOC_6H_3(—CH_2OH)—CH_2—C_6H_4(—OH)—CH_2—C_6H_4OH$ (M_n = 340). The average peak of M_n = 505 represented tetramers such as $HOC_6H_4—CH_2—[—C_6H_2(—OH)(—CH_2OH)—CH_2—]_2—C_6H_3(—CH_2OH)OH$ (M_n = 502), pentamers such as $HOC_6H_4—CH_2—[C_6H_4(—OH)—CH_2]_3—C_6H_4OH$ (M_n = 518), and some higher molecular mass species. A shoulder at M_n = 658 progressively appeared and increased in size as the reaction progressed, indicating that higher molecular mass oligomers were formed. A M_n of 655 corresponded to a momomethylolated hexamer according to the formula $HOC_6H_4—CH_2—[C_6H_4(—OH)—CH_2]_4—C_6H_4(—CH_2OH)OH$ (M_n = 655).

The higher molecular mass peaks did not correspond to compounds of masses as high as those indicated by the numerical values obtained (M_n's = 1990, 1614, and higher). As melamine resins,[35,36] higher oligomers of PF resins are known to form colloidal agregates[37,38] but less readily. The GPC analysis was intentionally done without filtration of the samples to observe if these aggregates did form. The higher molecular mass peaks in Figure 1(a,b) could then have just been these colloidal aggregates, formed by oligomers of slightly higher molecular mass than those of the last M_n = 658 peak. MALDI-TOF MS (discussed later) showed that this was indeed the case and that the longest oligomers present were no more than 10–12 repeating units long and were mainly 6–8 repeating units long.

Figure 2(a,b) shows the GPC of the same PF resin (F/P = 1.8) condensed after 30 and 60 min reaction

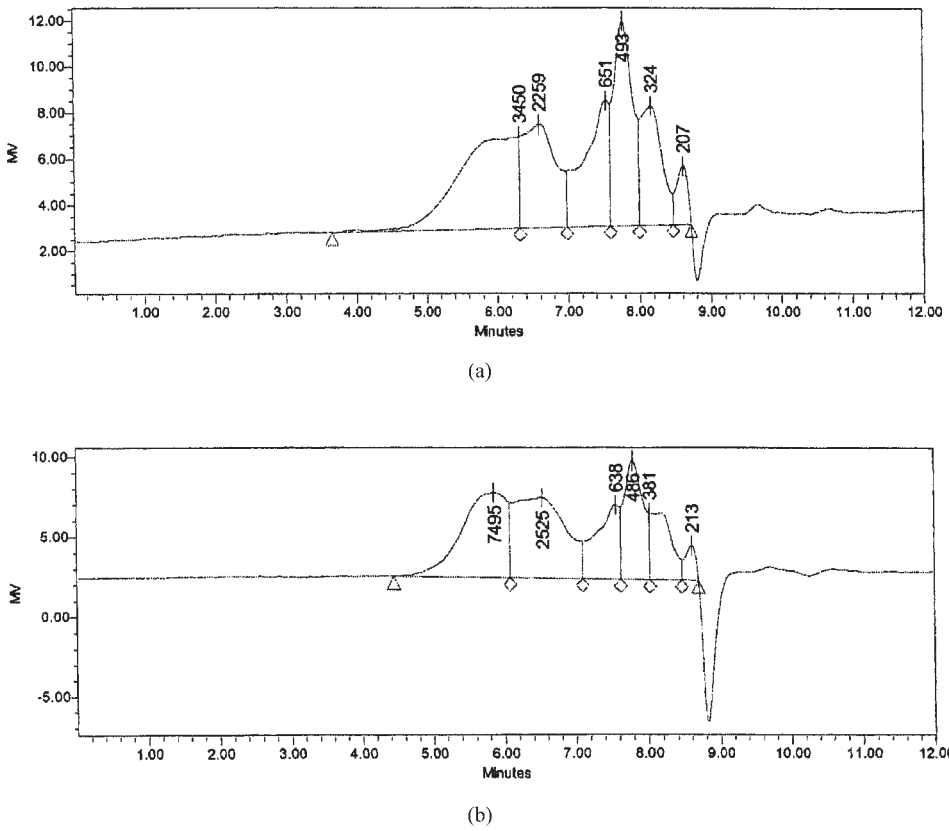
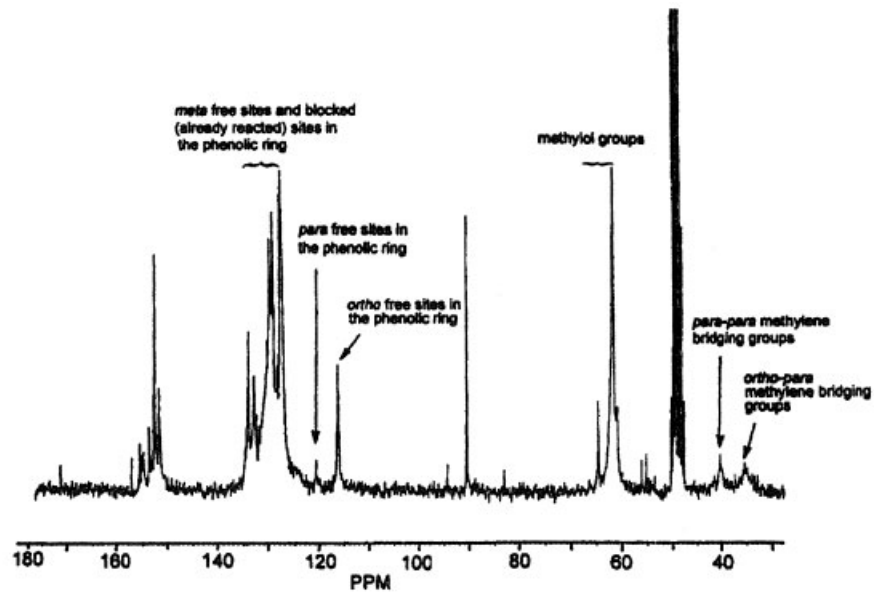


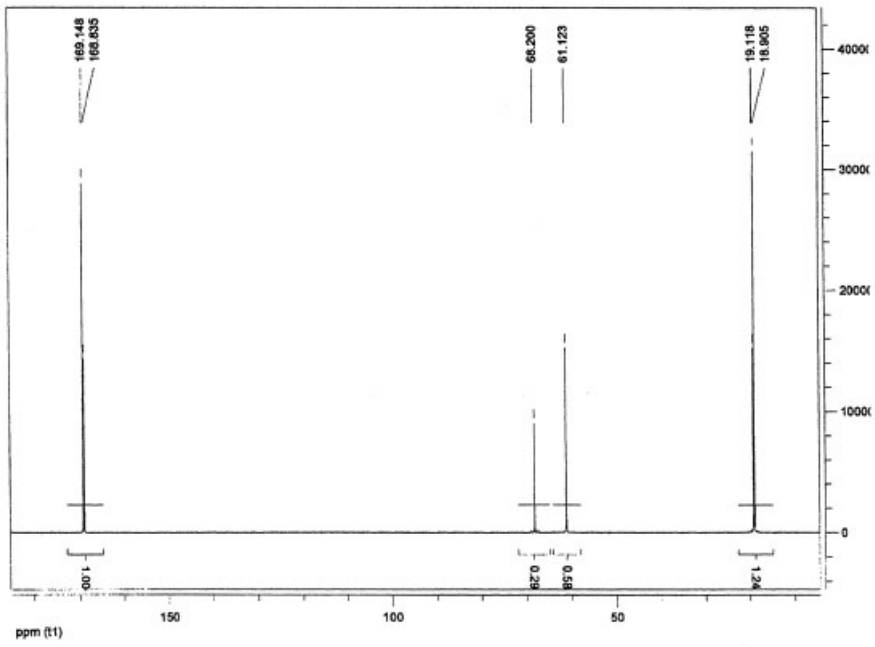
Figure 2 Gel permeation chromatogram of two triacetin-accelerated PF resins with (a) 1.5% triacetin after 30 min of reacting at pH 11 and 90°C and (b) 0.5% triacetin after 60 min of reacting at pH 11 and 90°C.

