

# Novolacs From Paraformaldehyde

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## Synopsis

Novolacs were prepared from phenol, paraformaldehyde, and variable amounts of water and methanol using oxalic acid as a catalyst. The retarding effect of water and methanol is clearly shown. Diffusion of reactants in the two-phase system does not seem to have a bearing on the measurements of reaction kinetics. A correlation between viscosity and refractive index of the polymer phase is shown. The advantages of using paraformaldehyde instead of aqueous formaldehyde solutions are summarized.

## INTRODUCTION

The most important commercial sources of formaldehyde are (1) aqueous solutions containing some methanol and small amounts of formic acid and (2) paraformaldehyde (solid polymeric hydrates). Both are used in the acid-catalyzed reactions with phenol for the production of novolacs.

Being a concentrated source of formaldehyde, the use of paraformaldehyde enhances the production per unit reactor volume as well as the heat which must be eliminated from the system. However, certain features, such as the optimum amounts, if any, of water and methanol to be added to the system or the possibility that the reaction be diffusion controlled when two phases appear, are not clearly stated in the related literature.

Water is necessary in order to depolymerize the paraformaldehyde. The presence of alcohols such as methanol also favors low degrees of condensation. As a counterpart, the effect of dilution on one hand and the formation of hemiformals on the other,



must have a retarding effect on the reaction kinetics. The change in the dielectric constant can also affect the reaction mechanism.

The aim of this paper is to present some illustrative results concerning the influence of water and methanol in the production of novolacs from paraformaldehyde. The influence of the stirring speed will also be discussed. Global, rather than mechanistic, trends will be emphasized. Conditions will be taken similar to those of industrial practice.

## EXPERIMENTAL

### Materials

A technical-grade paraformaldehyde with approximately 5.5% (w/w) H<sub>2</sub>O, and a 37.0% (w/w) aqueous formaldehyde commercial solution with 6% (w/w) methanol were the formaldehyde sources. Phenol was pure grade (PUREST), and the catalyst was oxalic acid with 99.5% minimum purity (BDH). Methanol was pure grade (PUREST).

### Reactor

The reactor was a 1-liter stainless steel vessel provided with an anchor impeller and a jacket for circulating oil or water coming from a thermostat. The vessel was hermetically sealed enabling the operation to be carried out under vacuum conditions (mechanical pump). When operating at atmospheric conditions a vertical condenser was used. A thermometer was placed in a sealed metallic tube entering the reaction mixture. Sampling as well as the final discharge of the polymeric mass was carried out by means of a 1/2-in. gate valve placed at the bottom.

### Polymerization

Let us call  $F$  = moles of formaldehyde,  $P$  = moles of phenol,  $A$  = moles of oxalic acid,  $W$  = moles of water,  $C$  = moles of methanol. The following ratios were always used:  $F/P = 0.80$ ,  $A/P = 0.01$ . When using the aqueous formaldehyde solution, water and methanol are automatically introduced in the reaction mixture in the following ratios:  $W/F = 2.57$ ,  $C/F = 0.15$ . When using paraformaldehyde, the water and methanol amounts could be arbitrarily varied. The following ratios were used:  $W/F = 0.26$ ,  $1.28$ , and  $2.57$ ;  $C/F = 0$  and  $0.15$ .

Polymerizations were carried out at 80°C and atmospheric pressure for several hours. The stirring speed could be varied between 200 and 1000 rpm. The usual value was 500 rpm unless otherwise stated. Samples were taken from time to time, and viscosity and refractive index were measured. When a predetermined viscosity had been reached the operation was followed under vacuum conditions for 2 hr at the same temperature. The novolac was then removed from the vessel.

### Viscosity

The polymer phase viscosity (after settling when two liquid phases were present) was measured at 25°C with a Brookfield Syncro-Lectric Viscometer RVT. The novolac-acetone solution intrinsic viscosity was measured at 20°C.

### Refractive Index

The polymer phase refractive index was measured with a Bausch & Lomb 334558 analyzer at 25°C.

