Statistical aspects for the production of novolacs

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Statistical parameters for the phenol (P)–formaldehyde (F) condensation under acid conditions are derived in the frame of Flory–Stockmayer's theory. Phenol is assigned an average functionality $f = 2.31$ as proposed by Drumm and Le Blanc (1972). Results show that a molar ratio (F/P) = 0.881 leads to gelation at full formaldehyde conversion. Free phenol and number and weight average molecular weights are calculated, showing a significant dependence on the final formaldehyde conversion and the selected molar ratio (F/P). A good agreement between theoretical predictions and experimental results is obtained

Keywords Statistics, condensation, novolacs, phenol, formaldehyde; gelation

INTRODUCTION

Flory[1] suggested than phenol (P)–formaldehyde (F) reactions could be considered as the polycondensation of trireactive phenol, with formaldehyde merely supplying the interunit linkage. This viewpoint is frequently quoted in the literature and used in statistical models for the production of novolacs[2]. However, Flory's simplifying assumptions: (1) equal reactivity of functional groups of the same type; (2) all groups react independently of one another; and (3) no intramolecular reactions occur in finite species, do not apply in the acid condensation of phenol with formaldehyde. Main restrictions are the unequal reactivity of *o* and *p* positions of phenol as well as the changes in reactivity as substitution continues[3]. A disagreement between experimental observations and Flory's theoretical predictions may be easily shown.

Trying to assign a correct average functionality for phenol, Drumm and Le Blanc[3] synthesized three novolacs, using different (F/P) molar ratios and similar formaldehyde conversions (from reported data they may be estimated as x_f: 0.936, 0.931 and 0.959). Molecular weight distributions, measured by g.p.c. showed a very good agreement with Stockmayer's weight distribution function[4] when an average functionality $f = 2.31 \pm 2\%$ was assigned to phenol.

The aim of this paper is to carry out statistical calculations for the production of novolacs, using Drumm and Le Blanc's proposition for the phenol functionality, and to compare theory with experimental observations. Equations valid in the frame of Flory–Stockmayer's model will be used, as derived by Macosko and Miller[5].

EXPERIMENTAL

Gelation conditions

Consider P moles of 2.31 functional monomer (phenol) reacting with F moles of bifunctional monomer (formaldehyde). Let the system polymerize until some fraction x_p of the P groups and some fraction x_f of the F's have reacted. These fractions are not independent but related through:

$$x_f = \frac{2.31\,P}{2F}\,x_p = r\,x_p \tag{1}$$

where r is the ratio of functionalities.

The branching coefficient is given by:

$$\alpha = x_p x_f = x_f^2 \cdot r \tag{2}$$

At the gel point

$$\alpha_c = \frac{1}{(2.31-1)(2-1)} = 0.763 \tag{3}$$

From equations (1) to (3), the $(F\ P)$ molar ratio which leads to gelation when $x_f = 1$, arises:

$$(F\ P) = 0.881 \tag{4}$$

Thus, the industrial production requires a formulation verifying $(F\ P) < 0.88$, in order to avoid gelation in the reactor. This is known from experience and values of $(F/P) \leqslant 0.85$ are always used[3,6]

Free phenol

The weight fraction of free phenol in the novolac is given by the first term of Stockmayer's weight distribution[4] as.

$$w_1 = (1-\alpha)^{2.31} \tag{5}$$

From equations (1), (2) and (5), we get

$$w_1 = \left\{1 - \frac{2x_f^2}{2.31}(F\ P)\right\}^{2.31} \tag{6}$$

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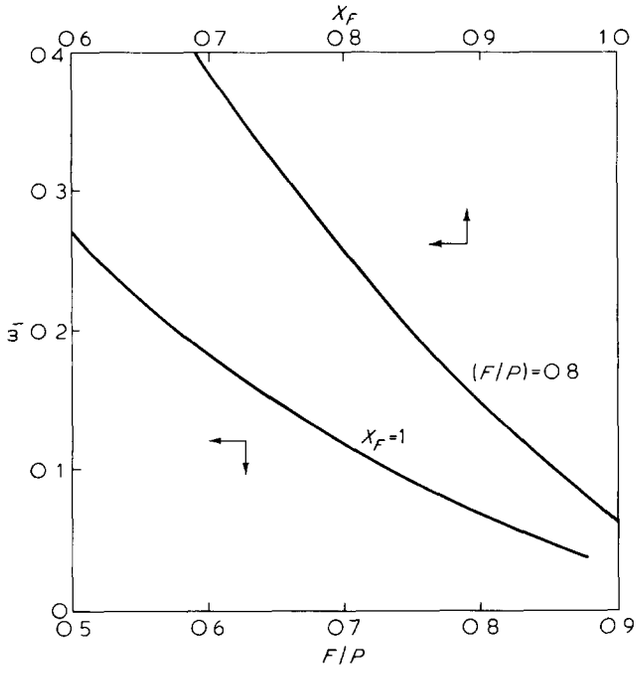

