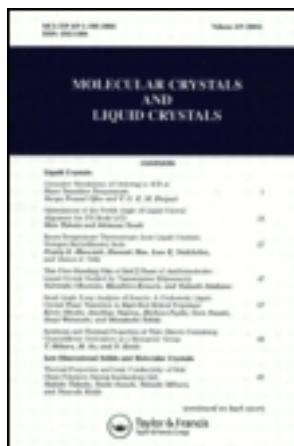


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Phenolic Resins Manufactured by Polycondensation in the Solid State from Pure Precursors: Crystallographic and ^{13}C NMR Investigations

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PHENOLIC RESINS MANUFACTURED BY POLYCONDENSATION IN THE SOLID STATE FROM PURE PRECURSORS ; CRYSTALLOGRAPHIC AND ^{13}C NMR INVESTIGATIONS.

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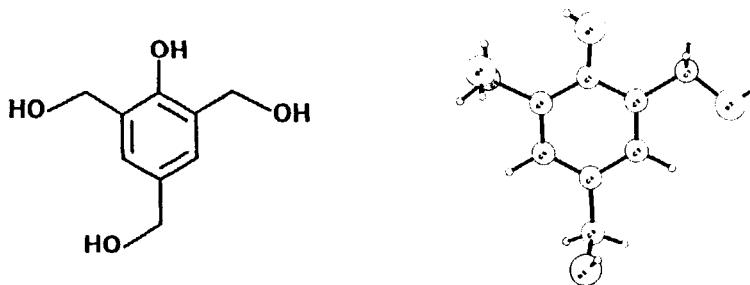
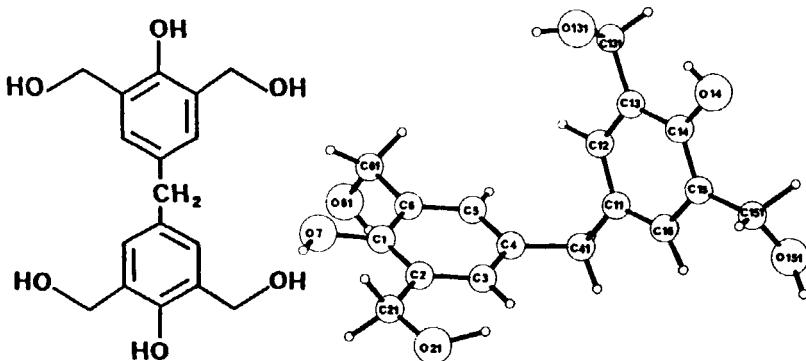
Abstract Two important precursors of phenolic resins manufactured from phenol are studied. Crystal structures and ^{13}C NMR spectra in solid state are determined for these pure compounds. The thermal polycondensation of one precursor is monitored by ^{13}C NMR.

INTRODUCTION

A number of precursors of phenolic resins have been prepared by condensation of phenols and formaldehyde. Single crystals of some precursors have been obtained (1) and their crystal structures determined. A full and particular study have been performed for 1 and 2 precursors which can be considered as important precursors of phenolic resins manufactured from phenol. The thermal polycondensation of precursor 1 is studied by ^{13}C NMR.

CRYSTAL STRUCTURES

Precursor 1 crystallizes in the monoclinic system with 4 molecules in the unit cell. The oxygen of one hydroxymethyl group in the ortho position lies in the benzene ring plane. The two other oxygen atoms of the hydroxymethyl groups are out of the ring plane and on the same side.

FIGURE 1. Precursor 1FIGURE 2. Precursor 2

Precursor 2 crystallizes in the triclinic system with 2 molecules in the unit cell.

On one benzene ring the oxygen atom of one hydroxymethyl groups is in the ring plane, the other is out of it. On the other benzene ring the two oxygen atoms of the hydroxymethyl groups are out of the plane and on both sides.

