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Functionality in phenol–formaldehyde step-growth polymerization

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Fundamental concepts of functionality within polymer systems are restated, with particular reference to the phenol–formaldehyde (P–F) step-growth polymerization. The functionality of both reactants is governed by the stoichiometry. A distinction between the number of functional groups (potential functionality) and actual functionality is made. At the extent of reaction used in practical systems when $P/F > 1$ (i.e. novolacs) the actual functionality of formaldehyde will always be two, while the actual functionality of phenol will approach a maximum of two. When $P/F < 1$ (i.e. resoles), a more complex situation arises, with formaldehyde never achieving an actual functionality of two while phenol may now attain an actual functionality greater than two. The functionality value for phenol within novolac resins of 2.31 quoted in the literature is shown to be in error. Results from an accurate molecular weight analysis of several industrial resins and using pure novolac-like compounds as g.p.c. standards give rise to actual functionality values of phenol in the range 1.49–1.72. This in turn can be used to calculate P/F ratios which range from 1.21 to 1.34. These compare well with typical starting P/F ratios used during the synthesis of P–F resins. © 1997 Elsevier Science Ltd.

(Keywords: functionality; step-growth; polymerization; phenol; formaldehyde; novolac; resole)

INTRODUCTION

Polymers derived from phenol (P) and formaldehyde (F) are the oldest reported synthetic polymer systems. They possess many desirable physical and chemical properties and this, coupled with their relative cheapness, has resulted in their extensive industrial use and numerous theoretical studies[1].

However, there is still confusion and contradiction in the literature on basic parameters such as molecular weight and structure of the polymers, and the functionality of the phenol residue incorporated into the polymer chains. In particular, an actual (or effective) functionality of 2.31 for phenol has been deduced[2] and subsequently used in analysis and modelling[3] of phenolic resins. As we will show in this paper, this value has no physical or chemical basis and in terms of the structure of phenol–formaldehyde (P–F) resins makes no sense. Because of this confusion, it seems desirable to restate some of the basic definitions pertaining to step-growth reactions and then to relate the functionality figures quoted with chemical structures consistent with these values.

Flory[4] and others[5], including our group[6], have detailed the classification of polymerizations based on kinetic parameters into step-growth and chain-growth reactions. Carothers[7,8] assigned functionality to compounds with regard to their potential to polymerize. For example, the double bond in styrene is assigned a functionality of 2, since styrene is capable of polymerizing to a linear polymer (in traditional organic jargon styrene has a functionality of one; hence we need to distinguish between the number of functional groups and actual functionality). The actual functionality of a molecule is determined by how many other molecules it can join. This, of course, is a function of the chemistry that takes place during the polymerization.

A case which clearly demonstrates the dependence of functionality upon the chemistry of the reaction is that of ring formation during the polymerization of diallyl compounds[9]. Here we have two double bonds per molecule, and it is tempting to assign a functionality of 4 to the molecule (2 per double bond). But some diallyl monomers (e.g. ethylene glycol divinyl ether) polymerize via a cyclopolymerization, so each monomer molecule joins only two other molecules, and hence the actual functionality is 2.

As with chain-growth reactions, the actual functionality of reactants in step-growth polymerization is also dependent upon the chemistry of these reactions. There are several examples of such step-growth polymerizations[6].

This definition of functionality also means that within step-growth polymerizations the actual functionality is dependent on stoichiometry. The P–F reaction is a typical step-growth reaction in which the reactants are not present in the required stoichiometric amounts for complete reaction of all functional groups and hence the actual and potential functionalities need to be considered. Although the potential functionality of individual phenol and formaldehyde units can be regarded as 3 and 2 respectively, when reacted in unequal stoichiometric amounts (with respect to the number of functional groups present) the actual functionality of these units vary. It appears that some previous studies on

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P–F systems have overlooked some of these basic concepts when considering functionality.

A contributing factor to this state of affairs has been the lack of suitable standards for gel permeation chromatography (g.p.c.) calibration during P–F resin analysis. G.p.c. is one of the major tools used in evaluating molecular weights and hence information on the structure and functionality of P–F resins. G.p.c. analysis of the two recognized classes of P–F polymers is complicated by extensive hydrogen bonding[10,11]. These classes of P–F resins reflect the reaction conditions, the extent of reaction and the ratio of phenol to formaldehyde (P/F) used in the synthesis. Novolacs are usually prepared under acid conditions using P/F ratios of >1 and all the F functional groups are reacted. On the other hand resoles are prepared under alkaline conditions at a P/F ratio of <1 and the reaction is stopped to give structures with free methylol groups.

