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Functionality and Observed Versus Predicted Gel Points

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SUMMARY

An ambiguity in use of the term functionality is pointed out. The two most widely used relations (Flory, and Stockmayer and Kahn) connecting extent of reaction at the gel point and functionality are examined. The relations are shown mathematically to lead to the same result when all assumptions and definitions are considered. Measured gel points of polyesters are compared with those predicted by the equation. Deviations were less than 10% of the predicted values.

An ambiguity in definition has been observed for the word functionality which has led to unnecessary confusion of thought. It is believed that this confusion has often occurred and has been seen in the literature quite recently [1, 2]. On the one hand, functionality has been used to mean the number of chain ends united at the branch points in a polymer network. Since branch points can unite no fewer than three chain ends, functionality in this sense can take on values of three or greater. Networks are most often three or four functional. If more than one type of branch point is present, the average functionality can be calculated as a fraction with a value above three.

On the other hand, we speak of the functionality as the average number of groups on a molecule, usually of a particular kind, capable of reaction. We say that glycerine has a functionality of three and adipic acid of two. In this sense average functionality can have any positive integral or fractional value including zero. In further discussion we will use a capital "F" to refer to functionality as a term describing the number of chain ends united at the branch points and a small "f" when referring to the number of reactive groups per molecule. Difficulty occurs when equations derived using one definition of functionality are used that employ functionality in the other sense. This situation has arisen in the application of relations connecting the gel point of polymerizing systems with functionality.

Two gel equations have been most widely used. The first due to Flory [3-5] is

$$\alpha_C = \frac{1}{F - 1} \tag{1}$$

where α_C = the critical value for α which leads to gelation, α being the probability that a polymer chain ends in a branch unit, and F = number of chain ends united at the branch points in the gelled polymer.

For the case where a difunctional B compound reacts with a mixture of difunctional and higher functionality A compound, Flory [3-5] found

$$\alpha = \frac{P_A P_B \rho}{1 - P_A P_B(1 - \rho)} = \frac{P_A^2 \rho}{r - P_A^2(1 - \rho)} \tag{2}$$

where P_A and P_B = relative degree of reaction of the A and B groups, respectively, ρ = ratio of A groups belonging to branch units to the total number of A groups, and r = ratio of B groups initially present to the initial A groups.

If no difunctional A compound is present $\rho = 1$, and Eq. (2) becomes $\alpha = P_A P_B = P_A^2/r$. However, in general α is not equal to the extent of reaction or the square of the extent of reaction, nor is F in Eq. (1) the functionality of the monomers used in the preparation of the polymers.

For the case where A consists of two and three functional materials only, one can derive:

$$\rho = \frac{3(f_A - 2)}{f_A} \tag{3}$$

where f_A is the number-average functionality of the A compounds. Then from Eqs. (1) and (2)

$$(P_A)_c^2 = \frac{r f_A}{4 f_A - 6} \tag{4}$$

where the subscript c refers to the value of P_A at the gel point.

This equation does connect the critical extent of reaction with the functionality of the monomers. In arriving at Eq. (4), F in Eq. (1) was given the value of three.

A general relationship for the extent of reaction at the gel point was not given by Flory. However, others [6, 7] have extended his theory to reactants of other functionalities.

The second gel equation that has been widely used is due to Stockmayer [8] and Kahn [9]. A generalized derivation has also been given by Fogiel and Stewart [10]. The relationship is in terms of weighted average functionalities of the reacting monomers which can take on any values. It has the simple form

$$(P_AP_B)_c = \frac{(P_A)_c^2}{r} = (f_A^1 - 1)^{-1}(f_B^1 - 1)^{-1} \tag{5}$$

where f_A^1 and f_B^1 are weighted average functionalities of the reacting monomers A and B defined by

$$f_A^1 = \frac{\sum_i f_{A-i}^2 n_{A-i}}{\sum_i f_{A-i} n_{A-i}} \tag{6}$$

$$f_B^1 = \frac{\sum_j f_{B-j}^2 n_{B-j}}{\sum_j f_{B-j} n_{B-j}} \tag{7}$$

where n_A and n_B are the number of moles of A and B consisting of a mixture of species bearing functionalities $f_1, f_2, f_3, \ldots f_i$ and $f_1, f_2, f_3, \ldots f_j$, respectively.

