Prediction of Molecular Weights for Condensation Polymerization of Polyfunctional Monomers

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ABSTRACT: Relatively simple expressions are derived for the number-average and weight-average degrees of polymerization of condensation polymers derived from polyfunctional monomers. The equations, which apply to systems up to the gel point, are derived with the assumption of equal reactivity of functional groups. Molecular weights for a hypothetical reaction mixture are compared with those obtained by numerical solution of the complete expression given by Stockmayer. The effect of polydispersity of reactants on the molecular weight of the polymeric product is also discussed.

Stockmayer[1] has derived an expression for the number of polymer molecules $N(m_i,n_j)$ containing m number of i index monomer units of type A and n number of j index units of type B. $N(m_i,n_j)$ is the distribution function for a condensation reaction between A species and B species from which the various moments of distribution and, in theory, the entire distribution of molecular lengths can be derived. The assumption of equal *a priori* reactivities of functional groups was made in the derivation of $N(m_i,n_j)$. However, when applied to the important task of predicting average molecular weights of reactant systems, the distribution function used by Stockmayer results in rather unwieldy expressions.

In this contribution we show that the individual summations contained in the function $N(m_i,n_j)$ can be brought into tractable form in terms of quantities and types of reactants. Then, by the use of a rather simple accounting technique, we obtain closed-form expressions for the number- and weight-average degrees of polymerization which are amenable to rapid and simple calculation. Finally, we compare the average molecular weights approximated by an extension of these simplified equations with a numerical evaluation of the complete expression derived by Stockmayer from the original distribution function.

Discussion

The distribution function, $N(m_i,n_j)$, is derived in terms of the functionalities of A and B species, f_i and g_j, and their molar amounts, A_i and B_j. The treatment which follows is for monodisperse (with respect to both molecular length and functionality) species, taking for illustrative simplicity difunctional B as the single B-type monomer. Therefore, $g_j = 2$, $\Sigma B_j = B$. The distribution function expression for this situation is eq 1

$$N(m_i,n_j) = \sum_{\substack{\text{all}\\ \text{species}}} f_iA_i \frac{(\sum f_im_i - \sum m_i)!}{[\sum f_im_i - 2\sum m_i + 2]!} P_A{}^{(\Sigma m_i - 1)} \times (1 - P_A)^{(\Sigma f_im_i - 2\Sigma m_i + 2)} \prod \frac{P_i{}^{m_i}}{m_i!} \quad (1)$$

(for simplicity the summation $\Sigma_{i=1}{}^N f_im_i$ is written as Σf_im_i).

In the above, species A is in excess and hence at the end of reaction P_B, the probability of B groups reacting, equals unity. In general identity 2 holds.

$$P_A \sum f_iA_i = P_B \sum g_jB_j \quad (2)$$

Thus, for A in excess, $P_A = 2B/\Sigma f_iA_i$, while for B in excess, $P_B = \Sigma f_iA_i/2B$. Also the probability of reaction of the ith species of type A is

$$P_i = f_iA_i/\sum f_iA_i \quad (3)$$

In the subsequent sections, eq 1 will be used to calculate the number- and weight-average degrees of polymerization from the initial reactant concentrations.

I. Number-Average Degree of Polymerization

We shall consider two cases: (I) species B in excess and (II) species A in excess. In either case we are faced with two alternate methods of establishing the degree of polymerization, counting all species or counting chains only. If either species is greatly in excess, then the resulting reaction product contains unreacted monomer (of the excess species) plus polymer chains of varying degrees of polymerization. The DP of the polymeric species isolated from the monomer will, of course, be different from the DP of the total mixture. If the excess monomer is to be removed, then obviously the DP of interest is that exclusive of unreacted monomeric units. If, however, the final product is used with the excess species, the total DP is of interest. The mathematical treatment of the two cases differs in the development of the term $\Sigma N(m_i)$ which represents the total number of species present at the end of the reaction. In general, $\Sigma N(m_i)$ are all the original species, A's and B's, minus those A units (not in excess) lost through reaction. If only the polymeric chains are to be counted, we subtract all the B units (originally in excess) which have not reacted at all.