when, respectively, 1.5 and 0.5% triacetin on PF resin solids were added during resin preparation. The lower molecular mass oligomer peaks observed were approximately in the same range of M_n indicated for the ones observed in Figure 1(a,b). The exception was the M_n = 64 peak pertaining to free formaldehyde forms, which disappeared. This already indicated that addition of the ester advanced the reaction to such a point that no free formaldehyde was present. The most evident difference, however, between the GPC chromatograms in Figure 2(a,b) and those in Figure 1(a,b) was the considerable increase in the very high molecular mass peaks. In Figure 2(a,b) are shown mass values of 2259 and 3450 [Fig. 2(a)] and 2525 and 7495 [Fig. 2(b)]. As these compounds were still in solution enough to be detected, they were not part of a gel (which could not be detected). As explained previously, they were likely to be part of colloidal aggregation of higher PF oligomers. This was unusual for an accelerator that was supposed to gel/harden the resin very rapidly.[20] It indicated that the severe limitation in the amount of ester accelerator limited the PF resin advance toward gelation and stopped it in an intermediate state. This was of interest: the ester acted, and the resin was stopped in its progress toward gelation and was rather advanced but still soluble and presented an evident colloidal state. This meant that there was a chance that (1) an intermediate of the reaction between the ester and the resin oligomers could be observed in this reaction-suspended resin state and (2) the existence of the colloidal state of the resin may have facilitated reactions that did not occur or were less likely to occur in solution, like when model compounds are used. Cases in which the colloidal state clearly changed the course of a phenolic resin polycondensation reaction have already been reported.[38,39]

Figure 3(a–e) shows the quantitative ^{13}C-NMR spectra (the integral values are indicated underneath the peaks) of a standard PF resin without any accelerator, the triacetin itself, and the triacetin-accelerated PF resin of Figure 2(a) and details of the 140–180, 110–165, and 20–70 ppm regions of the latter case. The spectrum of the triacetin-accelerated PF resin [Fig. 3(c)] appeared as a normal PF resin spectrum with the immediately evident exception of the four peaks between 160 and 162 ppm. Furthermore, there was an absence of any quinone peaks. In ^{13}C-NMR, the C═O of substituted and unsubstituted quinones and quinone methides showed up between 180.4 and 219 ppm.[40] There was only a very small signal at 180.063, and this could be ascribed to traces of any impurity so



(a)

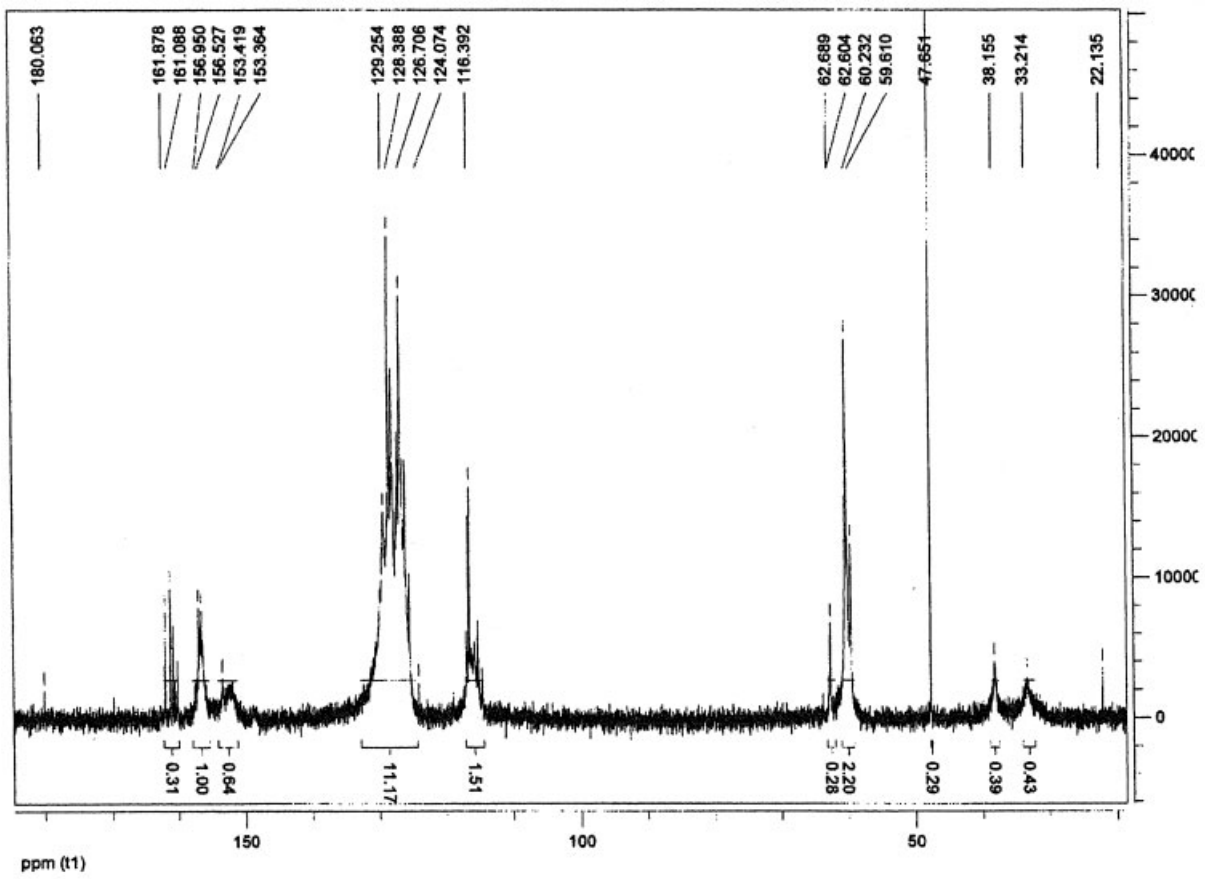


(b)

