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THE SYNTHESIS AND CHARACTERIZATION OF RESORCINOL-CROTONALDEHYDE RESINS

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ABSTRACT

The structure, course of the reaction, and molecular weight distribution for resorcinol-crotonaldehyde resins were determined by HET2DJ ^{13}C NMR, ^{1}H NMR, and GPC. In the first step of the reaction, the free reactive Positions 4 and 6 of resorcinol react with crotonaldehyde. Due to steric hindrance, Position 2 is less reactive in spite of its high electron density. In the next step, addition products react with themselves or monomers to form higher products. Water is eliminated during the reaction. The final molecular weight of the resins is up to 10 000.

INTRODUCTION

There are many possible reactions between phenols and unsaturated aldehydes. In the first step of the reaction, addition of the phenols to the carbonyl groups and to the double bonds of the aldehydes takes place. In the second step, the addition products react further with phenols or lower species to form products of higher MW. Cyclization of the unsaturated aldehydes and etherification of the phenol –OH groups are possible as well. The reaction

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*Part of this work is extracted from the PhD Thesis by M. Zigon.

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rate depends on the reactivity of reactants and on reaction conditions. Most of the products are red-colored resins which are soluble in polar organic solvents [1-3].

In this paper the study of the synthesis, structure, and mechanism of the reaction in acidic medium between resorcinol and crotonaldehyde in bulk and in solution is reported. For characterization of the reaction products, one- and hetero-two-dimensional ^{13}C, ^{1}H-NMR spectroscopy and GPC chromatography were used.

EXPERIMENTAL

Materials

Resorcinol and crotonaldehyde were Merck products. All chemicals were purified and dried before use.

Procedure and Apparatus

The synthesis of the resorcinol-crotonaldehyde resin solutions were performed in a reaction vessel at 55°C.

The molar ratio between resorcinol and crotonaldehyde was 1:1 and 1.5:1, and the concentration of hydrochloric acid was 1.0 mol%. The reaction time was 2 h. Methyl ethyl ketone and acetone as solvents were used. For bulk polymerization the syntheses were performed at room temperature with a molar ratio of 1:1 and concentrations of hydrochloric acid below 1 mol%.

For ^{13}C-NMR measurements a Varian superconducting magnet VXR 300 was used. The one-dimensional (1D) ^{13}C-NMR spectra were recorded with pulse width 16 μs (90°), pulse delay 2 s, and spectral window 16.5 kHz. The spectra were proton decoupled. The hetero-two-dimensional (HET 2DJ) ^{13}C-NMR spectra were taken with spectral windows 5 and 16.5 kHz, with double precession at normal temperature using the step program for incorporation of the high-power decoupler. For the second step of the accumulation, the decoupler was off. The proton spectra were recorded on a Varian EM360. For all NMR measurements, methanol-d_4 was used as solvent and TMS as the standard.

For GPC measurements, samples were taken from the reaction vessel at intervals of some minutes, dried, and then dissolved in THF. μ-Styragel columns with pore sizes of 10 and 50 nm and a UV detector at 254 nm wavelength were used. The columns were calibrated with polystyrene standards, resorcinol, and crotonaldehyde.

RESULTS AND DISCUSSION

The electron density of σ and π electrons of resorcinol contributes to the electrophilic substitution of protons on Positions 2, 4, and 6 of the benzene ring. Crotonaldehyde, as an unsaturated aldehyde, is a resonance hybrid of different structures. Its double bonds and aldehyde groups are depolarized, and positive centers are formed on Positions 1 and 3 of the carbon atoms.

In the HET 2DJ ^{13}C-NMR spectra of the resins, the ordinate represents the 1D ^{13}C-NMR spectrum and the abscissa the values of the carbon proton coupling of the carbon atom. In the spectra, two main regions can be seen: the region of crotonaldehyde and the region of the $-CH=$ and $>C=$ groups of resorcinol [4, 5].