A. Case I: B Species in Excess. We can show, from simple accounting techniques, that the value of DP for any number of units m is

$$\mathrm{DP}(m_i) = \sum_i f_im_i + 1 \quad (4)$$

Thus, from the definition of the number average

$$\overline{\mathrm{DP}}_n = \sum \mathrm{DP}(m_i)N(m_i\big/)\sum_{m_i} N(m_i)$$

For case I

$$(\overline{\mathrm{DP}}_n)_I = \frac{\sum_{m_i}\left(\sum_i f_im_i\right)N(m_i)}{\sum_{m_i} N(m_i)} + 1 \quad (5)$$

The summation in the numerator represents the total number of A-type functional units initially present, or Σf_iA_i.

The denominator sum is evaluated in two ways: (a) count-

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(1) W. H. Stockmayer, *J. Polym. Sci.*, 9, 69 (1952).

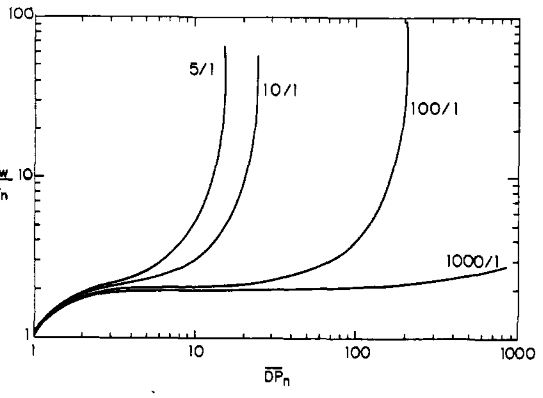

Figure 1. Effect of diol/triol ratio on polydispersity of product (A species in excess).

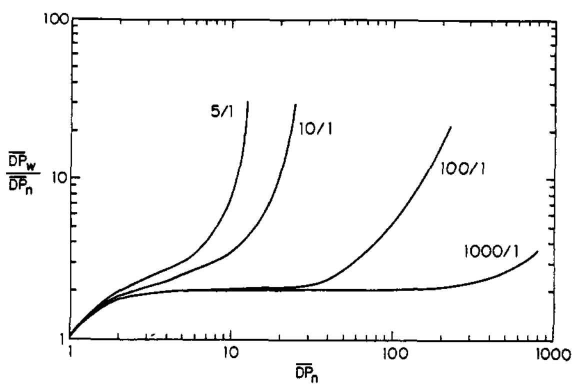

Figure 2. Effect of diol/triol ratio on polydispersity of product (B species in excess).

ing polymer chains only (*i.e.*, DP $\geq$ 2) or (b) counting all species. If we count only polymer chains

$$\sum_{m_i} N(m_i) = \sum A_i + B - \sum f_i A_i - \text{unreacted B} \quad (6)$$

which is the total original ($A + B$) minus the reacted B group from A functionality minus those left over. The unreacted B is simply the initial amount times the probability of both functional groups remaining unreacted, or

$$\text{unreacted B} = B(1 - P_B)^2 = B\left[1 - \frac{\sum f_i A_i}{2B}\right]^2 = B - \sum f_i A_i + (\sum f_i A_i)^2/4B \quad (7)$$

Thus, eq 6 becomes eq 8

$$\sum N(m_i) = \sum A_i - {}^1\!/_2 P_B \sum f_i A_i \quad (8)$$

and the number-average degree of polymerization for chains only is defined as: for case Ia

$$(\overline{DP}_n)_{Ia} = \frac{\sum f_i A_i + \sum A_i - {}^1\!/_2 P_B \sum f_i A_i}{\sum A_i - {}^1\!/_2 P_B \sum f_i A_i}$$

If we divide numerator and denominator by B and define $T = \Sigma A_i / \Sigma B_j$ as the initial molar ratio of reactants, we obtain

$$(\overline{DP}_n)_{Ia} = 1 + [2P_B/(T - P_B^2)] \quad (9)$$

The second accounting system includes unreacted excess monomer of type B

$$\sum N(m_i) = \sum A_i + B - \sum f_i A_i \quad (10)$$

Thus, for all species counted the DP is

$$(DP_n)_{Ib} = \frac{\sum f_i A_i + \sum A_i + B - \sum f_i A_i}{\sum A_i + B - 2P_B B} \quad (11)$$

which is equivalent to

$$(\overline{DP}_n)_{Ib} = [1 - 2P_B/(1 + T)]^{-1} \quad (12)$$

As expected, eq 12 and 9 converge at the high values of DP_n.