Figure 1 Weight fraction of free phenol as a function of the formaldehyde/phenol molar ratio (x_F = 1) or the formaldehyde conversion (F/P = 0.8)

Figure 1 shows the decrease in the weight fraction of free phenol, when increasing (F/P) at $x_F=1$, or increasing x_F at $(F/P)=0.8$. Note the significant dependence of w_1 on the fraction of reacted formaldehyde, x_F.

A proton magnetic resonance (p.m.r.) analysis of a commercial novolac[3] showed that for $(F/P)=0.85$, the unreacted phenol was 6.15%. This is to be compared with $w_1=4.61\%$, predicted from equation (6) when $x_F=1$. Minor variations in x_F produce a significant change in w_1 (i.e. for $x_F=0.976$, $w_1=6.15\%$).

Number average molecular weight

$$\bar{M}_n=\frac{M_P P+M_F F}{P+F-2.31\,P\,x_F/r} \tag{7}$$

where M_P is the molecular weight of phenol and M_F is the molecular weight of formaldehyde. However, the formation of a methylene linkage (CH_2) from two novolac hydrogen atoms (2 H) and a formaldehyde molecule (CH_2O) requires a water molecule to be deleted. In order to avoid correcting the $\bar{M}_n$ value accounting for the loss of weight from the condensate, we can arbitrarily assume that each formaldehyde molecule contributes with only the C atom to the novolac structure, the remaining H_2O being deleted. By taking $M_P=94$ and $M_F=12$, no correction to equation (7) is necessary.

Equation (7) may be rearranged with the aid of equation (1) to give:

$$\bar{M}_n=\frac{12(F/P)+94}{1-(F/P)(2x_F-1)} \tag{8}$$

Very often the polymerization is carried out under vacuum conditions (at the end of the process), distilling off practically all of the water and much of the unreacted phenol. The corresponding number average molecular weight, $\bar{M}'_n$, of the resulting novolac may be calculated as follows:

$$\bar{M}_n=x_1M_1+\sum_{i=2}^{\infty}x_iM_i \tag{9}$$

$$\bar{M}'_n=\sum_{i=2}^{\infty}M_ix_i/(1-x_1) \tag{10}$$

assuming that all phenol has been removed from the novolac. Combining both equations gives:

$$\bar{M}'_n=\bar{M}_n(1-w_1)/(1-x_1) \tag{11}$$

where

$$x_1=w_1\bar{M}_n/M_1 \tag{12}$$

is the molar fraction of unreacted phenol in the original novolac.

Figure 2 illustrates $\bar{M}_n$ and $\bar{M}'_n$ values as a function of the (F/P) ratio. For the normal (F/P) range, from 0.75 to 0.85[6], $\bar{M}_n$ varies between 400 and 700. However, if the reaction is stopped after 95% formaldehyde conversion, a considerable decrease in the resulting $\bar{M}_n$ is obtained, as shown in the figure. The dotted line represents the maximum possible value of the number average molecular weight of a novolac, prepared under normal practical conditions, after removing all the unreacted phenol. If the (F/P) gelation ratio is used $(F/P=0.881)$, the maximum number average molecular weight results. It is $\bar{M}_n=884$ (including free phenol) of $\bar{M}'_n=1286$ (after removing unreacted phenol).

For the commercial novolac already mentioned, a p.m.r. analysis showed that $\bar{M}_n=711$ (including unreacted phenol), for $(F/P)=0.85$[3]. Equation (8) predicts $\bar{M}_n=695$, in good agreement.

