

tivity peak at 250 °C. The 400 °C peak was eliminated after annealing above ~400 °C. After temperature cycling to ~600 °C in a nitrogen atmosphere, the resulting pyrolyzed (carbonized) material exhibited a blackish appearance and was fairly conductive [$\sim 10^{-6}$ (ohm-cm) $^{-1}$ at 600 °C]. In air above ~450 °C, the carbon was volatilized in reactions with oxygen and the residual material had a white color characteristic of the glass matrix [conductivity $\leq 10^{-9}$ (ohm-cm) $^{-1}$ at 600 °C]. Considerably higher conductances were observed following electrical breakdown.

Discussion and Conclusions

There is a direct correlation between thermal decomposition and temperature-dependent electrical conduction characteristics in phenolic materials. Peaks in the conductivity correlate with decomposition and the loss of volatiles from the material. The mass loss which occurs between 200 and 300 °C (water and/or ammonia and amines) correlates with the conductivity peak at ~250 °C. As the temperature is increased and volatilization occurs, the resulting residual material exhibits a decrease in the conductance (above ~250 °C) which produces a peak in the conductivity temperature dependence. The change in conductivity could be due to the loss of absorbed species and/or to a splitting out of polar species like water and ammonia which could lead to a more hydrocarbon-like material with a lower conductivity. As the temperature is further increased, the loss of other species occurs (phenolic and amine groups and higher molecular weight

species) and results in a second peak in the conductivity at ~400 °C. The position and magnitude of these peaks vary with heating rate. As the material pyrolyzes with heating to ~500 °C, the conductivity peaks are eliminated and the low-temperature conductivity is reduced (i.e., the materials are better insulators). At higher temperatures in nitrogen, however, the material carbonizes and becomes conductive. In air above ~450 °C, oxygen accelerates decomposition and the residual glass matrix material exhibits a low conductivity. The excellent correlation between thermal and electrical properties suggests that electrical conductivity (in the region of ohmic conduction) can be used as a thermal analytical tool in characterizing phenolic materials.

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Determination of Structure and Mechanism of Reactions between Unsaturated Aldehydes and Phenols

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The kinetics and mechanisms of reactions between acrolein or crotonaldehyde with phenol, cresols, and dimethylphenols and also structures of reaction products were studied in neutral and acid media. Beside addition of phenols to the double bonds and to the carbonyl groups of the unsaturated aldehydes and later formation of bi- and higher molecular species, side reactions of the unsaturated aldehydes also take place. From kinetic data for individual reaction systems tentative reaction schemes were determined.

Introduction

Reactions between unsaturated aldehydes and phenols lead to formation of resins which are soluble in polar solvents. The double functionality of the aldehydes and the functionalities of the phenols make many types of reactions possible: polymerization of the aldehydes double bonds, cyclization of the aldehydes, addition of the aldehydes to the free position of the phenols, and others. Some of these reactions have been already investigated, particularly the polymerization of acrolein and crotonaldehyde by Kubisa et al. (1980) and Schultz (1964). Smith and Dehnert (1975) cited that addition of the unsaturated aldehydes to the free position of phenols can take place through addition of the aldehyde groups to the benzene ring or through the addition of the aldehyde double bonds. The dominant reaction depends on reaction conditions and types of aldehydes and phenols used. Steric hindrances

can play an important role in determining which reactions will be prevailing.

Experimental Section

All reagent used were of analytical grade. Acrolein and crotonaldehyde were distilled before use.

The resins from acrolein or crotonaldehyde and phenol, *o*-, *m*-, *p*-cresol, 2,5-dimethylphenol, or 3,5-dimethylphenol were prepared at 20 °C in molar ratio between the unsaturated aldehydes and phenols from 1.7 to 1.0 in neutral and acid media (between 0.02 and 0.076 mol of HCl). The reaction time was 30 days. For ^{13}C NMR and GPC analysis samples were taken in time intervals of 6 h and 1 week. All the products were dark, viscous resins, soluble in acetone, chloroform, and other polar solvents. For GPC analysis in μ -Styragel columns (100 and 500 Å) dichloromethane was used as solvent (30 mL/h) and polystyrene standards, phenols, crotonaldehyde, acrolein, and α -for-