B. Case II: A Species in Excess. Since A species are in excess, $P_B = 1$ at the end of the reaction and $P_A = 2B/\Sigma f_i A_i$. For A units in excess the degree of polymerization is

$$DP(m_i) = 2\sum m_i - 1 \quad (13)$$

Therefore, the number-average DP is

$$(DP_n)_{II} = \left[2\sum_{m_i}\sum_{i} m_i N(m_i) - \sum N(m_i)\right] \Big/ \sum N(m_i) \quad (14)$$

The double sum $\Sigma_{m_i} \Sigma m_i N(m_i) = \Sigma A_i$, since it represents the total number of monomer units initially present. As in case I, there are two methods of counting $\Sigma_{m_i} N(m_i)$, either chains only (that is, species with DP greater than 1) or all species including unreacted monomer.

For chains only

$$\sum_{m_i} N(m_i) = \sum A_i + \sum B_j - \sum g_j B_j - \text{unreacted A}$$
$$= \sum A_i - B - \text{unreacted A}$$

The unreacted A of each functionality type can be obtained by considering either the group probability of reaction or the molecular probability.[2] Therefore

$$\text{unreacted } A_1 = A_1(1 - P_A)$$

For functionality of 2, the group concentration is $f_2 A_2$ or $2A_2$, and for the entire molecule to be unreacted both ends are unreacted. However, we have counted the molecule twice. So

$$\text{unreacted } A_2 = \frac{2A_2(1 - P_A)^2}{2}$$

By extension of the arguments unreacted A $= \Sigma_i A_i (1 - P_A)^{f_i}$. Hence

$$\sum N(m_i) = \sum A_i - B - \sum A_i(1 - P_A)^{f_i}$$

Substitution into eq 14 gives

$$(\overline{DP}_n)_{II} = \frac{T + 1 + \sum A_i(1 - P_A)^{f_i}/B}{T - 1 - \sum A_i(1 - P_A)^{f_i}/B} \quad (15)$$

If we count all species, $\Sigma N(m_i) = \Sigma A_i - B$, therefore

$$(\overline{DP}_n)_{II} = (T + 1)/(T - 1) \quad (16)$$

This result, which could have been determined by simple stoichiometry, serves to illustrate the applicability of the method outlined. We can now apply this technique to the more complex problem of $\overline{DP}_w$ and molecular weights.

II. Weight-Average Degree of Polymerization

The second moment of the DP with respect to the distribution $N(m_i)$ is defined as the weight-average degree of polymerization, or

$$\overline{DP}_w = \sum DP^2 N(m_i) / \sum DP N(m_i) \quad (17)$$

As in the treatment of number-average DP, two cases will be considered.

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[2] P. J. Flory, "Principles of Polymer Chemistry," Wiley, New York, N. Y., 1970, pp 318–320.

A. Case I: B Species in Excess. Since $\mathrm{DP}(m_i) = \Sigma f_i m_i + 1$, $\mathrm{DP}^2(m_i) = (\Sigma f_i m_i)^2 + 2\Sigma f_i m_i + 1$. Then, from eq 17

$$(\mathrm{DP}_\mathrm{w})_\mathrm{I} = \frac{\dfrac{\sum(\sum f_i m_i)^2 N(m_i)}{\sum N(m_i)} + \dfrac{2\sum\sum f_i m_i N(m_i)}{\sum N(m_i)} + 1}{\dfrac{\sum\sum f_i m_i N(m_i)}{\sum N(m_i)} + 1} \quad (18)$$

From eq 8 and 10 we have

$$(\overline{\mathrm{DP}}_\mathrm{w})_\mathrm{Ia} = \frac{\bar{f}_\mathrm{w}(1 + P_\mathrm{B})/[1 - P_\mathrm{B}(\bar{f}_\mathrm{w} - 1)] + 2 + T/2P_\mathrm{B} - P_\mathrm{B}/2}{1 + T/2P_\mathrm{B} - P_\mathrm{B}/2} \quad (19)$$

$$(\overline{\mathrm{DP}}_\mathrm{w})_\mathrm{Ib} = T + 1 + 2[(\bar{f}_\mathrm{w} + 1 + P_\mathrm{B})/(1 - \bar{f}_\mathrm{w} + 1/P_\mathrm{B})]/(T + 1) \quad (20)$$

The effective, or weighted-average, functionality, $\bar{f}_\mathrm{w}$, is defined by Fogiel[3] as $\bar{f}_\mathrm{w} = \Sigma f_i^2 A_i/\Sigma f_i A_i$.