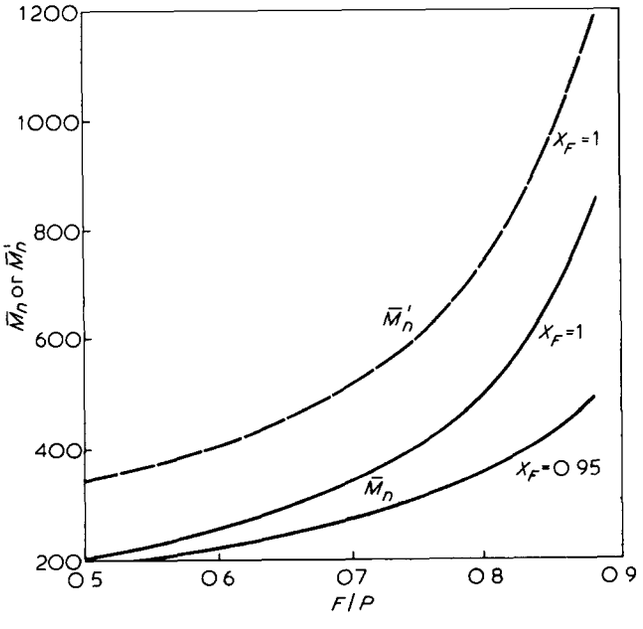

Figure 2 Number average molecular weight as a function of the formaldehyde/phenol molar ratio, for different formaldehyde conversions ($\bar{M}_n$ includes all unreacted phenol, $\bar{M}'_n$ is for a novolac free of phenol)

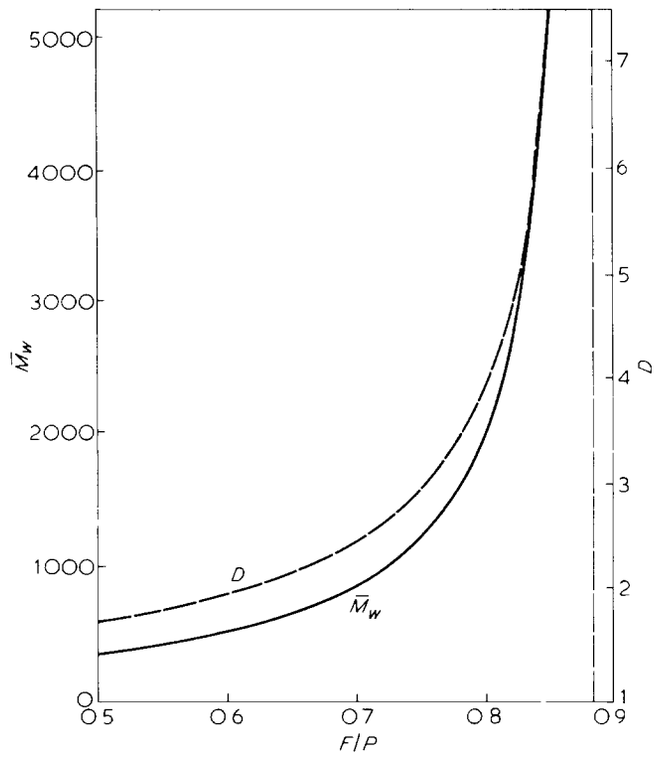

Figure 3 Weight average molecular weight and dispersion index, at full formaldehyde conversion, vs. the formaldehyde/phenol molar ratio

However, a novolac was prepared in our laboratory, using a reactor previously described[7], a molar ratio $(F/P) = 0.80$, and oxalic acid as catalyst. The reaction was carried out until $x_F \rightarrow 1$. Gentle vacuum conditions were applied in order to remove water, but trying to keep the unreacted phenol in the reactor (a small amount was, however, removed). The novolac was then dried over four hours at 140°C. Under these conditions, the theoretical number average molecular weight is $\bar{M}_n = 518$ (including all unreacted phenol). The experimental value, obtained with a cryoscopic method using dioxane as solvent, was $\bar{M}_n = 557$. The remaining unreacted phenol was then removed by heating the novolac to 160°C under vacuum (3 h). An i.r. spectrum (Perkin–Elmer 599) of the distilled product showed that it was mainly phenol, with traces of oxalic acid. The theoretical number average molecular weight is $\bar{M}'_n = 757$. The experimental value as determined by cryoscopy in dioxane was $\bar{M}'_n = 745$. The agreement is good.