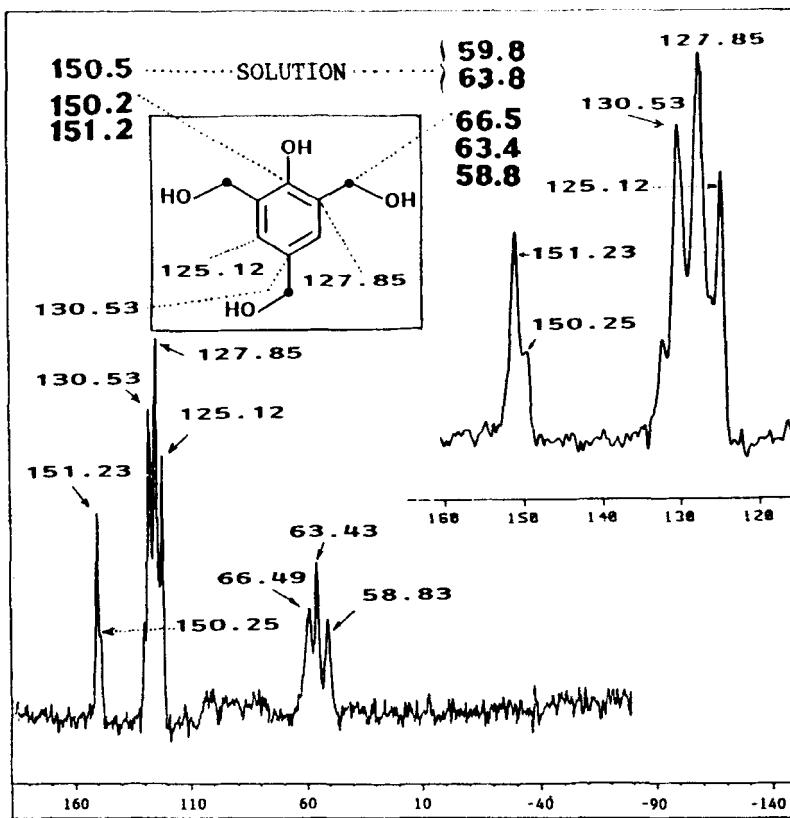


FIGURE 3. ^{13}C NMR Spectrum of precursor 1

¹³C NMR

The study of the ^{13}C NMR spectra of compound 1, Figure 3, shows that the carbons of the three hydroxymethyl groups correspond to three distinct peaks in the solid state (58.83 ; 63.43 ; 66.49 ppm) and only two peaks in solution (59.82 ; 63.84 ppm).

The first observed peak in solution corresponds to the two groups at ortho positions while the second corresponds to the group at para position. In the solid state the different orientations of hydroxymethyl groups given by X ray diffraction explain the three observed peaks without any assignment being possible.

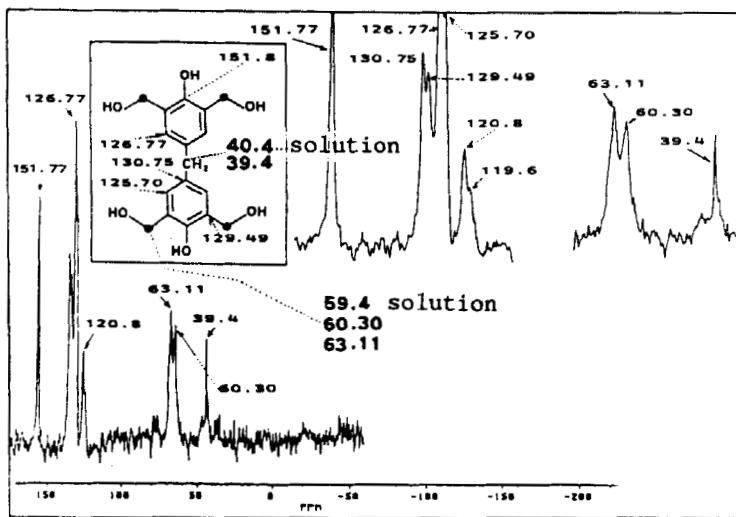


FIGURE 4. ^{13}C NMR spectrum for precursor 2

For compound 2, Figure 4, the four carbons of the hydroxymethyl groups correspond to only one peak in solution (59.4 ppm). In the solid state two peaks are observed (60.30; 63.11 ppm) due to different spatial orientations of these four groups.

The pure thermal polycondensation of 1 for 30 minutes at 120°C gives a peak at 73.4 ppm, Figure 5, which corresponds to the carbons of an ether bridge $-\text{CH}_2-\text{O-CH}_2-$ (2) (3). Indeed, the same peaks are

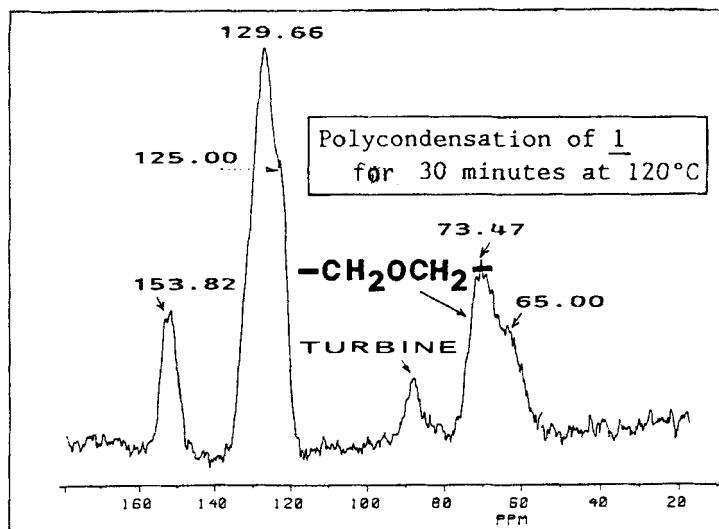


FIGURE 5. ¹³C NMR of the product of thermal polycondensation of 1

observed on the spectrum of di(2-hydroxybenzyl) ether, Figure 6. This substance has been specially synthesized to obtain this information.