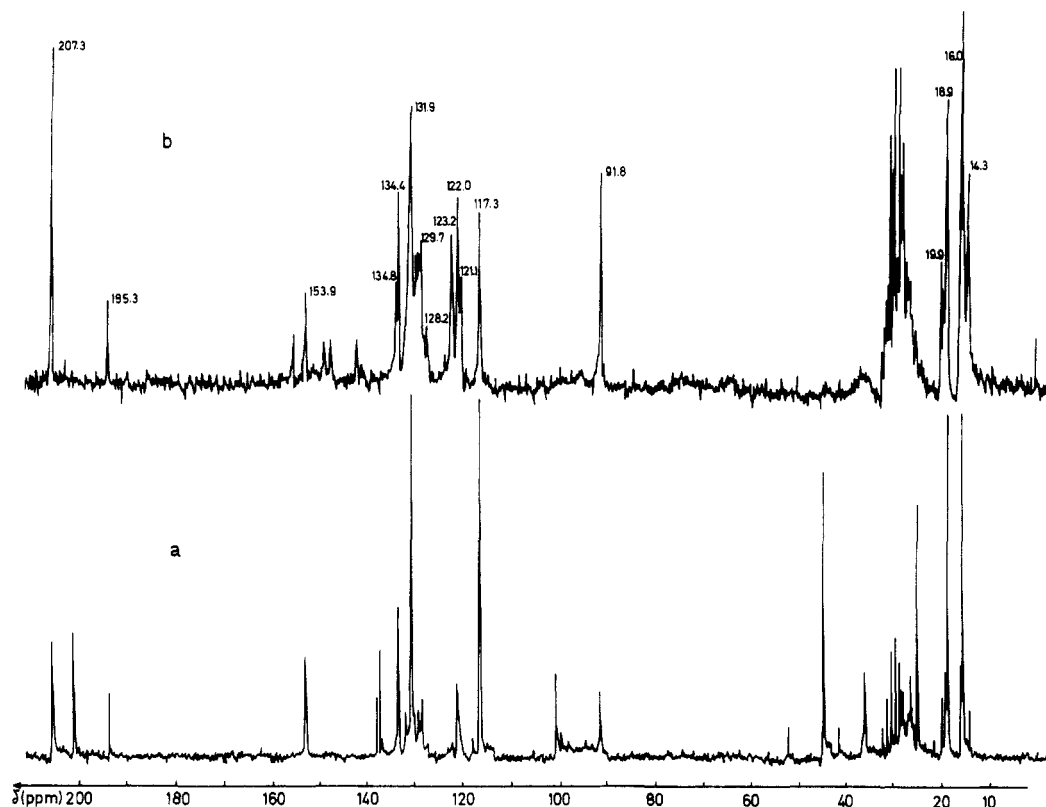


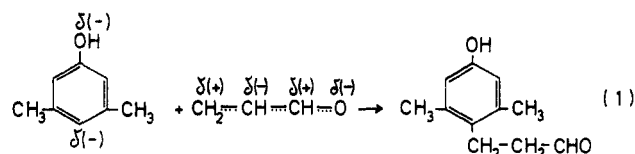
Figure 1. ^{13}C NMR spectra of the reaction products between acrolein and 3,5-dimethylphenol: (a) neutral medium; (b) acid medium.

mylethyl phenols were used for calibration. A UV spectrometer (λ 254 nm) was used as detector. All NMR spectra chemical shifts were quoted with respect to TMS as standard. ^{13}C NMR spectra were recorded on a JEOL FT 90 Q spectrometer. Spectra were cumulated between 5000 and 6000 times, pulse with was 14 μs (90° angle) and spectral with was 5000 Hz. The samples were dissolved in acetone- d_6 and chloroform- d_1 (~20% solution). All signals were proton decoupled.

Results and Discussion

In ^{13}C NMR spectra of the products of the reactions between unsaturated aldehydes and phenols three characteristics regions of addition products were determined by Šebenik et al. (1981), Šebenik and Osredkar (1983): (i) the region between 25 and 45 ppm belonging to $-\text{CH}_2-$ and $>\text{CH}-$ groups bonded to phenols; (ii) the region between 60 and 80 ppm belonging to $>\text{CHOH}$ groups of the aldehydes groups bonded to the phenols and the $-\text{CH}_2\text{O}-$ groups of the double bonds which are bonded to the $-\text{OH}$ groups of phenols. (iii) The third characteristic region is between 194 and 204 ppm belonging to bonded or unbonded aldehydes. Signals belonging to the aromatic C atoms or other side-reaction products can be seen as well.