Weight average molecular weight

$$\bar{M}_w = \frac{(2r/f)(1 + x_F^2/r)M_P^2 + [1 + (f-1)x_F^2/r]M_F^2 + 4x_F M_P M_F}{(M_I + 2rM_P/f)[1 - (f-1)x_F^2/r]} \quad (13)$$

which, for our case ($f = 2.31$), may be rearranged to:

$$\bar{M}_w = \frac{1.532 + (P/F)94 + [81.385 + 1.737(F/P)]x_F^2 + 48x_F}{[0.128 + (P/F)][1 - 1.1342(F/P)x_F^2]} \quad (14)$$

Figure 3 shows the variation of $\bar{M}_w$ for $x_F = 1$, as well as the dispersion index:

$$D = \bar{M}_w / \bar{M}_n \quad (15)$$

as a function of the formaldehyde/phenol molar ratio. As expected, $\bar{M}_w \rightarrow \infty$ when $(F/P) \rightarrow 0.881$ (gelation molar ratio). Also, D increases significantly with (F/P). This means that the resulting novolac may vary substantially from batch to batch if extreme care is not taken to make a precise control of the (F/P) molar ratio. This is particularly important in the range 0.80–0.85, which is widely used for the industrial production. Another factor which is closely related to $\bar{M}_w$ is the viscosity of the novolac. As $\bar{M}_w$, it may change significantly from batch to batch if (F/P) is not exactly reproduced each time. Viscosity changes will lead to variations in the reactor's discharge time

Figure 4 shows the increase in $\bar{M}_w$ with the degree of conversion x_F, for $F/P = 0.8$. There is a great sensitivity of the $\bar{M}_w$ value, and the associated viscosity, with the selected end point.

The increase in $\bar{M}_w$ due to the removal of unreacted phenol may be easily calculated:

$$\bar{M}_w = \sum_{i=1}^{i'} w_i M_i = w_1 M_1 + (1 - w_1) \sum_{i=2}^{i'} M_i w_i / (1 - w_1) \quad (16)$$

and

$$\bar{M}'_w = \sum_{i=2}^{i'} M_i w_i / (1 - w_1) = (\bar{M}_w - w_1 M_1)/(1 - w_1) \quad (17)$$

CONCLUSIONS

By using the average functionality $f = 2.31$[3] for phenol in its condensation with formaldehyde under acid conditions, equations valid in the frame of Flory–Stockmayer's model provide statistical parameters which are useful for analysing aspects related to the industrial production of novolacs. Several polymer characteristics (average molecular weights, free phenol amount) showed a strong dependence on the formaldehyde conversion level and the selected molar ratio (F/P). This is particularly relevant in ranges used in the production of

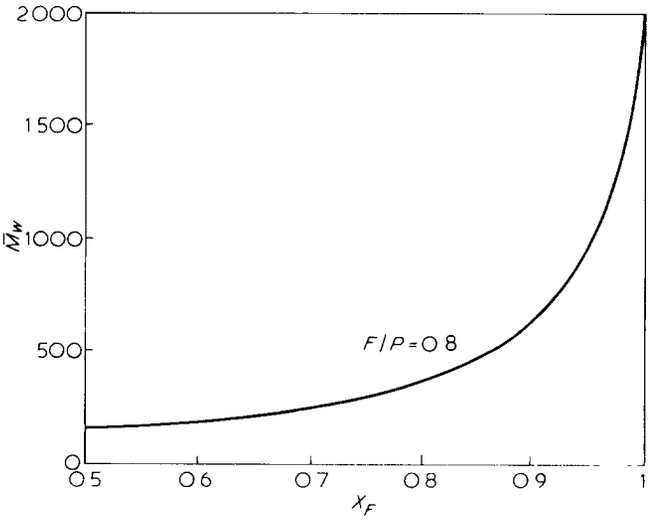

Figure 4 Weight average molecular weight vs. formaldehyde conversion for $(F/P) = 0.8$

commercial novolacs ($0.9 < x_F < 1$; $0.75 \leqslant F/P \leqslant 0.85$). It was also shown that a molar ratio (F/P) = 0.881 leads to gelation at full formaldehyde conversion.

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