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Polycondensation of Higher Phenols and Unsaturated Aldehydes

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Dedicated to Prof. Dragutin Fleš on the occasion of his 60th birthday

SUMMARY

The reactions of o-, m-, p-cresol, 2,5- and 3,5-dimethylphenol with acrolein and crotonaldehyde were studied by means of cmr spectroscopy and GPC in acid and alkaline medium in the temperature range of 300 to 340K. The addition of phenols to double bonds of the unsaturated aldehydes and the addition of aldehyde groups to the free positions of phenols seem to be the two dominant reactions. The signals for aldehyde groups and for double bonds decrease with increasing reaction time.

INTRODUCTION

The reaction between phenols and formaldehyde or higher saturated aldehydes have been investigated by many authors[1]. They reported that addition only occurs of aldehyde groups via the phenolate forms and that addition products can further react with each other forming high molecular products which are mostly insoluble.

The intention of our investigation was to determine the mechanism of reactions between unsaturated aldehydes and higher phenols. In our case four types of reactions are possible: addition of the aldehyde group to free ortho and para positions of phenols; addition of double bond of aldehyde to free ortho and para positions of phenols; polymerization of the unsaturated double bonds; polymerization of aldehyde groups[2].

In our paper the results of structural studies by cmr and GPC of isothermal reactions of o-, m-, p-cresol, 2,5-and 3,5-dimethylphenol with acrolein and crotonaldehyde in acid and alkaline medium are reported.

EXPERIMENTAL

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

Mixtures of different phenols and different unsaturated aldehydes in the molar ratio 1:2 with HCl or sodium hydroxide as catalyst were heated in the temperature range between 300 to 340K. The products were dark viscous resins, soluble in acetone, THF and chloroform. After quick cooling, the samples for cmr were dissolved in deuterated acetone while the samples

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for GPC were dissolved in THF. The cmr spectra were cumulated above 3000 times. Pulse width was 14 μs (90° angle). For all spectra chemical shifts were quoted with respect to TMS as standard. The columns for GPC were filled with μ-Styragel 100 and 500 Å. The columns were calibrated by 2,2'-dihydroxydiphenylmethane, 4,4'-dihydroxydiphenylmethane and bis (4-hydroxyphenyl)2-propane.

RESULTS AND DISCUSSION

As mentioned before, four types of reactions between phenols and unsaturated aldehydes can take place. Experimentally we found, that the rate of polymerization of the double bonds and aldehyde groups under the selected conditions is lower as compared to the rate of addition of the unsaturated aldehydes to phenols. The mixtures of compounds formed in the reactions were separated by means of GPC. A representative GPC chromatogram resulting from the reaction between 2,5-dimethylphenol and crotonaldehyde is presented in Fig. 1.

Four peaks belong to compounds with molecular weights 120, 235, 380 and 590. From this result it can be concluded, that compounds between one to four phenols bonded to unsaturated aldehyde were formed. Quantities of compounds of different molecular weight depend on the reaction conditions and on the type of phenols and aldehydes used in the reaction. The most reactive were akrolein and 3,5-dimethylphenol, the least were p-cresol and crotonaldehyde.

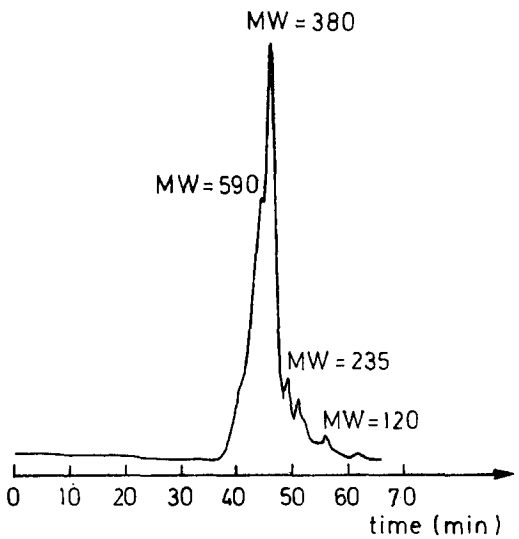

Fig.1:GPC chromatogram of reaction products between 2,5-dimethylphenol and crotonaldehyde

The rates of reactions in acid medium are higher than the rates in alkaline medium for all phenols and unsaturated aldehydes which were studied. In alkaline medium less reactive phenols react only at temperatures above

340K, while in acid medium they react allready at 300 (3,5-dimethylphenol) and 340K (p-cresol).

The cmr spectrum shows (Fig.2) four different regions of chemical shifts for the system of 2,5-dimethylphenol and crotonaldehyde. The signals between 35 and 45 ppm belong to methylene bridge bonded to one or two aromatic rings. The signals between 60 to 95 ppm belong to hydroxy and ether groups bonded to the primary and secundary carbon atom. The group of signals between 100 and 160 ppm belong to double bonds of unsaturated aldehydes and aromatic rings of phenols. The aldehyde groups have signals between 190 and 200 ppm. These groups of signals are similar for all phenols used. In table 1 chemical shifts of different groups are given. The identification of signals was made by using compound with similar characteristic groups[3,4], or by comparing phenols and aldehydes used for reaction and by calculation.