In the following, the behavior of individual reactivity is given. The methyl groups of crotonaldehyde do not react with resorcinol. They only change the position of the chemical shift. After 2 h of reaction time, six quartets are found in the region between 20.4 and 21.3 ppm with intensity ratio 1:3:3:1 belonging to $-CH_3$ groups. The signals for the double bond of crotonaldehyde, before the beginning of the reaction, are two doublets at 134.9 and 153.7 ppm with the intensity ratio 1:1. After the addition of resorcinol, Carbon 2 ($=CH-$) changes to $-CH_2-$ at 36.4 ppm to form a triplet with the intensity ratio 1:2:1. The doublet of Carbon 3 appears at 28.0 ppm. After the addition of resorcinol, the signal of Carbon 1 shifts to 70.6 ppm. Further on, $-CH(OH)-$ groups react with resorcinol to form $>CH-$ groups. After elimination of water, new doublets form between 30 and 33 ppm.

The aromatic carbon atoms of resorcinol have signals between 100 and 160 ppm, as doublets for $-CH=$ and singlets for the quaternary $>C=$ atoms. In the reaction with crotonaldehyde, the carbon atoms in Positions 1 and 3 do not react but only shift to form three new singlets between 153 and 159 ppm. All these singlets are split in fine structure in a long-range coupling with the doublet of the proton on Position 2. The coupling constant is 16 Hz. Carbon 2 is a doublet at 103.5 ppm. There is no long-range coupling since Carbon 2 has no neighboring protons on Positions 1 and 3. With reaction, this signal disappears and new doublets form between 103.3 and 104.0 ppm. The change in the chemical shifts is due to the reaction on Positions 4 and 6, which means that Carbon 2 does not react with crotonaldehyde. This is confirmed by the behavior of Carbons 1 and 3 as well. Carbons 4 and 6 react with crotonaldehyde to form new singlets at 120 ppm. On reaction with crotonaldehyde, the doublet of the carbon on Position 5 only shifts to give signals at 124 to 129 ppm. A representative spectrum of the reaction product of crotonaldehyde and resorcinol in molar ratio 1:1 is given in Fig. 1.

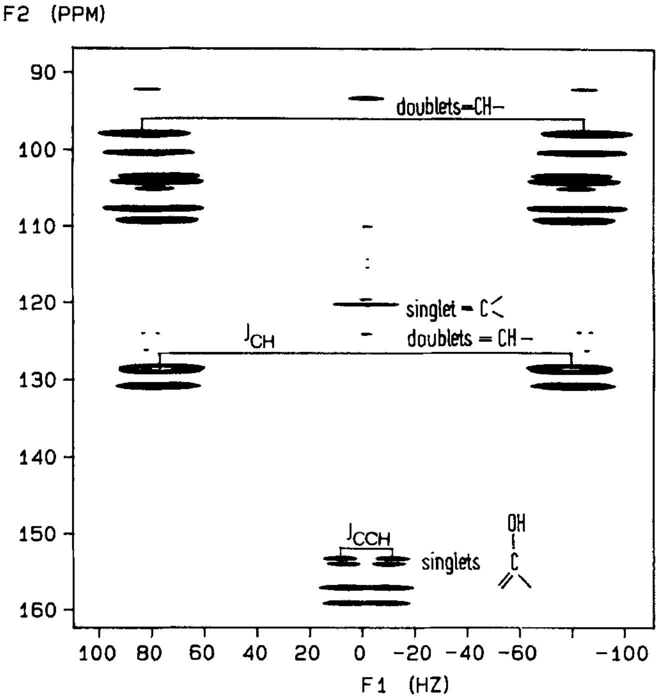


FIG. 1. Hetero 2DJ ^{13}C-NMR spectrum of the reaction products between resorcinol and crotonaldehyde in the molar ratio 1:1. Solvent: methyl ethyl ketone.

The coupling constants are given in Table 1. On the basis of all data, Scheme 1 can be predicted.

