Note on the Paper "A General Equation in Polycondensation"

It was recently claimed in this journal[1] that a new general equation for polycondensation had been derived that could replace all equations for polycondensation other than Flory's statistical expression for gelation. It is the purpose of this note to show that the new equation for predicting the gel point in polycondensations has, in fact, been known to manufacturers of polyesters such as alkyds for many years[2] and that the equations derived in Ref. 1 are simple restatements of the well-known equations of step-growth polymerization.

In Ref. 1, the relationship derived between the extent of conversion, P, of the minor component and the number-average degree of polymerization, $\bar{X}_n$, is as follows:

$$P = \frac{\bar{F} - Q - 2/\bar{X}_n}{\bar{f}} \qquad (1)$$

where

$$\bar{F} = \frac{\Sigma N_{ai} f_{ai} + \Sigma N_{bi} f_{bi}}{\Sigma N_{ai} + \Sigma N_{bi}}$$

where N_{ai} = number of moles of the A-functional ith species and f_{ai} = the functionality of the A-functional ith species, and similar definitions apply to the B-functional species. In the derivation, the B groups were assumed to be more abundant than were the A groups:

$$Q = \frac{\Sigma N_{ai}(f_{ai} - 2) + \Sigma N_{bi}(f_{bi} - 2)}{\Sigma N_{ai} + \Sigma N_{bi}}$$

$$\bar{f} = \frac{2 \Sigma N_{ai} f_{ai}}{\Sigma N_{ai} + \Sigma N_{bi}}$$

It is clear that eq. (1) may be simplified by noting that $Q = \bar{F} - 2$. Thus,

$$P = \frac{\bar{F} - (\bar{F} - 2) - 2/\bar{X}_n}{\bar{f}}$$

Substituting for $\bar{f}$ gives

$$P = \frac{2(1 - 1/\bar{X}_n)(\Sigma N_{ai} + \Sigma N_{bi})}{2 \Sigma N_{ai} f_{ai}}$$

$$P = \frac{(\Sigma N_{ai} + \Sigma N_{bi})(1 - 1/\bar{X}_n)}{\Sigma N_{ai} f_{ai}} \qquad (2)$$

At gelation, $\bar{X}_n \rightarrow \infty$ and $P = P_c$, the critical extent of reaction at gelation (based on the number-average), and so eq. (2) may be written

$$P_c = \frac{(\Sigma N_{ai} + \Sigma N_{bi})}{\Sigma N_{ai} f_{ai}} \qquad (3)$$

This is simply the total number of molecules in the system initially divided by the total number of equivalents of the minor species initially in the system and is precisely the definition of "Patton's Alkyd Constant" given in Ref. 2, which as been widely used for more than 30 years in the coatings industry as a measure of "safety" in formulating step-growth polymers.

Equation (1) may also be shown to be a simple restatement of well-known equations,[3] since the number-average degree of polymerizations is defined as

$$\bar{X}n = \frac{\Sigma N_{ai} + \Sigma N_{bi}}{N_p}$$

where N_p = number of molecules in the mixture at any extent of reaction P of the minor component.

Substituting in eq. (2) and rearranging gives

$$P = \frac{(\Sigma N_{ai} + \Sigma N_{bi}) - N_p}{\Sigma N_{ai} f_{ai}}$$

or

$$N_P = (\Sigma N_{ai} + \Sigma N_{bi}) - P \Sigma N_{ai} f_{ai} \qquad (4)$$

This simple rearrangement of eq. (2) is a familiar equation to be found in many polymer texts and papers, such as that by Macosko and Miller[3], and shows that the equations given in Ref. 1 are simple restatements of the basic equa-

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tions of step-growth polymerization. However, it is not to be denied that the derivations and equations in Ref. 1 are very simple and it is clear that the approach of the author represents a valuable teaching aid.

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