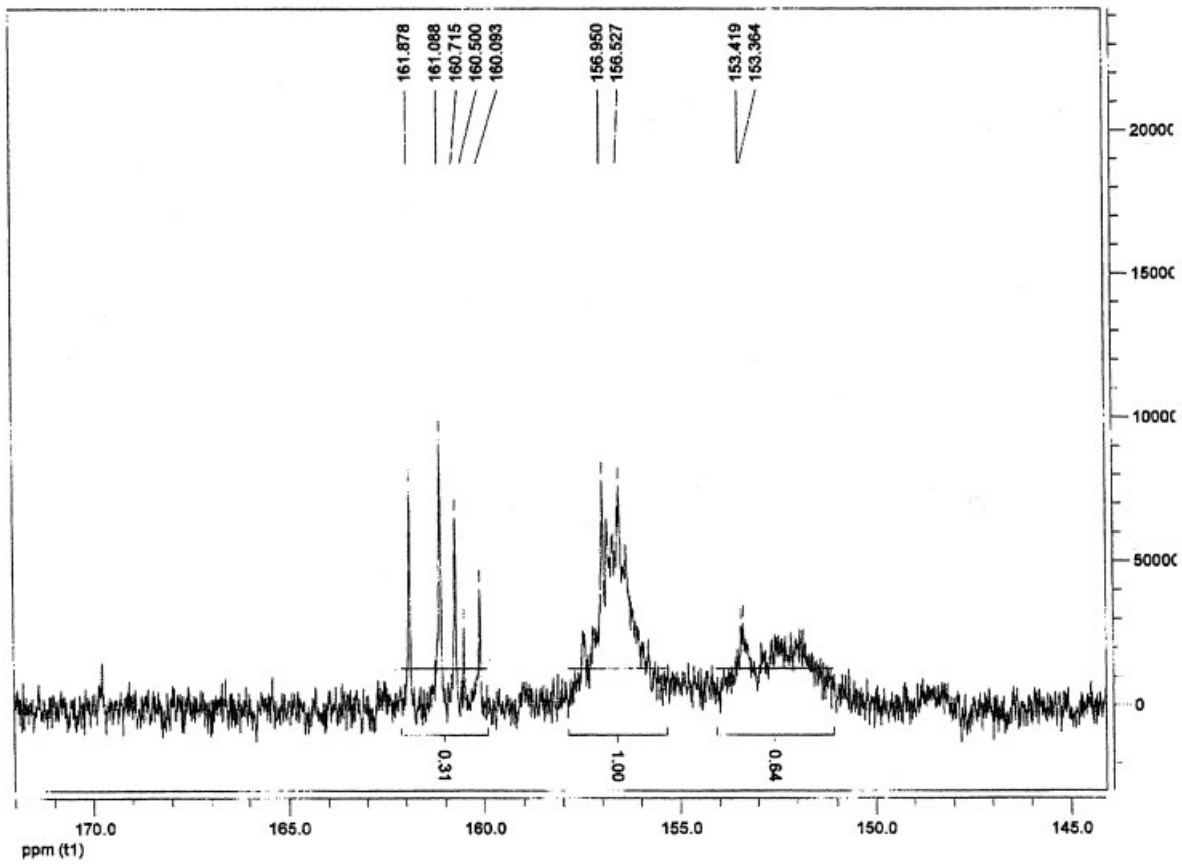
Figure 3 ^{13}C-NMR spectra of (a) a control PF resin prepared without the addition of an accelerator, (b) glycerol triacetate (triacetin) alone, (c) a PF resin accelerated with 1% triacetin during resin preparation, and (d) the detailed 140–180 ppm range of the triacetin-accelerated PF resin. Spectra (b), (c), and (d) are quantitative, and the relative integral values are shown in the parentheses underneath the main bands.

insignificant it was. Even if it was a quinone methide (and it was just out of the correct ppm range), this would be quite normal due to the oxidation that PF resins undergo on preparation.

First of all, there was no 120-ppm peak, which indicated that there were no para-free sites. All the para sites reacted. There were only free ortho sites. This might appear unusual in a resin where ortho substitution has been considered by all the researchers involved to be vastly favored by the accelerator. In reality, as the amount of ortho sites was double the para sites, a number of ortho sites may very well have still been free. In this respect, the absence of the free para sites signal could be taken to mean that the resin



(c)



(d)

Figure 3 (*Continued*)

was rather advanced, which was the case. This was supported by the absence of any hemiformal signals around 90–95 ppm, signals instead noticed by Park and Riedl[29] and in other standard PF resins spectra.[41] This means the resin was very advanced, as befits ester-induced acceleration.

The methylene signals were noted at 33.2 and 38.1 ppm. The 33.2-ppm signal could have been due to the rare ortho–ortho methylene bridge (theoretical 33.1 ppm), which was also found for solid-phase cross-polarization/magic-angle spinning ^{13}C-NMR in PC-accelerated PFs by Park and Riedl.[29] This might well have been so, but we do not think this was the case here because there appeared to be in this region of the spectrum a shift of slightly less than 2 ppm. The 38.2-ppm peak was definitely the signal of para–para methylene bridges, which generally appear at 40 ppm. Thus, the 33.2-ppm peak was, in reality, the signal of the ortho–para methylene bridge usually appearing at 35 ppm.

Very small signals of triacetin are noticeable in Figure 3(c) as compared to Figure 3(b). Thus, traces of triacetin were still present, as observed by the very small peak of –C═O at 168–169 ppm [Fig. 3(c)]. This could not have been acetic acid, as the signal would have been at 177 and 182.6 ppm for the nonionized and ionized forms, respectively, nor could it have been formic acid obtained from the formaldehyde by a Cannizzaro reaction, as these signals would have been at 166.3 and 171.3 ppm, respectively.[40] The residual —CH_3 of triacetin was noted by the very small peak at 22.1 ppm, although this appeared slightly off in relation to its shift in unreacted triacetin (19.1 ppm).

The real difference, however, were the four peaks between 160 and 162 ppm in Figure 3(c,d). They did not appear in a standard PF resin without triacetin [Fig. 3(a)] and were definitely a reaction product very possibly belonging to the intermediate we were looking for to explain the mechanism. They did not belong to triacetin because the signals of this appeared elsewhere [see Fig. 3(b); –C═O of triacetin appeared at 168–169 ppm]. To try to explain these four signals, in Table I, we report the shifts that the intermediates proposed by the different research groups would have, if they existed. In the series of structures listed in Table I, we consider the different intermediates as possible intermediates, included the quinone methide of Detlefsen's mechanism, and their cyclic precursors.[12] The ester obtained by transesterification proposed by Detlefsen[12] and Conner,[31] the transient structures of the catalyzed intermediate proposed by Higuchi and coworkers,[26,27] the hemiformal structure considered by Park Riedl,[29] the acyl structures proposed by Park and Riedl[29] and Pizzi and coworkers,[20,24] the esters and the anhydride structures proposed by Pizzi et al.,[24] and a number of other structures that one might think could exist, are listed.[24] The shifts of all these structures were calculated by ChemWindow.[42] A comparison of the results shown in Table I indicated that none of the shifts of the C═O of the compounds proposed by Detlefsen, Conner, Higuchi, Riedl, and Pizzi appeared in the spectrum. Their shifts had values too high (between 168 and 201 ppm) in relation to the 160–162 ppm peaks noticed, and furthermore, the shifts of the C═O of the proposed compounds were not present in the spectrum shown in Figure 3(c,d). This means that none of the compounds and the mechanisms proposed could be the correct intermediate of reaction and the correct mechanism, respectively. The exceptions were the *m,m* and *p,p* anhydride bridges proposed later by Pizzi et al.,[24] which corresponded rather closely to the shifts at 160–162 ppm shown in Figure 3(c,d). These anhydrides presented shifts between 162.15 and 162.30 in unsubstituted phenolic rings and could go as low as 159.9 ppm for the *p,p* case with a methylol substituents in ortho to the phenolic —OH. They were then very close to the experimental values of 161.88, 161.09, 160.7, and 160.1 and the very small peak at 160.4 ppm, especially if one considers that the precision of this quantitative spectrum was ±1 ppm. Both anhydrides appeared at first sight possible from the other carbon shifts. The *p,p* presented a C1 shift of 162.06 ppm that could explain one more peak in the 160–162 ppm range. However, the *p,p* isomer did not present the peaks at 156.9 and 156.5 ppm in Figure 3(d). The *m,m* isomer did instead, at 156.9 ppm. This did not mean that only the *m,m* isomer occurred. On the contrary, two of the shifts of the *m,m* isomer, those at 120.2 and 121.2 ppm, were clearly not in the spectrum. As attractive as the idea of a *m,m* bridge can be, it is evident that this may not have been there and that the idea could be discarded. However, the shifts at 120 and 121 ppm were those of the sites ortho and para to the phenolic —OH of the metasubstituted nuclei (Table I). Hence, these were the sites to which would be linked the normal methylene bridges and methylol groups in a PF resin. At least for the ortho site, this would alter the shifts from 120.2 to 129.9 ppm, which was present. A methylene/methylol-substituted, mixed *m,p* bridge would also give all the shifts noted even more closely, including the 156.9-ppm shift. The 156.9-ppm peak then was either just the shift of a hydroxyl carrying aromatic carbon of a substituted ring of the PF resin or the indication that a *m,m* or *m,p* anhydride bridge was also present. Thus, the indications from the NMR shifts observed were those of a standard PF resin, which also presented *p,p, m,m,* and *m,p* anhydride bridges somewhere in its structure.