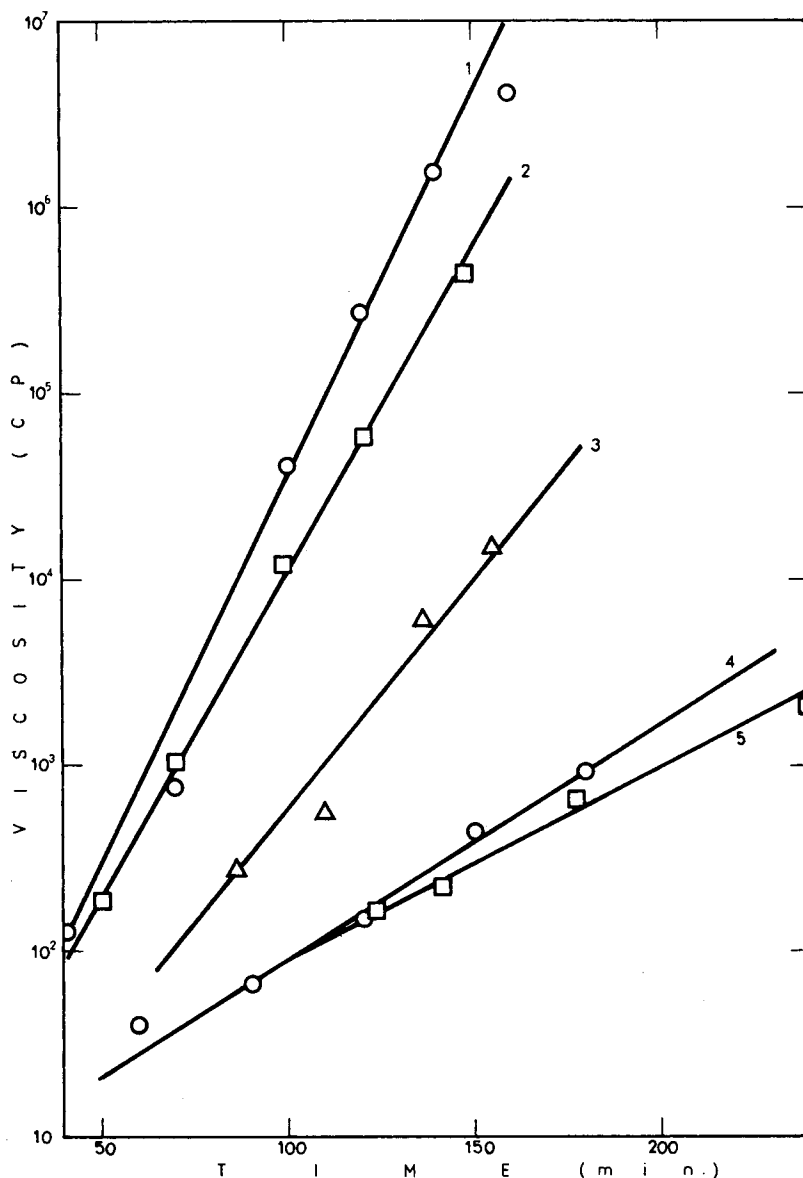


Fig. 1. Polymer phase viscosity as a function of reaction time: (1)  $W/F = 0.26$ ,  $C/F = 0$ ; (2)  $W/F = 1.28$ ,  $C/F = 0$ ; (3)  $W/F = 2.57$ ,  $C/F = 0$ ; (4)  $W/F = 2.57$ ,  $C/F = 0.15$  (starting from paraformaldehyde); (5)  $W/F = 2.57$ ,  $C/F = 0.15$  (starting from the aqueous formaldehyde solution).

## RESULTS AND DISCUSSION

### Kinetics

Figures 1 and 2 show the evolution of the polymer phase viscosity and refractive index. Viscosity increases exponentially with time. Note that both water and methanol have a very marked retarding effect on the kinetics. The two slowest runs were the ones using aqueous formaldehyde and a synthetic analogous mixture starting from paraformaldehyde. The small departure between them