The proton spectra confirmed the elimination of water during the reaction. In the resin with molar ratio 1:1, the number of protons at the beginning of the reaction was 12 and decreased to 10.4 after 2 h of reaction. The signal of the $-CH_3$ group, which did not react and was not influenced by other signals, was used for normalization. The signals of the $-CH(OH)-$ group decreased in both proton and carbon spectra after 2 h of reaction.

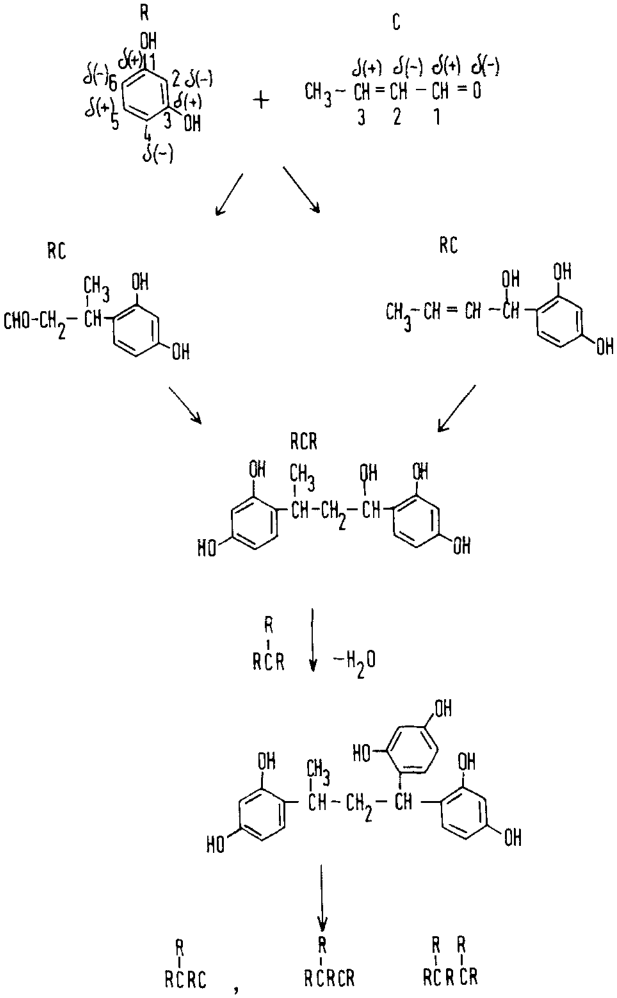
Four molecular weight fractions were detected in the GPC chromatograms: molecular weights under 200 (belonging to unreacted monomers), between 400 and 650, between 700 and 2500, and higher molecular weights up to 10 000 (Fig. 2).

TABLE 1. Carbon-Proton Coupling Constants of the Aliphatic and Aromatic Carbons in the Resorcinol-Crotonaldehyde Resin

Group	Chemical shift, ppm	Type of coupling	Coupling constant, Hz	
			J_{CH}	J_{CCH}
$-\overset{\vert}{C}H-$	28-33	Doublet	130	
$-CH_2-$	36-41	Triplet	128	
$-CH_3$	20-24	Quartet	127	
Benzene ring				
C_1, C_3, quaternary	153-159	Singlet-doublet		16-21
C_2	103-104	Doublet	161	
C_4, C_6	108-109	Doublet	161	
C_4, C_6, quaternary	120-121	Singlet		
C_5	124-129	Doublet	157	

The fraction of molecular weight between 400 and 550 corresponds to forms RCR, $R\overset{R}{\overset{|}{C}}R$, or RCRCR of the reaction scheme. The form RCRC is less probable since the signals in the proton and carbon spectra corresponding to end groups like $-CHO$ or $-CH{=}CH-CH_3$ are very small. This can be explained by the high reactivity of the aldehyde groups and of the double bonds, which form $-\overset{|}{C}H-$ or $-CH_2-$ groups. The fraction of molecular weight between 700 and 1500 corresponds to the form $R\overset{R}{\overset{|}{C}}R\overset{R}{\overset{|}{C}}R$ or $R\overset{R}{\overset{|}{C}}R\overset{R}{\overset{|}{C}}R\overset{R}{\overset{|}{C}}R$. Partly crosslinked or branched species are also possible. The fraction of molecular weight higher than 1500 increased with reaction time and is present after only 1 h of reaction. This fraction corresponds to more than 8 monomer units in the chain.