Based on chemical shifts of reaction products determination of reaction schemes for individual reactions are possible. In a neutral medium the addition of the double bond of acrolein to the free position of phenols is very fast with 2,5-, 3,5-dimethylphenol (1), and *m*-cresol, but slow with phenol, *o*- and *p*-cresol. In these reactions α -formyl



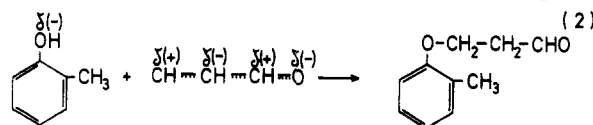
ethyl phenols are formed which can later react with $-\text{CHO}$ or with free positions of phenols to form bi- or higher

Table I. Relative Reactivities of Acrolein with Different Phenols

type of phenol	neutral medium	acid medium
phenol	1.0	1.0
<i>o</i> -cresol	0.7	0.7
<i>m</i> -cresol	2.1	2.5
<i>p</i> -cresol	0.4	0.3
2,5-dimethylphenol	2.3	3.0
3,5-dimethylphenol	2.5	4.0

molecular products. These reactions can be followed via the decreasing signals of the $-\text{CHO}$ groups and by the increasing signals of the $-\text{CH}-\text{OH}$ and $-\text{CH}_2\text{O}-$ groups with time.

Phenol and *o*- and *p*-cresol have strong ^{13}C NMR signals in the region between 60 and 80 ppm, belonging to $-\text{CH}_2\text{O}-$ and $>\text{CH}-\text{OH}$ groups. These groups are formed with the addition of $-\text{CHO}$ groups to the benzene rings or with the addition of the double bonds to the $-\text{OH}$ groups (2).



Reaction 2 is more probable in the case of phenols in which the negative centers on *o*- and *p*-positions are not very strong.

Spectra of reaction products in strong acid medium have a strong ^{13}C NMR signal at 91.5 ppm which can be ascribed only to $-\text{OCHOCHO}-$ groups, as were reported by Breitmaier et al. (1979), Ebdon and Heaton (1977), and De Breet et al. (1977). This signal could be ascribed to $-\text{OCHO}-$ group of the cyclic or polymeric acrolein (Figure 1). These cyclic compounds can further react with phenols via the addition of the double bonds.

The relative reactivities between phenols and acrolein were determined by GPC on the basis of unreacted phenols in reaction mixture at same reaction conditions (Table I).

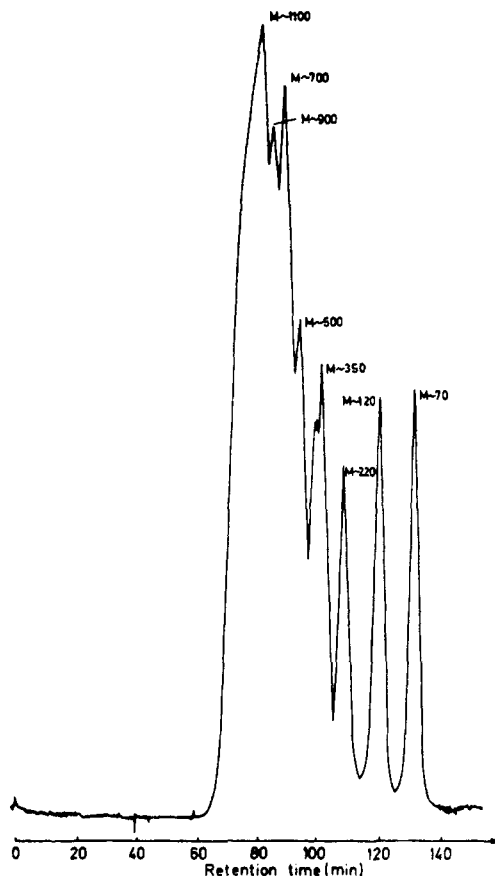
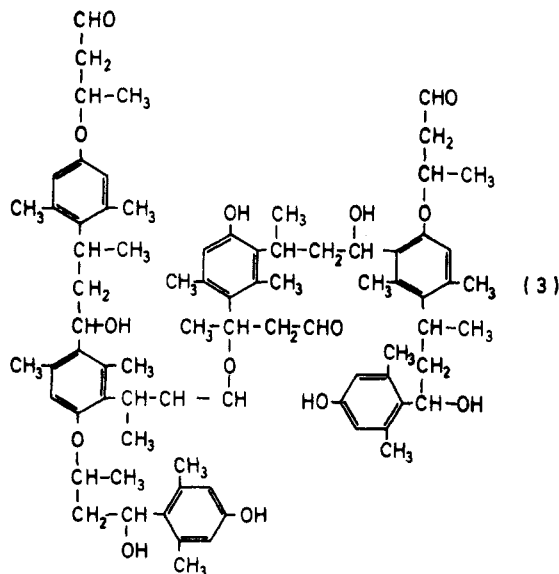


Figure 2. GPC chromatogram of the reaction products between crotonaldehyde and 3,5-dimethylphenol in acid medium; molar ratio: 1.7:1:0.072.