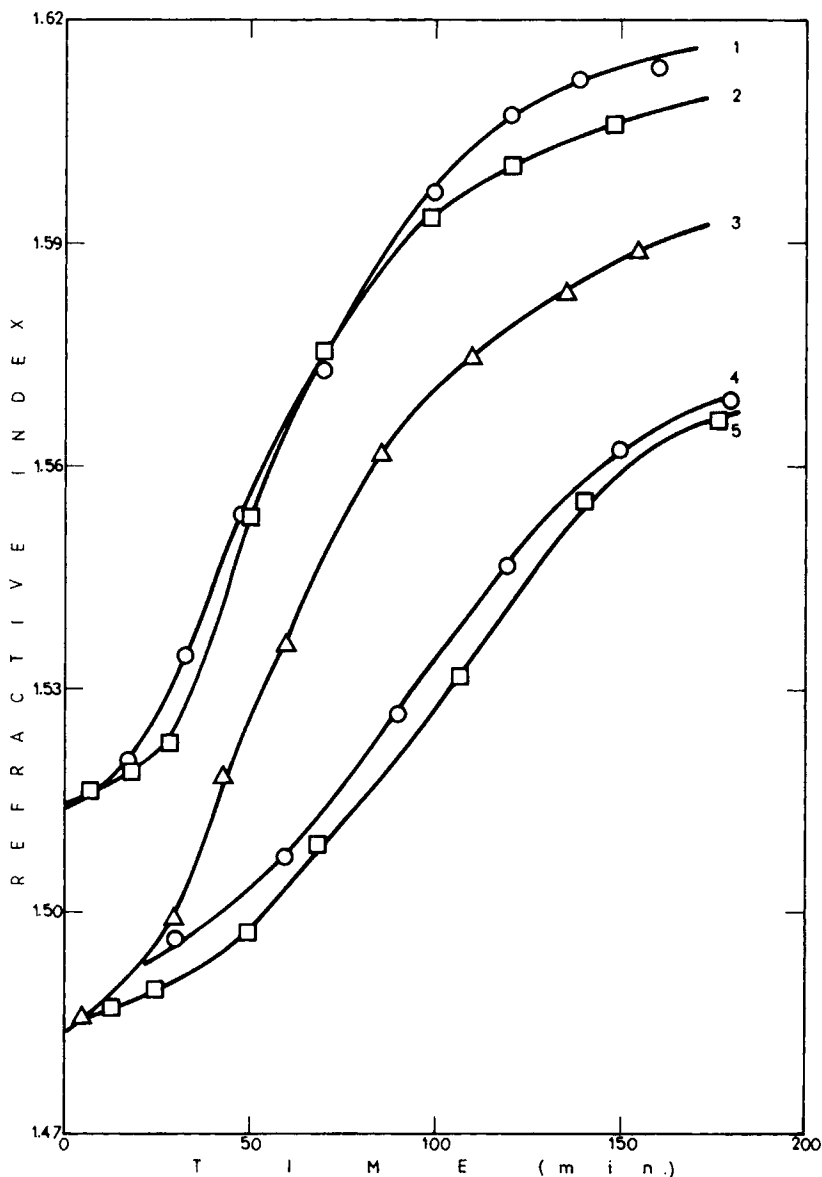


Fig. 2. Polymer phase refractive index as a function of reaction time: (1)  $W/F = 0.26$ ,  $C/F = 0$ ; (2)  $W/F = 1.28$ ,  $C/F = 0$ ; (3)  $W/F = 2.57$ ,  $C/F = 0$ ; (4)  $W/F = 2.57$ ,  $C/F = 0.15$  (starting from paraformaldehyde); (5)  $W/F = 2.57$ ,  $C/F = 0.15$  (starting from the aqueous formaldehyde solution).

may be entirely due to slightly different formulations. Though the run with the least amount of water (curve 1) shows the highest final conversion, initial values somewhat overlap with the second curve. Suggestively, solid paraformaldehyde appeared in initial samples of run 1. Runs in anhydrous conditions had severe limitations for the complete disappearance of solid paraformaldehyde. In every case, the higher the reaction rate, the less the observed time for the appearance of two liquid phases.