Because g.p.c. separates molecules according to their hydrodynamic volume it is necessary to calibrate the system with standards of known molecular weight that have similar molecular characteristics and architecture to the sample polymer. Otherwise a 'universal' calibration[12] is required, which accounts for the differences in the hydrodynamic volumes of the standard and sample polymers. Unfortunately, reliable data (e.g. Mark–Houwink parameters) are not always available to perform the 'universal' calibration, hence g.p.c. calibration can be a major stumbling block in obtaining molecular weights of some polymers.

Such problems can be observed in the molecular weight analysis of novolacs, where varying molecular weights have been reported using the g.p.c. technique[13–19]. These variances can be attributed *inter alia* to the lack of suitable standards[10,15], and such results should be interpreted on a qualitative basis only. To overcome this problem, we have synthesized[20] a series of pure compounds which model the structural residues typically found in novolac polymers. These have been used as standards for g.p.c. analysis of commercial resins allowing us to be confident of the molecular weights obtained[11]. From this accurate molecular weight analysis we can then draw conclusions about the structure and functionality of the novolac resins.

The reaction of phenol with formaldehyde has been modelled by numerous workers using either statistical (i.e Flory/Stockmayer[3,4,16,21,22] or Monte Carlo[23–25] methods) and/or kinetic[26–28] approaches. Such studies attempt to predict the molecular weight distributions, amount of branching and gel points of P–F polymerizations. Functionality is particularly important to the Flory/Stockmayer-type model, where functionality values need to be assigned to both phenol and formaldehyde. The approach of Drumm and LeBlanc[2] was to use this method assuming that the P–F system could be modelled by treating phenol as exclusively trireactive and that the formaldehyde only supplies the interlinking unit[29]. After synthesizing novolac resins and analysing their molecular weight Drumm and LeBlanc[2] deduced a value of 2.31 for the actual (or effective) functionality of phenol in novolacs. This figure has been used and quoted by others since[1,3] even though it has been noted that 'the method has no reliable scientific foundation'[22].

In this paper we reassess the literature values on functionality and structure of phenol–formaldehyde systems. Initially this is based upon simplified structures, and then using the accurate molecular weight averages of phenolic resins extrapolated to more complex industrial resins. Actual functionality values obtained can then also be used to calculated P/F ratios used to synthesize the resins.

RESULTS AND DISCUSSION

Functionality of some simple models

In the aqueous environment used in the preparation of most novolacs or resoles, formaldehyde can be considered as methylene glycol. This has a potential functionality of 2. Phenol has a potential functionality of 3. In the preparation of a typical novolac the P/F ratio is >1. In functionality terms, the methylene glycol reaches its potential functionality of 2 (i.e. actual functionality = potential functionality) whereas phenol will have a functionality < 2. Consider the compound depicted in *Figure 1*, a model for a novolac.

Then the actual functionality (f_{actual}) of phenol can be derived from

$$f_{\text{actual}} = \frac{2+2n}{n+2} \qquad (1)$$

Here it is necessary to consider the contribution to the functionality of both end units (functionality of 1) and internal phenolic units (functionality of 2). If the novolac contains $(n+2)$ phenolic units, then there are n internal units and only two end units. For novolacs of less than 15 phenolic units, the actual functionality increases rapidly with the number of units added. However, for longer linear chains, the actual functionality approaches a limiting value of 2. That is, as the ratio of P/F approaches 1, the actual functionality of phenol approaches 2. This means that in a novolac the structure is controlled by limiting the functionality of the phenol, or in other words, controlling the stoichiometry. The influence of the chain length upon the actual functionality of a linear novolac is depicted in *Figure 2*. This calculation holds

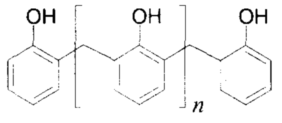

Figure 1 A linear novolac structure where $f_{\text{actual}}(\text{phenol}) \rightarrow 2$ as $n \rightarrow \infty$