For the particular case used by Flory [3-5] cited above where a bifunctional B monomer reacts with a mixture of two functional and three functional A monomer, Stockmayer's and Kahn's relation becomes

$$(P_A)_c^2 = \frac{r}{(f_A^1 - 1)} \tag{8}$$

and

$$f_A^1 = \frac{4n_2 + 9n_3}{2n_2 + 3n_3} \tag{9}$$

Table 1. Observed vs. Predicted Gel Points

Stearic acid (moles)	Sebacic acid (moles)	1,2,3-Tri-carboxy-propane (moles)	1,3,5-Tri carboxy-pentane (moles)	1,1,1-Tri-methylol-propane (moles)	1,4-Butane-diol (moles)	Actual COOH reacted, gel point (%)	Predicted COOH reacted gel point (%)	f_A	$f_A{}^1$	f_B	f_{AV}
0.100	0.100			0.100		94.9	86.7	1.50	1.67	3.00	2.00
0.067	0.100			0.089		86.1	81.5	1.60	1.75	3.00	2.08
0.050	0.100			0.083		82.9	79.1	1.67	1.80	3.00	2.14
0.025	0.100			0.075		77.7	75.0	1.80	1.89	3.00	2.25
0.13	0.100			0.071		75.2	72.3	1.89	1.94	3.00	2.32
	0.100			0.067		71.6	70.7	2.00	2.00	3.00	2.40
	0.100	0.025			0.138	87.9	88.8	2.20	2.27	2.00	2.10
	0.100	0.050			0.175	83.3	83.7	2.33	2.43	2.00	2.15
	0.050	0.050			0.125	79.0	79.1	2.50	2.60	2.00	2.22
	0.050	0.100			0.200	76.0	75.6	2.67	2.75	2.00	2.29
	0.025	0.100			0.175	73.5	73.3	2.80	2.86	2.00	2.33
		0.100		0.100		55.0	50.0	3.00	3.00	3.00	3.00
			0.100	0.100		54.2	50.0	3.00	3.00	3.00	3.00

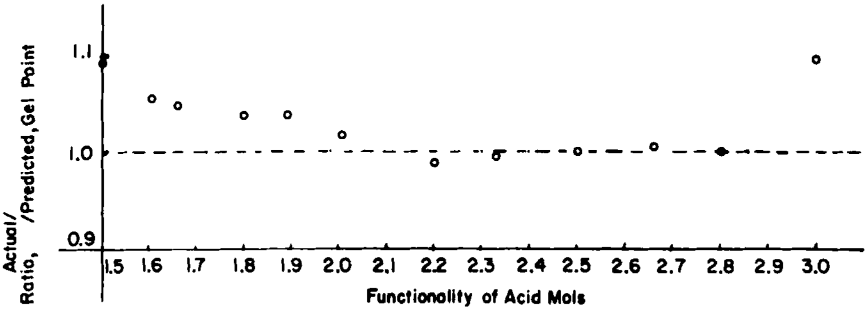

Fig. 1. Observed vs. predicted gel points.

where n_2 and n_3 are the number of moles of two and three functional A compound present, while the number-average functionality is

$$f_A = \frac{2n_2 + 3n_3}{n_2 + n_3} \tag{10}$$

By suitable algebraic manipulation it can then be shown that

$$f_A^1 = \frac{5f_A - 6}{f_A} \tag{11}$$

Placing this value of f_A^1 in Eq. 8 we obtain

$$(P_A)_c^2 = \frac{rf_A}{4f_A - 6} \tag{12}$$

which is identical with Eq. (4) found using Flory's equation. Thus Stockmayer's and Kahn's approach leads to the same result as that of Flory when all assumptions and definitions are considered.