Also, the methyl group of triacetin disappeared from the spectrum of the reaction product. The methyl group disappearance could be possibly explained by the peak at 47.7 ppm, indicating formation of methanol (with a theoretical shift at 49–49.5 ppm). How-

TABLE I
Calculated ^{13}C-NMR Shifts of the Structures of All of the Intermediates Advanced by Different Groups

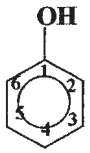
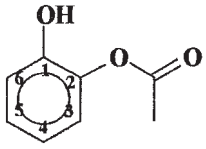
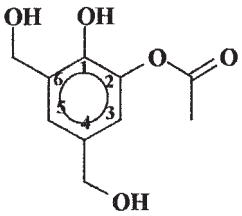
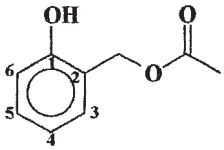
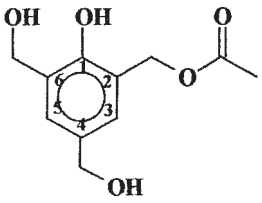
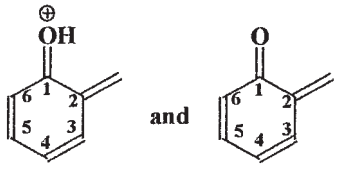
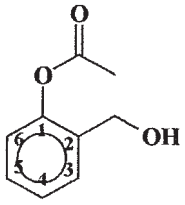
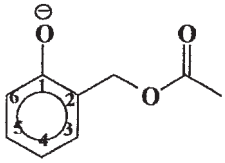
	C═O	—CH_3	—CH_2— bridge	C1	C2	C3	C4	C5	C6	—CH_2OH	—CH_2OH
	—	—	—	155.0	115.60	129.80	121.10	129.80	115.6	—	—
	—	—	—	150.80	127.40	125.86	131.70	125.86	127.40	60.50 (*o*)	60.35 (*p*)
2,4,6 trihydroxymethyl phenol											
Intermediates:[12,31,32] Detlefsen and Conner											
	168.45	20.71	—	149.3	138.9	123.0	122.53	122.04	115.88	—	—
	168.45	20.71	—	141.97	149.40	112.97	131.40	121.78	127.85	60.21	62.15
	170.74	20.68	62.30	155.30	127.85	128.64	121.25	128.37	115.60	—	—
	170.74	20.60	62.30	152.08	127.85	125.86	131.70	125.86	127.40	60.50	65.35
	182.65	—	—	182.65	140.30	127.43	127.40	140.80	—	—	—
	168.7	—	—	155.4	130.84	128.8	121.3	128.2	114.7	60.2	
Intermediates:[26,27] Higuchi's group											
	170.74	20.68	68.53	—	117.52	128.50	126.97				