The same results, in respect to the structure and molecular weight distribution, were obtained with both solvents and for bulk synthesis. Differences were observed only in the rate of reaction, with much higher rates for bulk


R
OH
δ(+)
δ(-)
δ(+)
δ(-)
δ(+)
δ(-)
1
2
3
4
5
6
OH
+
C
δ(+) δ(-) δ(+) δ(-)
CH3 - CH = CH - CH = O
3 2 1
RC
CHO-CH2- CH
CH3
OH
OH
RC
CH3- CH = CH - CH
OH
OH
OH
RCR
HO
OH
CH3
CH-CH2- CH
OH
OH
OH
RCR with R above
-H2O
OH
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CH - CH2 - CH
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SCHEME 1.

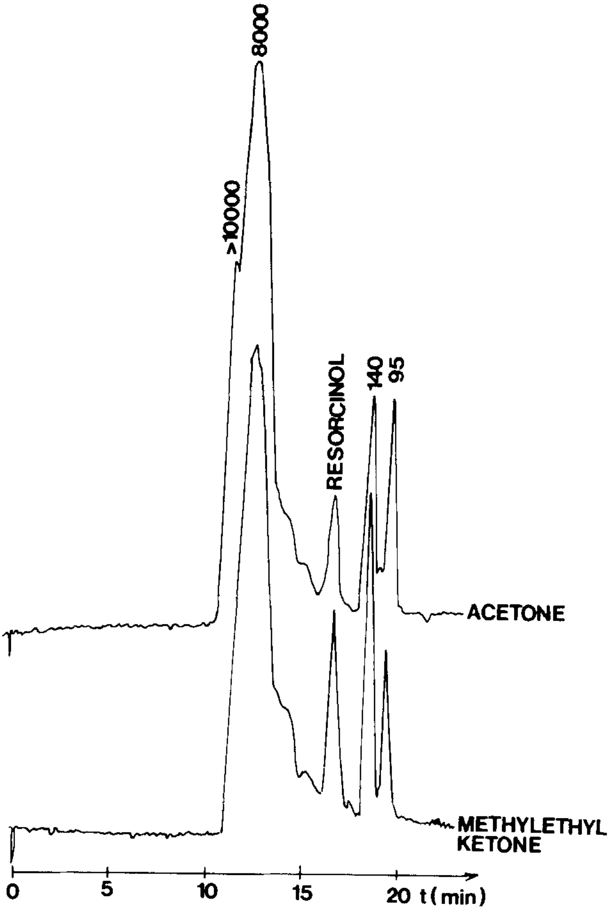

FIG. 2. GPC chromatogram of the resorcinol-crotonaldehyde resin: molar ratio 1:1. Solvents: acetone and methyl ethyl ketone, reaction time 2 h, temperature 55°C.

synthesis. The similarity in structure can be attributed to the fact that acetone and methyl ethyl ketone are unreactive solvents.

CONCLUSIONS

In solutions at 55°C, in acidic medium, the highly reactive resorcinol and the less reactive crotonaldehyde produce resins in 2 h with average molecular weights between 5000 and 9000. The resins are soluble in alcohols and ketones. During the reaction, water is eliminated and branched resins are formed. After 2 h of reaction, no free double bonds or –CH(OH)– groups are detected. The reaction rate for bulk synthesis is much higher than for solution synthesis.

The HET 2DJ ^{13}C-NMR spectroscopy in combination with GPC is a good method for determination of the mechanism and course of polycondensation.

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