It seemed of interest to compare actual measured gel points with those predicted by the use of Eqs. (4) and (5), which as just shown yield the same results. Experiments were carried out with 1) mixtures of sebacic acid and 1,2,3-tricarboxy propane in various ratios, reacting these with 1,4-butanediol at 150°C; and 2) mixtures of sebacic acid and stearic acid in various ratios, reacting these with 1,1,1-trimethylolpropane at 150°C. Two other reactions were also carried out: 1) 1,2,3-tricarboxypropane with 1,1,1-trimethylolpropane and 2) 1,3,5-tricarboxypentane with 1,1,1-trimethylolpropane, both at 150°C. The ratio of carboxyl to hydroxyl

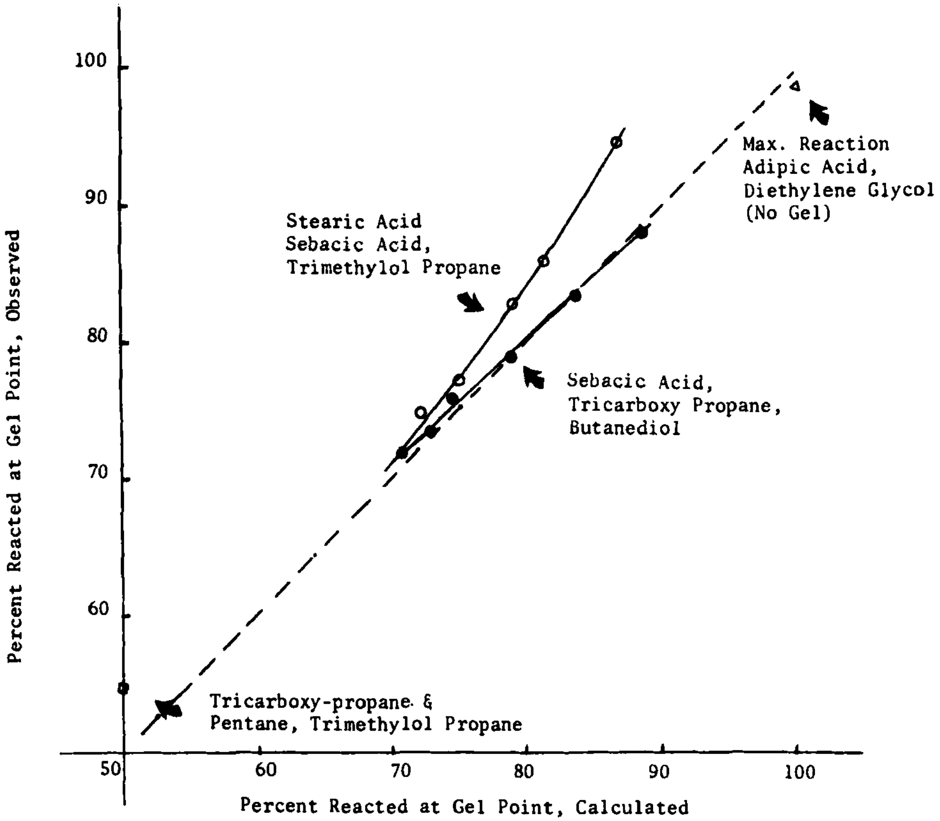

Fig. 2. Deviation from predicted gel points vs. functionality of acid moles.

groups was one-to-one in all cases. No catalyst was employed. The extent of reaction at the gel point was determined by acid-base titration as described in a previous publication [11].

Results are shown in Table 1 and Fig. 1, where the actual and predicted gel points are compared. Some of these data have been previously reported in a different form [11]. Also given in Table 1 are the functionalities f_A; the number-average functionality of the acid moles, f_A^1 ; the weight-average functionality of the acid moles from Eq. (6), f_B; the number-average functionality of the hydroxyl containing moles; and f_{AV}, the number-average functionality of the whole system. The ratio of the actual to the predicted extents of reaction at the gel point is shown in Fig. 2 vs. the number-average functionality of the acid moles. Deviation is always less than 10% of the predicted value. The measured value is nearly always greater than the predicted.

It would seem that the general equation of Stockmayer and Kahn adequately predicts the extent of reaction at the gel point in the systems employed here.

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