TABLE I *Continued*

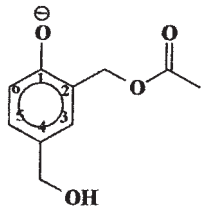
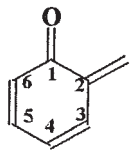
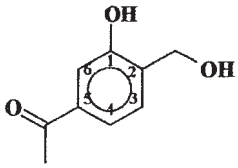
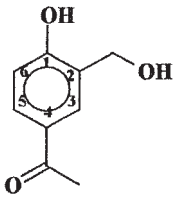
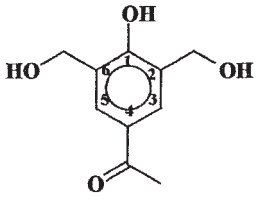
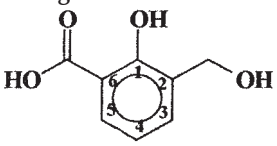
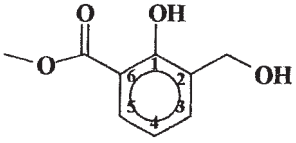
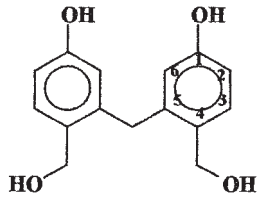
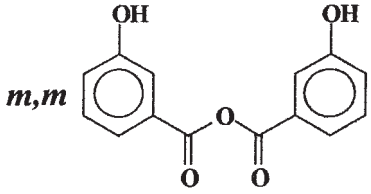
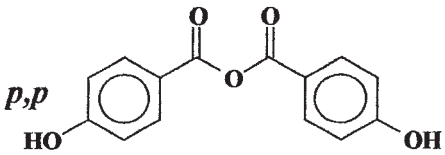
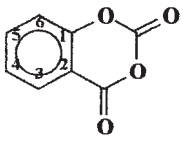
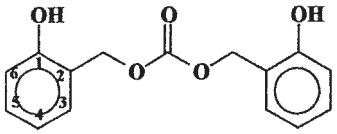
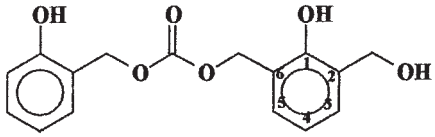
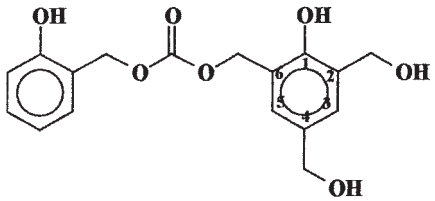
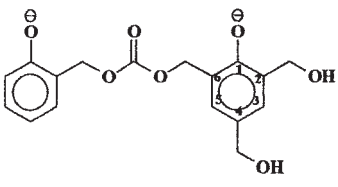
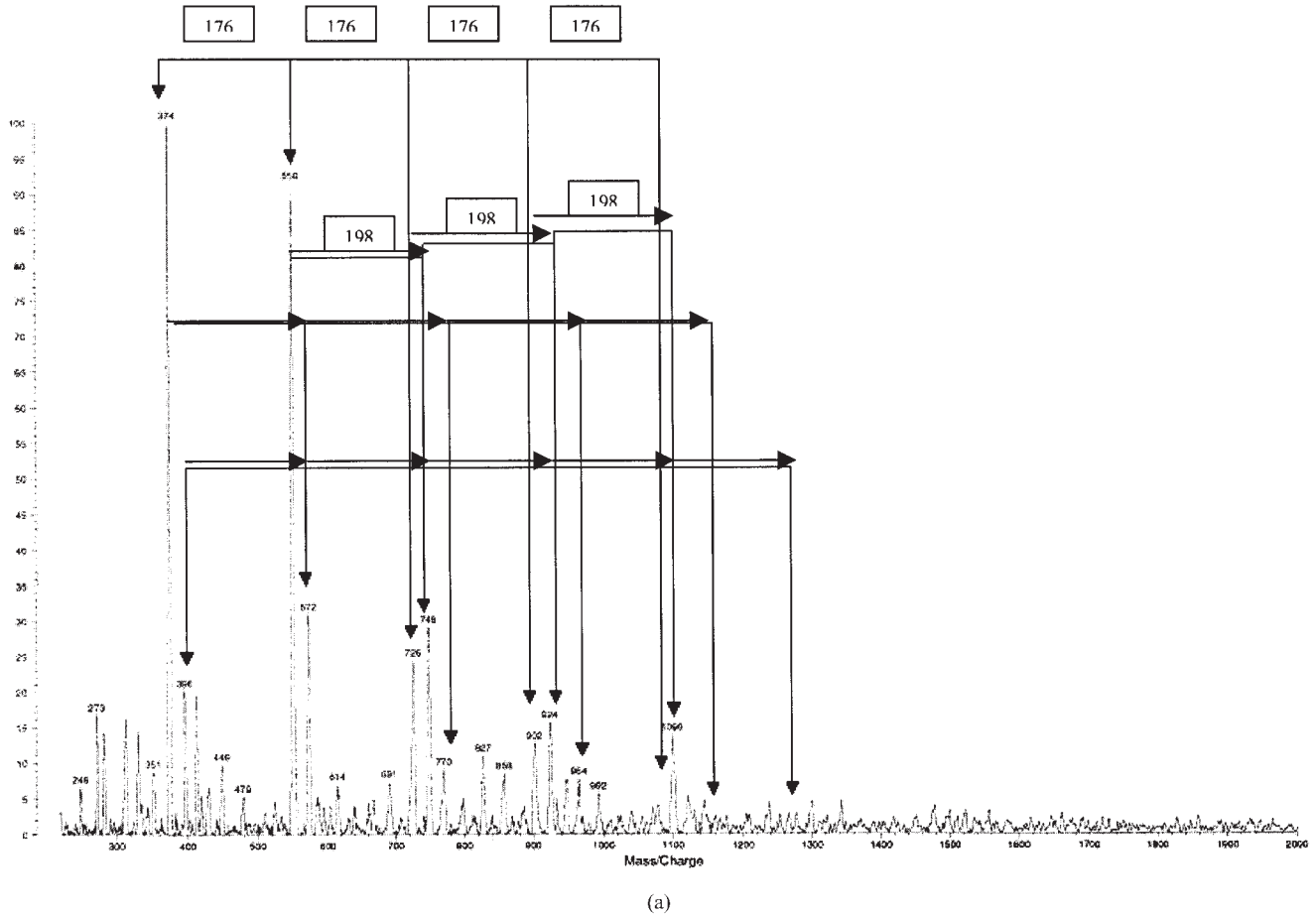
	C═O	—CH_3	—CH_2— bridge	C1	C2	C3	C4	C5	C6	—CH_2OH	—CH_2OH
	170.74	20.68	68.53	—	117.52	129.30	126.84			63.78	
	182.65	—	—	182.65	140.30	127.43	127.40	140.80	—	—	—
Acyl intermediates:[20,24,] Riedl and Pizzi											
	196.56	26.27	—	154.7	129.9	128.5	123.29	135.66	114.56	61.1	—
	196.87	26.27	—	160.3	127.85	130.3	123.90	130.13	116.70	60.21	—
Ortho isomer (of the previous)	201.20	28.29	—	160.97	127.85	133.83	121.81	128.75	122.79	60.21	—
	196.50	26.27	—	157.94	127.40	128.46	129.72	128.46	127.4	60.50	60.50
Acid on ring intermediates:[24] Pizzi											
											
Ortho acid	172.95	—	—	160.97	127.85	133.83	121.81	127.90	112.70	60.2	—
Meta acid	168.2	—	—	154.6	129.9	128.5	121.17	129.3	117.85	61.1	—
Para acid	168.02	—	—	160.3	127.85	129.16	122.8	130.58	116.17	60.21	—
											
Ortho ester	171.20	52.21	—	160.97	127.85	133.83	121.81	127.5	111.80	60.21	—
Para ester	166.81	52.21	—	160.30	127.85	129.16	121.34	131.08	116.17	60.21	—
Dimer intermediates: Meta substitution:[5,20,24] Pizzi											
o,o-Dyhydroxydiphenyl methane			30.90								
o,p-Dihydroxydiphenyl methane			34.65								
p,p-Dihydroxydiphenyl methane			39.80								
m,m-Dihydroxydiphenyl methane			40.58	157.80	115.48	138.88	120.79	129.46	114.05		
m,o-Dihydroxydiphenyl methane			35.45								

TABLE I *Continued*

	C═O	—CH_3	—CH_2— bridge	C1	C2	C3	C4	C5	C6	—CH_2OH	—CH_2OH
			38.05	154.3	113.1	128.5	129.96	136.37	115.17	62.4	62.4
m,m											
m,p											
			38.84 with methylol groups next to —CH_2—bridge								
m,o			37.33 with methylol groups next to —CH_2— bridge								
o,o			31.78 with methylol groups next to —CH_2— bridge								
o,p			35.45 with methylol groups next to —CH_2— bridge								
Temporary anhydride bridges:[24] Pizzi											
	162.15	—	—	156.9	120.2	129.9	121.2	131.2	116.6		
m,m											
	162.3	—	—	162.06	115.6	131.9	123.0	131.9	115.6		
p,p											
with a CH_2 ortho to —OH	159.9										
o,o	166.7										
	166.9/152.6			157.8	116.4	130.7	120.7	134.32	114.7		
Intermediates:[24] Pizzi, Zhao and Pilato											
	155.00	—	68.53	155.3	127.85	128.64	121.25	128.37	115.60	—	—
	155.00		68.53	150.80	127.85	126.84	121.81	126.84	127.85	60.21	—
	155.00		68.53	152.08	127.40	125.86	131.70	125.86	127.85	60.50	65.35
	155.0		68.53	—	117.52	125.86	—	125.86	117.52	62.23	65.35



(a)

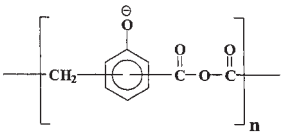
Figure 4 MALDI-TOF mass spectra of the triacetin-accelerated PF resin: (a) full extent of the spectrum with the indication of the repeating mass patterns, (b) detail of the 200–800 Da region, and (c) detail of the 800–1350 Da region.

ever, even this would, nonetheless, entail major rearrangements in the reaction, indicating that a very complex mechanism was indeed at work in the ester acceleration of PF resins, a mechanism that was likely to be far more complex than any of the mechanisms proposed up to now.