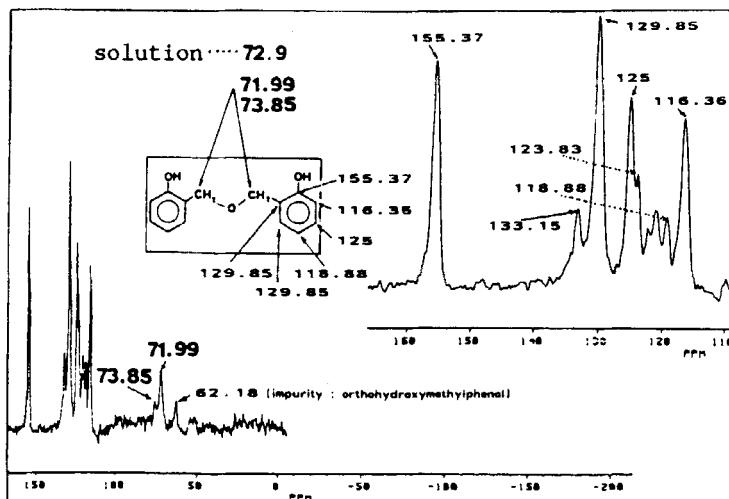


FIGURE 6. ^{13}C NMR spectrum of di(2-hydroxybenzyl)ether.

The same behaviour is observed during thermal polycondensation at 250°C and 30 minutes but, in this case, peaks begin to appear between 40 and 46 ppm, probably due to the formation of methylene bridges $-\text{CH}_2-$, Figure 7.

Thus the pure thermal polycondensation of 1 for a limited time leads to a polymer with a tridimensional structure essentially provided by ether bridges. In the solid state, 1 also leads to the formation of ether bridges.

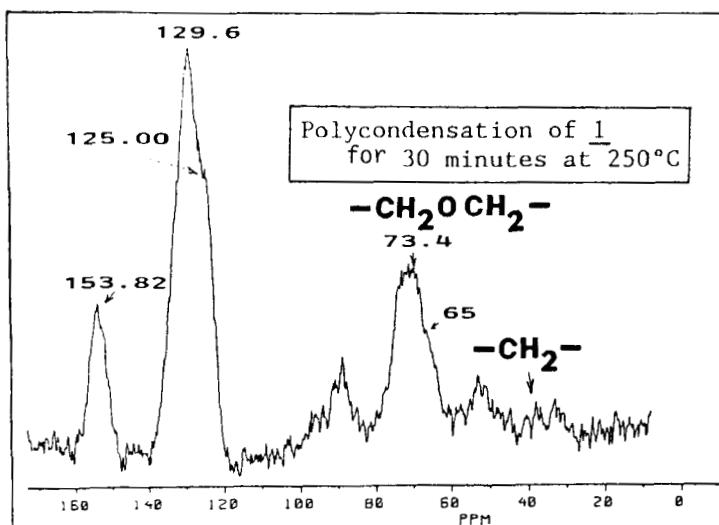
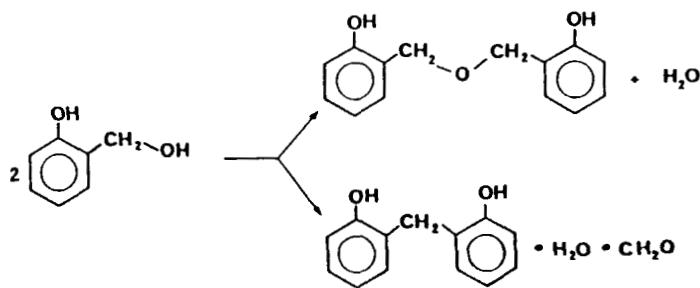


FIGURE 7. ^{13}C NMR spectrum of product of thermal polycondensation of 1

The reactions, written simply, in the case of 2-hydroxymethylphenol are as follows :



These basic studies, now in progress, should allow better understanding of the structures of phenolic resins and the ensuing properties.

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