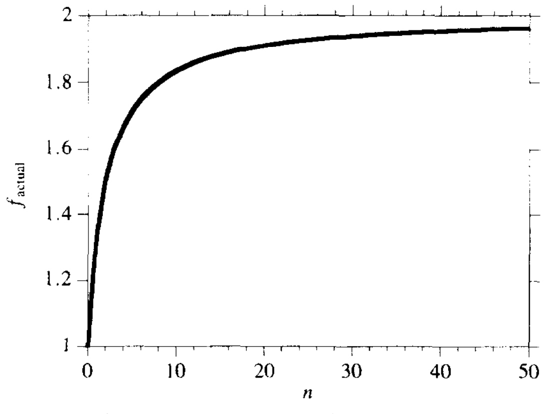

Figure 2 The effect of chain length (n, as defined in text) upon f_{actual} for novolacs

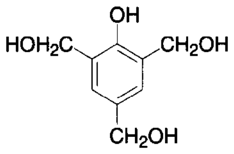

Figure 3 A model compound for resoles where f_{actual}(phenol) = 3 and f_{actual}(formaldehyde) = 1

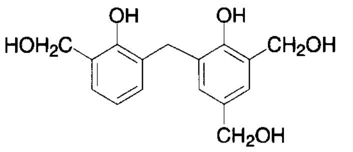

Figure 4 A model resole structure which has f_{actual}(phenol) = 2.5 and f_{actual}(formaldehyde) = 1.25

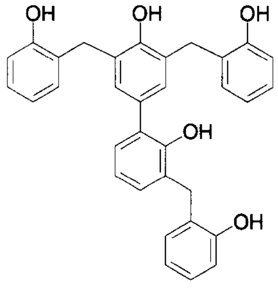

Figure 5 A model novolac structure containing a branching unit

irrespective of the substitution pattern (i.e. the percentage of *ortho–ortho′*, *ortho–para′* and *para–para′* methylene linkages) present.

The case of a resole is more complicated in functionality terms. Consider the simplified example of 1 mole of phenol (3 equivalents) reacted with 3 moles of methylene glycol (aqueous formaldehyde) to give the idealized structure in *Figure 3*.

Then in terms of functionality we have the opposite to the novolac. That is the phenol achieved its full functionality of 3 (i.e. potential and actual functionality are the same). The methylene glycol has an actual functionality of 1. Resoles with two or three phenyl residues and with some unsubstituted aromatic *ortho* or *para* positions are even more complex, but in no resole system does the formaldehyde achieve an actual functional of 2, as is the case with novolacs. The resole in *Figure 4* has functionality for phenol of $f_{\text{actual}} = 5/2 = 2.5$, whereas the methylene glycol has $f_{\text{actual}} = 5/4 = 1.25$.

Effect of branching and crosslinking

In the case of a novolac, the introduction of chain branching such as illustrated in *Figure 5* cannot increase the f_{actual} of phenol to greater than 2.

Each branched phenyl residue ($f_{\text{actual}} = 3$) is counterbalanced by a chain end ($f_{\text{actual}} = 1$). The branch point and the chain end average out to 2. If we now consider the calculated value of f_{actual} for phenol of 2.31 it is clear that a highly crosslinked structure is required. That is, it is necessary to have extensive crosslinking to minimize end groups with f_{actual} of phenol = 1. Furthermore, to approach this functionality figure for phenol (2.31) within the number average molecular weight figures quoted by us[11] and others[13–17] (i.e. less than 1000), a structure as depicted in *Figure 6* (which has a f_{actual} of 2.22) is required. Such a structure is extremely unlikely and in any case would not be expected to be soluble.

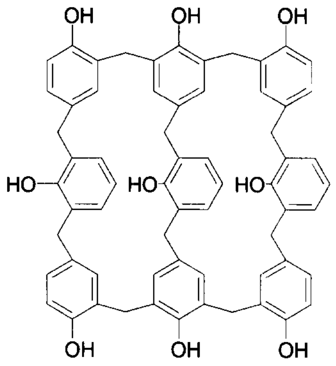

Figure 6 A novolac-type structure required to give f_{actual}(phenol) = 2.22

Thus we conclude that the actual functionality of phenol in a novolac must be less than 2. The figure of 2.31 deduced by Drumm and LeBlanc[2] therefore has no chemical or physical meaning in terms of the structure of P–F resins, and so must be an artifact of the model and mathematical treatment undertaken. An actual functionality of above 2 for phenol can only eventuate when the P/F ratio exceeds 1/1, that is, when gelation can occur. Literature reports[30] suggest that the synthesis of novolacs requires a P/F ratio of greater than ~1.15 to avoid gelation within the reactor. Thus, considering that free phenol remains at the completion of the P–F polymerization, often up to 15% (by weight), the actual ratio of P/F in the polymer approaches or even exceeds 1/1. Hence, at these ratios, gelation is possible and the phenol is now able to exceed an actual functionality of 2.