Clearly, on the basis of the NMR results, one could also argue that the anhydride bridges could neither be nor have anything to do with an intermediate of the ester acceleration mechanism.

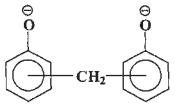
MALDI-TOF MS was used to confirm that these *p,p* anhydride bridges not only did exist (this was already confirmed by the NMR spectrum) but that they were (1) an integral part of the structure of the PF resin and (2) an integral part of some stage of the ester acceleration mechanism. They may or may not have been temporary bridges, as previous work appears to indicate,[24,31] and perhaps may not exist in the final resin network.[24,31] MALDI-TOF spectra of the GPC fractions of low and high molecular weight (MW) in Figures 2(a,b) were also done. The results obtained were the same.

Figure 4 shows the MALDI-TOF mass spectrum of the triacetin-accelerated PF resin used. Table II shows the breakdown of the species formed. The repeating 176- and 198-Da motives in the PF resin were the most noticeable features. For oligomers composed of up to 5–6 phenolic nuclei, the 176-Da repeating motive was, by far, the dominant one. The only repeating structure fitting a 176-Da motive was the following

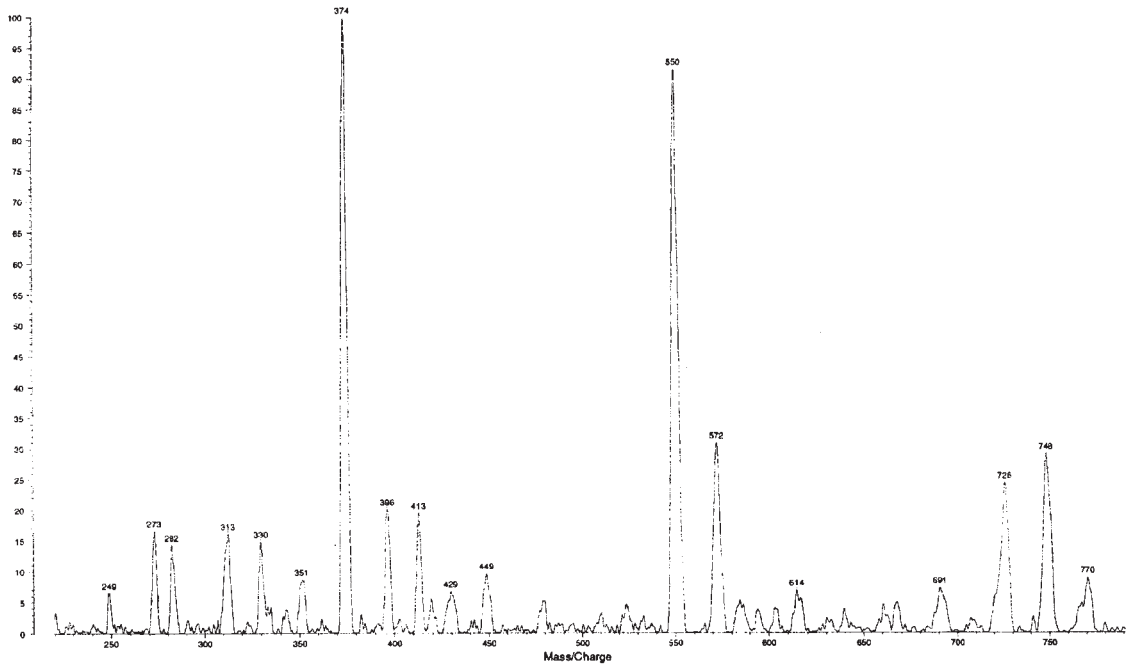


at a theoretical value of 177 Da. This pattern is noticeable in Figure 4(a–c) as being repeated four times up to 1077 Da and an added time up to 1275 Da [Fig. 4(a,c)].

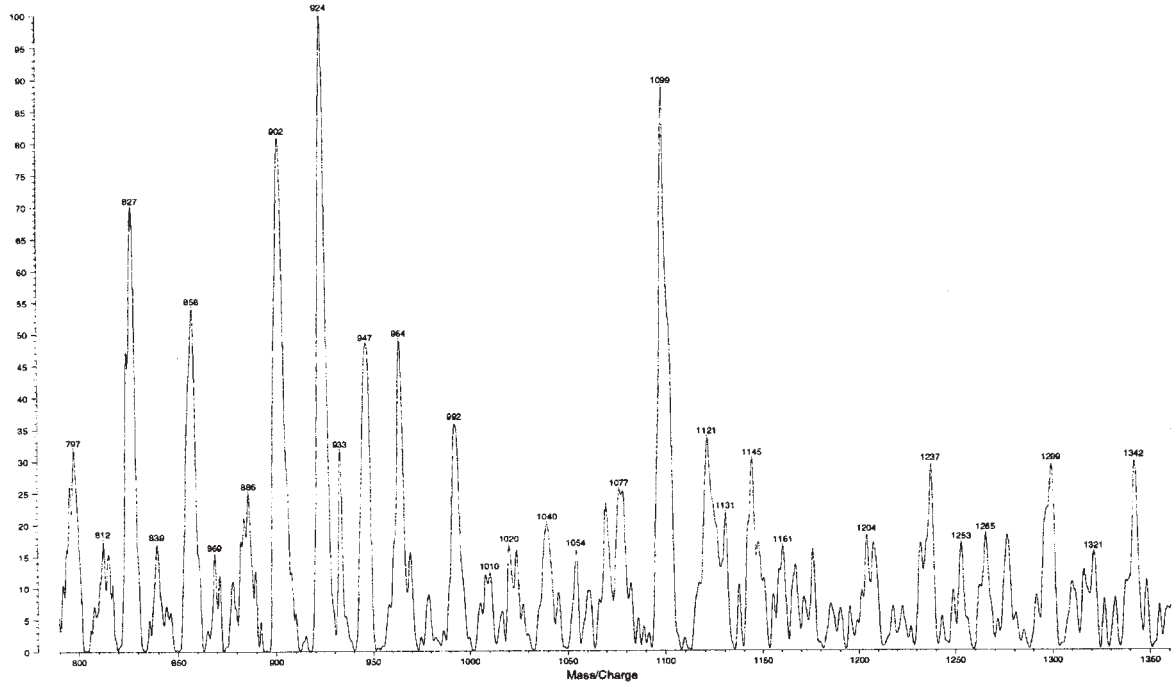
The pattern of 198 Da corresponds to a PF dimer of the type



The main peak at 374 Da was calculated as 350 (MW of compound) + 23 (MW of Na^+ used as matrix) for a



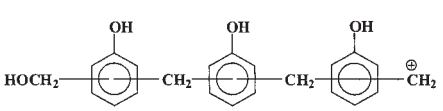
(b)