The most reactive is 3,5-dimethylphenol which is due to the formation of strong negative centers on *o*- and *p*-positions.

Crotonaldehyde reacts with phenols in neutral and acid media at a lower rate than acrolein but the reaction mechanisms are similar. In Figure 2 the GPC chromatogram of the reaction product between crotonaldehyde and 3,5-dimethylphenol is shown. The molecular weight of 1200 corresponds to six benzene rings bounded together by crotonaldehyde. A possible reaction product (3) follows.



The concentration of the lower oligomers in reaction systems has a maximum after three days and decreases after that time. 3,5-Dimethylphenol (Figure 3) is more

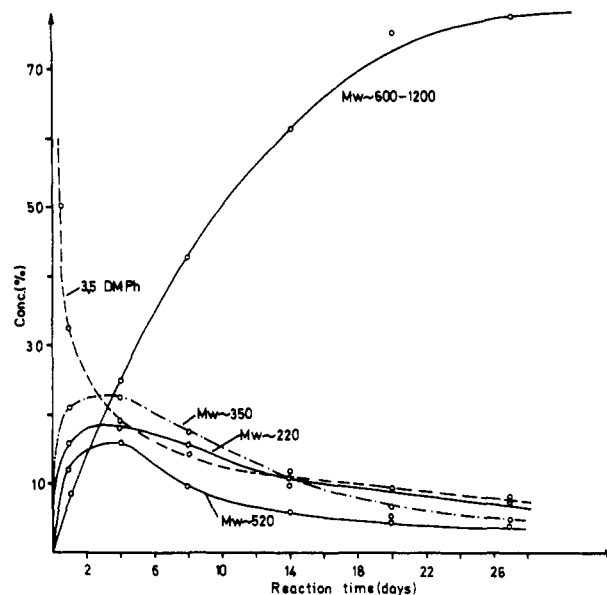


Figure 3. Concentrations of different products as time function in the reaction between crotonaldehyde and 3,5-dimethylphenol in acid medium; molar ratio: 1.7:1:0.072.

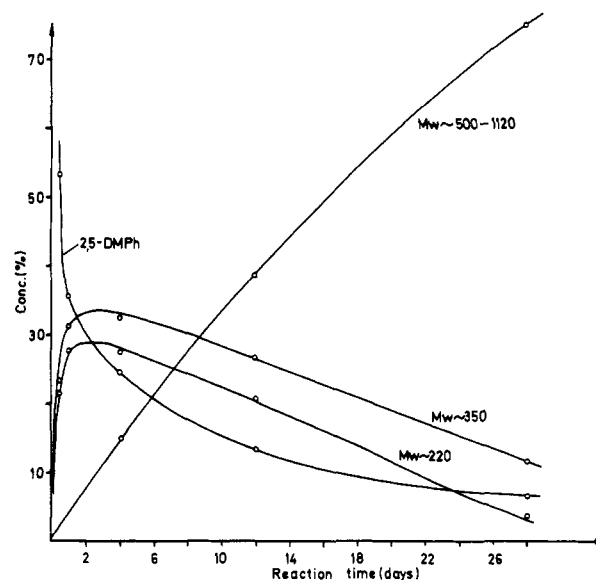


Figure 4. Concentration of different products as time function in the reaction between crotonaldehyde and 2,5-dimethylphenol in acid medium; molar ratio: 1.7:1:0.072.

Table II. The Rate Constants for the Reaction of Crotonaldehyde and 2,5- or 3,5-Dimethylphenol in Acid Medium

	$K \times 10^3 \text{ L}/(\text{mol s})$
2,5-dimethylphenol	0.012
3,5-dimethylphenol	0.014

reactive than 2,5-dimethylphenol (Figure 4). In both cases in two weeks of reaction time the molecular weight grows to values between 600 and 1200. Other phenols react in a similar way but with different reaction rates. Based on measurements of concentrations of 2,5- and 3,5-dimethylphenols as a function of the reaction time by GPC, the rate constants for these two phenols with crotonaldehyde in acid medium were calculated (Table II)

$$\frac{d[\text{Ph}]}{dt} = -K[\text{Ph}][\text{Cr}] \quad (4)$$

where Ph is 2,5-dimethylphenol or 3,5-dimethylphenol and Cr is crotonaldehyde.

