the theoretical ones, but for penta- and hexa-oxyethylene glycol were smaller than the theoretical ones.

As is mentioned above, it is noticeable that in the cryoscopic determination of molecular weight of polyoxyethylene glycol and its derivatives the observed value varies with the solvent. Although the concentration dependence of the value of Mc has a close relation with the interactions between solute molecules, and solute and solvent molecules, no further detailed discussion on these interactions or solvent effects can be given from the present results alone.

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11. Studies on the Heat Stability of Polyvinylacetals

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Heat stability of polyvinylacetals was measured by the weight loss during heat-treatment at various temperatures. Polyvinylformal and --butyral were found to decompose measurably at 180-220°C. But the rate of decomposition was markedly retarded by boiling in aqueous solution of Na_2CO_3 or NaOH.

For polyvinylalcohol, as the raw material of acetals, and for various acetals such as formal, acetoacetal, butyral, octylacetal and laurinacetal, the decomposition curves were obtained and shown in Figure 1.
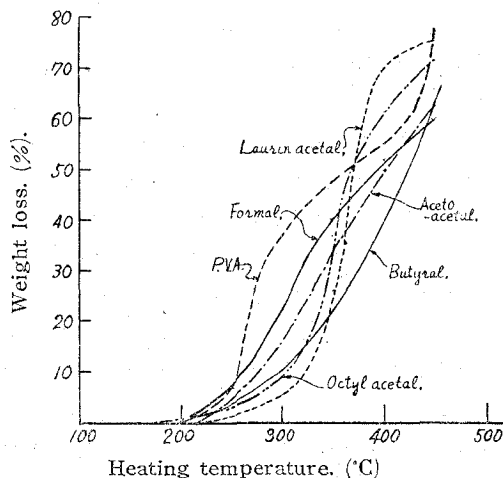

Fig. 1. Decomposition curves. (Acetalization degree 65~70%)

The maximum rate of decomposition falls in the series laurin acetal > octyl acetal > butyral > formal and acetoacetal. The decomposition of polyvinylalcohol occurs at relatively lower temperature and at slightly faster velocity. The viscometric measurements in 80% formic acid solution were

performed for the heat treated formals and these results were shown in Table 1.

Table 1. Viscosities of heat treated formals.

Treatment	$[\eta]$	k'
none	0.094	0.21
200°C 5 min.	0.091	0.72
250°C 3 min.	0.077	0.77
250°C 5 min.	0.065	0.75
250°C 10 min.	0.052	0.74

in 80% HCOOH at 20°C

It was found from Table 1 that some degradation occured at 250°C. and the k'-value in Huggins' viscosity equation slightly increased.

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12. Activation of Methyl Group by Nitro Group. (V)

Some Rate Studies and Their Results

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Paranitrotoluene, by acting on methanolic alkali, absorbs oxygen to give rise to p,p'-dinitrodibenzyl and dinitrostilbene. The authors have traced kinetically the course of oxygen absorption. Results obtained are as follows.

(1) Total oxygen absorbed is much more than the expected theoretical amount. This suggests that a certain fraction of oxygen absorbed has been employed elsewhere than in the self- condensation of p-nitrotoluene. Our examinations have identified several oxidation products of methanol in the reaction mixture. Theoretical amount of oxygen consumed has been calculated from the analytical data on the oxidation products as well as the yields of dinitrodibenzyl and dinitrostilbene. A little discrepancy between the observed and the theoretical in oxygen balance is probably due to the formation of a resinous matter which has been observed contaminating the main products.

Nitrobenzene or m-nitrotoluene does not absorb oxygen under the same experimental conditions.

(2) The absorption of oxygen proceeds according to the first order with respect to the concentration of p-nitrotoluene.

(3) The absorption rate does not decrease even if the air instead of oxygen is used as a reactant. This suggests, at least in a certain range, that the variation in partial pressure of oxygen little affects the rate; and so oxygen probably can not participate in the rate determining step of the reaction.