(c)

Figure 4 (*Continued*)

theoretical value of 373 Da and corresponded to a PF trimer structure presenting a methylol and a $—CH_2^+$ group, of repeating unit $—C_6H_4—CH_2—$



The combination of the 176 and 198 repeating units with the 374-Da unit yielded molecules of the type

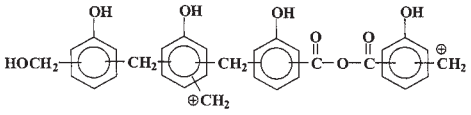


TABLE II
MALDI-TOF Fragmentation Peaks of a PF Resin Accelerated by a Small Percentage of Triacetin Ester

Experimental $M + Na^+$	Relative proportion	Unit type 106	176	198	Oligomer type	Calculated $M + Na^+$
249	7	2	—	—	$^+CH_2PCH_2PCH_2^+$	249
273	17	2	—	—	$(^+CH_2)_2PCH_2P(CH_2^+)_2$	273
282	14	2	—	—	$HOCH_2PCH_2P(CH_2^+)_2$	279
313	17	2	—	—	$(HOCH_2)_2PCH_2P(CH_2^+)_2$	309
330	15	2	—	—	$(HOCH_2)_2PCH_2P(CH_2^+)(CH_2OH)$	326
374	100	3	—	—	$HOCH_2PCH_2PCH_2PCH_2^+$	373
449	10	2	1	—	$(^+CH_2)_2PCH_2P(CH_2^+)CH_2P(CH_2^+)(CO)O(CO)$	450
550	92	3	1	—	$HOCH_2PCH_2P(CH_2^+)CH_2P(CO)O(CO)PCH_2^+$	550
572	31	3	—	1	$HOCH_2P[CH_2P]_3CH_2P$	571
726	25	3	2	—	$HOCH_2PCH_2P(CH_2^+)CH_2P[(CO)O(CO)P]_2(CH_2)_2^+$	726
748	29	3	1	1	$HOCH_2PCH_2P(CH_2^+)CH_2P(CO)O(CO)P[CH_2P]_2$ and/or $HOCH_2P[CH_2P]_3CH_2P(CO)O(CO)PCH_2^+$ and/or $P[CH_2P]_5CH_2P$	747 753
770	10	3	—	2	$HOCH_2P[CH_2P]_5CH_2P$	770
902	13.5	3	3	—	$HOCH_2PCH_2P(CH_2^+)CH_2P[(CO)O(CO)P]_3(CH_2)_3^+$	902
924	16	3	2	1	$HOCH_2PCH_2P(CH_2^+)CH_2P[(CO)O(CO)P]_2[CH_2P]_2CH_2^+$ and/or $HOCH_2P[CH_2P]_4[(CO)O(CO)P]_2(CH_2)_2^+$	923
964	7	3	—	3	$HOCH_2P[CH_2P]_7CH_2P$	965
1077	4	3	4	—	$HOCH_2PCH_2P(CH_2^+)CH_2P[(CO)O(CO)P]_4(CH_2)_4^+$	1078
1099	15	3	3	1	$HOCH_2PCH_2P(CH_2^+)CH_2P[(CO)O(CO)P]_3[CH_2P]_2(CH_2^+)_2$ and/or $HOCH_2P[CH_2P]_4[(CO)O(CO)P]_3(CH_2^+)_3$	1099
1275	3	3	4	1	$HOCH_2PCH_2P(CH_2^+)CH_2P[(CO)O(CO)P]_4[CH_2P]_2(CH_2^+)_3$ and/or $HOCH_2P[CH_2P]_4[(CO)O(CO)P]_4(CH_2^+)_4$	

The phenolic —OH was taken as —OH in some cases and as $—O^-$ in other cases to calculate the masses nearer to the experimental results.

at 550 Da, obtained as 350 + 177 + 23 (Na^+) and higher molecular mass oligomers of a similar type. The series of higher oligomers of this type, hence containing anhydride bridges, and standard PF oligomers not containing any anhydride bridges but only methylene bridges obtained experimentally by MALDI-TOF in Figure 4(a–c) are shown in Table II. The relative abundances up to 1099 Da of these different oligomers shown in Table II indicated that mixed oligomers containing both methylene bridges and anhydride bridges constituted up to 48% of the total oligomers present with the methylene bridges still in great majority.

The existence of PF oligomers of molecular mass up to 1099 and of higher molecular mass in very small amounts confirmed that the much higher masses observed by GPC in Figure 2 were nothing other than colloidal aggregates of the higher oligomers. This confirmed the existence of a colloidal state of the PF resins, as already determined for melamine-urea-formaldehyde (MUF) resins.

The repeating 176-Da pattern inserted onto normal methylene-linked PF oligomers clearly demonstrated that the anhydride bridges were (1) an integral part of the structure of the PF resin and (2) an integral part of some step in the ester acceleration mechanism. This means that it was demonstrated that

1. An alternative bridge to methylene and methylene ether bridges did form at some step of the ester acceleration mechanism.
2. This type of bridge appeared to just exist temporarily at some stage of the acceleration mechanism, temporarily because all researchers involved[24,26,29,31] appear to have noted the absence of these structures in the final PF resin.
3. This bridge appeared to link phenolic nuclei *p,p* and *m,m* and even *m,p* but not ortho. At least at some intermediate moment in the reaction, when these bridges exist, the effective functionality of the phenolic nuclei increases, which was one of the earlier hypothesis advanced.[5,20,22,24] This could possibly be one of the causes that leads to an eventual higher level of crosslinking[24,31] through methylene bridges and, consequently, a higher strength of ester-accelerated PF resins.
4. The mechanism was evidently much more complex than any of the mechanisms that were proposed earlier.
5. The ester acceleration mechanism had nothing to do with the carbonate acceleration mechanism.
6. The difference in the reaction conditions of monomeric model compounds such as hydroxy-