Table III. The Relative Reactivities of Different Aldehydes with Phenols

	phenol	2,5-dimethylphenol	3,5-dimethylphenol
acrolein	1.0	2.3	2.5
crotonaldehyde	0.1	0.3	0.3
formaldehyde	0.5	1.5	3.5

In Table III the reactivities of acrolein and crotonaldehyde with phenols are given. For comparison, reactivities determined for formaldehyde are also included. Due to different reaction conditions, e.g., the presence of water in formaldehyde, the values in the Table III are only illustrative. As can be observed, acrolein is more reactive than crotonaldehyde.

Conclusions

Reactions between unsaturated aldehydes and different phenols are very complex and three kind of reactions are possible: addition, polymerization, and cyclization. Besides the main reaction a number of side reactions of the

unsaturated aldehydes take place. The mechanisms of the reactions are strongly influenced by reaction conditions and by the type of aldehydes and phenols.

Registry No. Acrolein, 107-02-8; crotonaldehyde, 4170-30-3; phenol, 108-95-2; *o*-cresol, 95-48-7; *m*-cresol, 108-39-4; *p*-cresol, 108-39-4; 2,5-dimethylphenol, 95-87-4; 3,5-dimethylphenol, 108-68-9.

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Nontransition Metal Assisted Regio- and Stereoselective Synthesis of Alkylidene-Bridged Oligomeric Phenolic Compounds

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A method has been developed for the regio- and diastereo-controlled synthesis of alkylidene-bridged novolac-type oligomers. The procedure consists of condensation of bromomagnesium phenolates with racemic α -substituted salicyl alcohol derivatives in aprotic nonpolar media. A variety of all-ortho ethylidene-bridged, isobutylidene-bridged, and mixed ethylidene-isobutylidene-bridged trimers as well as syndiotactic pentanuclear ethylidene-bridged pentamer are conveniently prepared in this manner. A template mechanism involving both the reacting species and the metal ion is suggested to account for the exclusive ortho-specificity of the reactions as well as their stereochemical behavior.

Introduction

Phenolics, despite its maturity, continues to attract the interest of academic and industrial workers while the spectrum of practical applications broadens more and more (Knop and Scheib, 1979; Taylor, 1983). Although there have been numerous studies on phenol-formaldehyde condensation products and related methylene-linked polyphenols, there has been little investigation on the use of aldehydes other than formaldehyde as the bridging reactant in the synthesis of novolac-type oligomers (Kiegel, 1963).

In principle, by using prochiral aldehydes, a study can be undertaken directed toward the stereocontrol of the phenol-aldehyde condensation process and similar reactions. If this goal could be reached, then a viable access would be opened not only to many regular alkylidene-linked polyphenols but also to unsymmetrical oligomers bearing mixed bridges.

As part of our project aimed at regiocontrol of electrophilic substitution reactions on phenol systems by using nontransition metal promoters (Casnati et al., 1983), we also tried to prepare some regular all-ortho alkylidene-

bridged oligomers by controlling the direction of diastereo-differentiation in the condensation reactions.

A recent paper from this laboratory (Casiraghi et al., 1984) has shown that, in the synthesis of all-ortho ethylidene-linked polyphenols, the nature of the organometallic promoter as well as the substrate to promoter ratio played a dominant role in controlling the relative stereochemistry of produced oligomeric compounds.

In the present work we report a more detailed study on the diastereoselection of some model reactions and preliminary results on the stereocontrolled synthesis of ethylidene-linked tetranuclear and pentanuclear oligomers.

Result and Discussion

The reactions in Scheme I were chosen as models of the condensation reaction leading to regular all-ortho alkylidene-linked novolacs.

Our experiments include preparation of symmetrical meso and racemic ethylidene-linked trimers **3maa** and **3raa** and isobutylidene-linked trimers **3mbb** and **3rbb** by growth of dinuclear compounds **2a** and **2b** with the corresponding racemic α -substituted salicyl alcohol **1a** and **1b** and the synthesis of unsymmetrical ethylidene-iso-