Functionalities in novolac resins

Research conducted by our group has highlighted how the measurement of molecular weight distribution by g.p.c. can be greatly improved by using structurally identical molecules to novolac resins as standards[11]. Having a number of novolac resins at our disposal, we have measured their molecular weight distributions by g.p.c. using the structurally identical units as calibration standards. The resins used consisted of both statistical resins RESA1–RESA6 and high *ortho*-linked resins (RESB1 and RESB2). From the number average molecular weight ($\bar{M}_n$) the degree of polymerization ($\bar{x}_n$) can be calculated using

$$\bar{x}_n = \frac{\bar{M}_n + 12}{106} \tag{2}$$

The actual functionality can then be computed using this $\bar{x}_n$ value, via equation (3) [note that equation (3) is equivalent to equation (1) when $\bar{x}_n$ is substituted for $(n+2)$].

$$f_{\text{actual}} = 2 - \frac{2}{\bar{x}_n} \tag{3}$$

Note that the limiting value for f_{actual} as $\bar{x}_n \rightarrow \infty$ is 2. Values of $\bar{M}_n$, $\bar{x}_n$ and f_{actual} for each resin are presented in *Table 1*. These are industrial resins, therefore we do not know whether the free phenol content measured by us accurately reflects the free phenol remaining at the end of the polymerization (i.e. we do not know if some or all the free phenol has been removed from these resins). Thus, the $\bar{M}_n$ values, and subsequently $\bar{x}_n$ and f_{actual} values, do

Table 1 Percentage free phenol, number average molecular weight ($\bar{M}_n$), degree of polymerization ($\bar{x}_n$), actual functionality (f_{actual}) and P/F ratios of resins studied

Resin	% Free phenol	$\bar{M}_n$	$\bar{x}_n$	f_{actual}	P/F ratio
RESA1		599	5.76	1.65	1.21
RESA2		447	4.33	1.54	1.30
RESA3		404	3.92	1.49	1.34
RESA4	4.7	639	6.14	1.67	1.20
RESA5	3.9	680	6.53	1.69	1.18
RESA6	4.4	735	7.05	1.72	1.16
RESB1		595	5.73	1.65	1.21
RESB2	7.7	642	6.17	1.68	1.19

not include the free phenol content (where applicable) of each resin.

The f_{actual} values range from 1.49 to 1.72, much lower than 2.31 suggested by Drumm and LeBlanc[2], and also lower than the limiting value of 2. Using these f_{actual} values we can calculate the ratio of phenolic units to formaldehyde residues of each resin. This is simply obtained using equation (4) (again assuming that the maximum f_{actual} is 2).

$$\mathrm{P/F} = \frac{2}{f_{actual}} \tag{4}$$

These P/F ratios are also listed in *Table 1*. If the amount of free phenol for these resins were known it would be a trivial exercise to adjust the P/F ratios to obtain the starting P/F ratio used for the polymerization. A free phenol content of, say 10% by weight, would increase the P/F ratios in *Table 1* by approximately 0.1–0.2. In any case, these P/F ratios are of the order 1.21–1.34, typical of industrial P/F starting ratios.

CONCLUSIONS

By considering the fundamental aspects of functionality in step-growth polymerizations, we have shown that the actual functionality of phenol in phenol–formaldehyde novolac resins approaches a limiting value of 2. Only when there is substantial crosslinking involved can this value be increased. Analysis of a range of commercial novolac resins gives results consistent with this limiting value. This leads us to question a number of literature reports where a functionality of 2.31 has been used to calculate number and weight average molecular weights. This value is in our view wrong and misleading. In the quoting of molecular weights for novolacs or resoles, due consideration should be given to the concept of actual functionality and the resultant chemical structures which must exist to contribute to such values. In many cases, discrepancies would be observed between actual functionalities and molecular weights and in these cases analysis of resins, by g.p.c. for example, should be conducted on a qualitative basis alone.

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