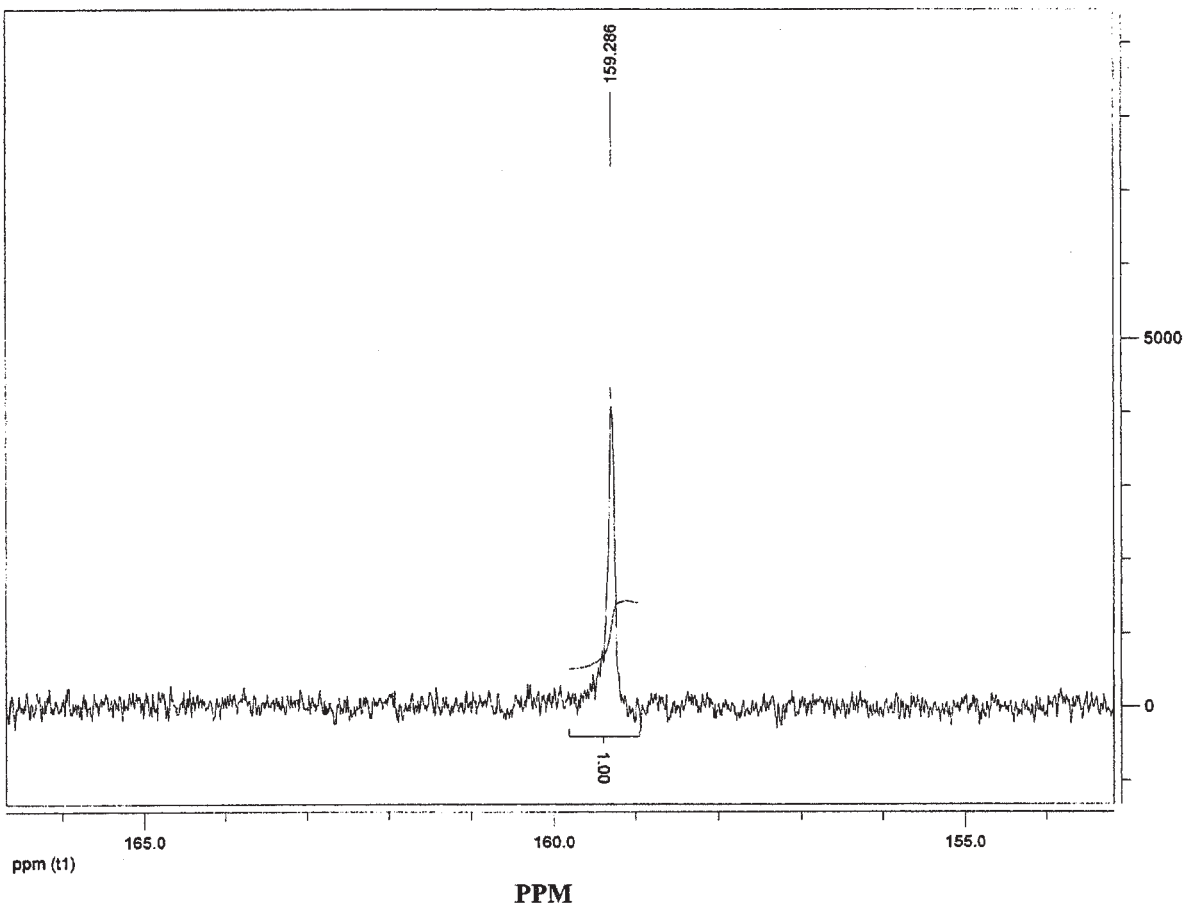


Figure 5 Quantitative ^{13}C-NMR spectrum of $NaHCO_3$ in a diluted water solution. The spectra were the same both at ambient conditions and after heating.

methyl phenols, carried out in dilute in solution, were rather different than the colloidal aggregation environment in which the reaction of a higher average molecular mass PF resin was carried out. The colloidal state of a polycondensation resin has been shown several times before to affect intensely the route a reaction can take.[35,38,39]

As a consequence of the evident complexity of the mechanism, it is not really possible to advance at this stage a complete and exhaustive mechanism of the reaction but only to propose simplified and, by necessity, incomplete hypothesis of what occurs, a hypothesis, however, based this time on some solid experimental evidence of something really new.

In Figure 5 is shown the ^{13}C-NMR spectrum of $NaHCO_3$ in solution. The spectrum was the same after the solution was heated. Only one peak at 159.3 ppm was noted. This did not correspond, of course, to any of the peaks reported in the spectra of the PF resin accelerated with triacetin, as shown in Figure 3. It is reported for another reason: in a previous work[4] several bands in the 160–162 ppm region were observed for both carbonate-accelerated (viz., sodium carbonate and guanidine carbonate) and triacetin-accelerated resins. The bands were small but well defined and had rather different shifts and shift patterns according to the accelerator used. They were in the same interval of the 160–162 ppm bands shown in Figure 3. These were in that work ascribed to carbonates being present in the water. This proved later not to be the case, and it was not the case for the spectra presented now. It means that in the spectra presented in this article, as in those presented in previous work,[4] for the triacetin and organic and inorganic carbonates, the intermediate species involved in the acceleration reaction were observed by NMR. In all cases, the NMR band pattern indicated that the relative proportion of esters or even anhydrides attached to the aromatic rings was small at any given time. This confirmed previous observation with regard to the presence on the ring of acyl groups[29] and carbonyl and/or carboxyl groups.[20,24] It must be stressed that these structures were evidently temporary, as remarked by several authors and as confirmed here by the low intensity of the peaks. They were formed and disappeared continuously as the reaction occurred. This is why only small-intensity

bands were observed, when one was fortunate enough to observe them, as in Figure 3 and in three of the spectra reported in a previous work.[4]

It was the addition of the accelerators during the synthesis of the resin that allowed us to observe the intermediates described. As the PF resin had a relatively high viscosity at the end of the triacetin-catalyzed reaction, the reaction was, at this stage, diffusion controlled, and it was only this slow down of the reaction that seemed to allow sufficient stabilization of the anhydride bridges for observation.

Also, the similarities of the likely mechanism of the reaction of PF resin acceleration with what is known of the mechanism of the Kolbe–Schmitt reaction are rather striking. Both reactions need the phenate ion obtained from the phenolic hydroxyl to occur. Both reactions by addition of CO_2 are accelerated[43] (for PF resins) or occur (Kolbe–Schmitt).[25] Even more important, shift of the carboxyl groups introduced on a phenate ring by a Kolbe–Schmitt reaction from the ortho site to the para site can indeed readily occur according to the alkali metal catalyst and in considerable proportion.[44] This, too, has been observed by the change in reactivity of ortho and para sites in the acceleration of PF resins, as observed by several authors.[27,29,31] In the PF resin acceleration mechanism, it was then equally probable that the use of different carboxyl compounds, organic and inorganic, would enhance the possibility of rearrangements of the type observed for the anhydride bridges.

CONCLUSIONS

As a consequence of the evident complexity of the mechanism, it is not really possible for us to advance at this stage a complete and exhaustive mechanism of the reaction but only to propose a summary of a simplified and, by necessity, incomplete hypothesis of what occurs. The hypothesis, however, is based this time on some solid experimental evidence of something really new. The mechanism involves the phenate ion of the resin to apparently give an ortho carbonyl or carboxyl group on the ring. This apparently undergoes rapid rearrangement shifting to sites different to the ortho position. The appearance gathered from NMR shifts calculation indicates preferential repositioning to the para site and, very surprisingly, to the meta sites of the phenolic ring. Anhydride-like bridges form and have been shown by MALDI-TOF MS to contribute to oligomeric structure with or without methylene bridges. These structures appear to be temporary; hence, they are in small proportion at any given moment of the reaction. This indicates a dynamic equilibrium of some sort, whatever these structures accelerating role of PF resins might be. MALDI-TOF analysis clearly indicated that these structures were, at some moment, an integral part of the structure of the liquid resin and that they existed parallel to the methylene bridges pertaining to a normal PF resin structure. If the higher strength of the final network, due to higher density of crosslinks, is due only to a greater proportion of methylene linkages as a consequence of these structure catalysis, whatever this may be, as sustained by certain authors, or to the inducement of a higher functionality of the ring, it is not possible to say because the next steps of the mechanism from these structures to the final network cannot be deduced from any of the data available up to now.

In conclusion, whatever the complete mechanism might be, the confusion generated by the number of possible interpretations that all authors have advanced already indicates clearly that the mechanism is much more complex than anyone has thought up to now, that none of the facile interpretations advanced are a complete solution, and that the sum of what has been ascertained up to now does not allow us either to advance a complete mechanism or to conclude what the real causes of the acceleration are.

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