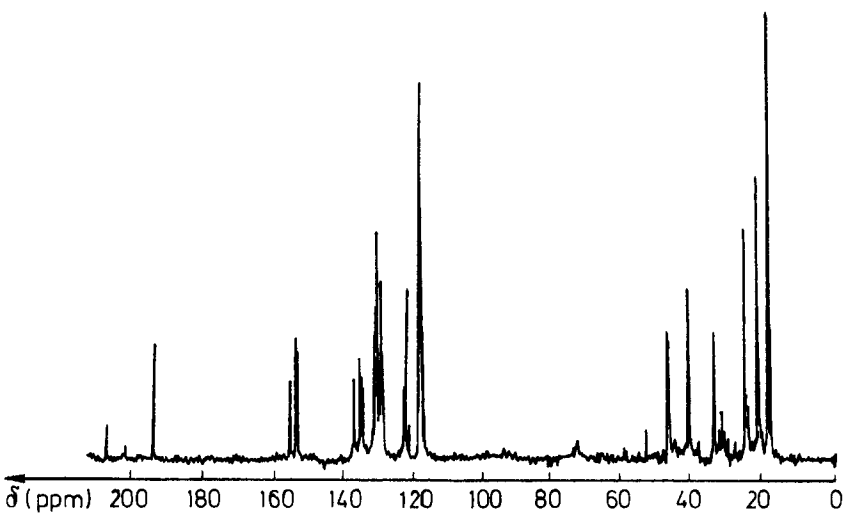

Fig.2: cmr spectrum of reaction products, between 2,5-dimethylphenol and crotonaldehyde

On the basis of the identified signals in the spectra, the reaction scheme for 2,5-dimethylphenol and crotonaldehide shown in Fig.3 can be predicted.

Reaction schemes for other phenols and acrolein are similar as for 2,5-dimethylphenol and crotonaldehyde. They differ only in which partial reaction is dominant.

Addition of the double bond to free ortho and para positions of phenols is dominant in the case of 3,5- and 2,5-dimethylphenol. Cresols react slightly more intensively than the addition of aldehyde groups. Products react further to form two, three and four benzene rings compounds and also high molecular weight compounds, structures of which are more complex.

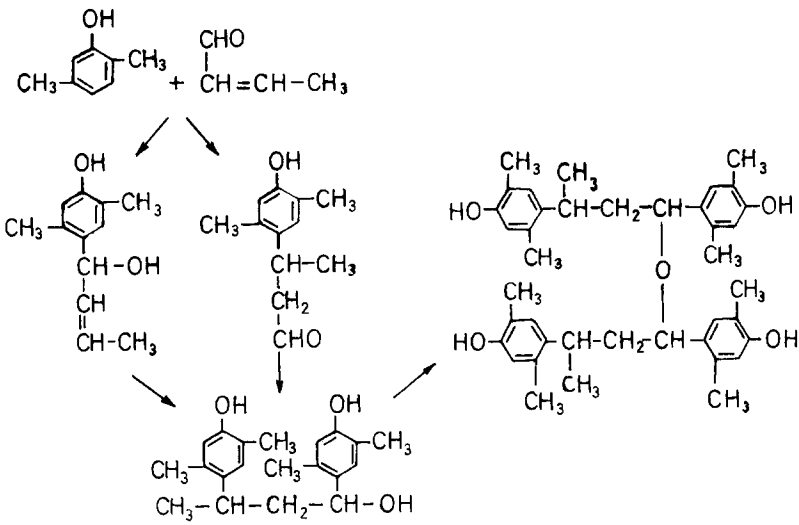

Fig.3: Scheme of the reaction between 2,5-dimethylphenol and crotonaldehyde

In Table 1 chemical shifts for different reaction products between higher phenols and unsaturated aldehydes are given.

TABLE 1

Chemical shifts for different reaction products between higher phenols and unsaturated aldehydes

Type of substituent		Chemical shifts (δ,ppm)
Ar-CH(OH)-CH=CH-CH_3	-CH-OH	72-74
	-CH-CH_3	150-155
	OH =C -CH	133-136
Ar-CH(CH_3)-CH_2-CHO	-CHO	191-192
	-CH-	30-35
	CH_2-	40-45
Ar-CH-O-CH-Ar	-CH-O-CH-	85-95
Ar-CH(OH)-CH=CH_2	=CH_2	101-103

The use of cmr and GPC methods provides rapid information about structure of reaction products between higher phenols and unsaturated aldehydes. The investigation on the structure and kinetics of unsaturated resins is being continued and further results will be reported later on.

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