By varying the stirring speed from 200 to 1000 rpm, no significant change

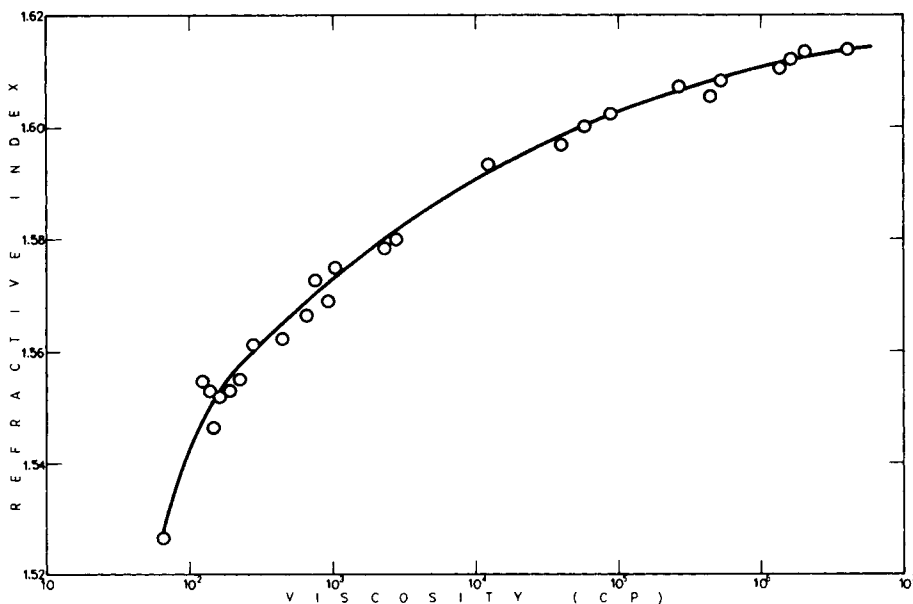


Fig. 3. Correlation between refractive index and viscosity at 25°C.

in the position of the kinetic curves was observed. At least in this range, diffusion of reactants in the two-phase system does not seem to have a bearing on the measurement of reaction kinetics. It is worth noting that the Reynolds number in the selected speed range is of the same magnitude as the one characterizing the industrial process.

Runs with a high reaction rate show an initial temperature rise of 2° or 3°C. An impeller speed lesser than 200 rpm magnified the temperature difference.

Figure 3 shows the observed correlation between the refractive index and the viscosity, both at 25°C.

### Properties of Novolacs

The intermediate products show good properties as wood adhesives. This quality disappears with vacuum treatment, denoting the possible influence of free phenol in the adhesive character.

A typical novolac was prepared by reaching a viscosity of 10<sup>7</sup> cp under atmospheric pressure, followed by 2 hr under vacuum conditions. A colorless solid was obtained which yielded a white powder upon grinding. Its intrinsic viscosity in acetone at 20°C was  $[\eta] = 3.88 \times 10^{-2}$  dl/g. For this case, the following  $[\eta]-\bar{M}$  relationship has been proposed<sup>1</sup>:

$$[\eta] = 1.08 \times 10^{-2} \bar{M}^{0.2} \quad (3)$$

Then,

$$\bar{M} = 612 \text{ g/g-mole}$$

## CONCLUSIONS

Novolacs can be prepared with very good rates by using paraformaldehyde as a formaldehyde source and the following reactant ratios:  $F/P = 0.80$ ,  $A/P = 0.01$ ,  $W/F = 0.26$ , and  $C/F = 0$ . Greater amounts of water and/or methanol decrease the reaction rate significantly. Lesser amounts of water cause severe limitations in the complete dissolution of the solid paraformaldehyde.

The reaction does not appear to be diffusion controlled in the two-phase system (the impeller speed has no influence on the reaction rates).

Summarizing, by using paraformaldehyde instead of aqueous formaldehyde, not only the production per unit reactor volume is greater, but the rate is considerably increased. As a counterpart, the heat flux to be eliminated also increases the difficulty of using typical reactors for the high-rate production of novolacs. However, the use of a reactor with great external area-to-volume ratio, at least for the initial polymerization period, will give convenient heat dissipation enabling the operation to be carried out in a considerably lesser time than it frequently takes in industrial practice.

This research has been financed in part by a grant of the Comision Nacional de Estudios Geofisicos, Argentina.

## References

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Received September 26, 1977