B. Case II: A Species in Excess. Since $\mathrm{DP}^2(m_i) = 4(\Sigma m_i)^2 - 4\Sigma m_i + 1$, one obtains

$$(\overline{\mathrm{DP}}_\mathrm{w})_\mathrm{II} = \frac{4\sum\limits_{m_i}\left(\sum\limits_i m_i\right)^2 N(m_i) - 4\sum\limits_{m_i}\sum\limits_i m_i N(m_i) + \sum\limits_{m_i} N(m_i)}{2\sum\limits_{m_i}\sum\limits_i m_i N(m_i) - \sum\limits_{m_i} N(m_i)} \quad (21)$$

Evaluation of eq 21 for chains only requires the use of

$$\sum N(m_i) = \sum A_i - B - \sum_i A_i(1 - P_\mathrm{A})^{f_i}$$

The summations simplify to

$$(\mathrm{DP}_\mathrm{w})_\mathrm{IIa} = \frac{8/[1 - P_\mathrm{A}(f_\mathrm{w} - 1)] + T - 1 - (1/B)\sum A_i(1 - P_\mathrm{A})}{T + 1 + (1/B)\sum A_i(1 - P_\mathrm{A})^{f_i}} \quad (22)$$

$$(\overline{\mathrm{DP}}_\mathrm{w})_\mathrm{IIb} = \{8/[1 - P_\mathrm{A}(\bar{f}_\mathrm{w} - 1)] + T - 1\}/(T + 1) \quad (23)$$

The preceding results can be used, in addition to estimating the DP, to evaluate the breadth of the molecular weight distribution curve, $\overline{M}_\mathrm{w}/\overline{M}_\mathrm{n}$. It will be shown that this ratio is approximately $\overline{\mathrm{DP}}_\mathrm{w}M/(\overline{\mathrm{DP}}_\mathrm{n}M)$ where M is the appropriate average chain weight. Hence, the simple ratio of DP's determines the polydispersity index.

The question of the effect of polyfunctional reactants (greater than 2) on the polydispersity of the resulting polymer can be illustrated graphically through the use of equations derived in the previous sections. Consider, for example, the reaction of a difunctional isocyanate, the "B" species, with a mixture of diols and triols. Figures 1 and 2 show a plot of $\overline{\mathrm{DP}}_\mathrm{w}/\overline{\mathrm{DP}}_\mathrm{n}$ *vs.* $\overline{\mathrm{DP}}_\mathrm{n}$ for the two cases of B in excess and A in excess. The sharp upturn of each curve represents the onset of gelation, occurring at different values of $\overline{\mathrm{DP}}_\mathrm{n}$ depending on the net diol to triol ratio. It will be noted that the curves tend towards a value or $\overline{\mathrm{DP}}_\mathrm{w}/\overline{\mathrm{DP}}_\mathrm{n} = 2$, as predicted for normal distribution of molecular sizes. The value of $\overline{\mathrm{DP}}_\mathrm{w} = \overline{\mathrm{DP}}_\mathrm{n} = 1$ represents 0 extent of reaction and is consistent with the definition of $\overline{\mathrm{DP}} = 1$ for unreacted monomer.

III. Calculation of Average Molecular Weight

The average degree of polymerization, as discussed in the preceding sections, is generally sufficient to characterize the size of a polymer chain. In some cases, however, the actual molecular weight is desired. This can be estimated with considerable accuracy from the appropriate average DP value by multiplying by the number-average molecular weight of the monomer mixture, or $\Sigma X_k M_k$, where X_k is the mole fraction of the kth species and M_k is its molecular weight. Hence

$$M_\mathrm{w} = \mathrm{DP}_\mathrm{w}\sum_k M_k X_k \quad (24)$$

and the summation is over all species (A_i's and B_j's).

Stockmayer has derived an expression for the weight-average molecular weight of a polymer which, because of its complexity, is best evaluated by means of a computer program with molar amounts and functionalities as input.

It is possible, then, to compare the value of $\overline{M}_\mathrm{w}$ obtained by direct evaluation of Stockmayer's equation with that obtained from the relatively simple expressions for $\overline{\mathrm{DP}}_\mathrm{w}$, each multiplied by the average chain weight, $\Sigma M_i X_i$. Thus, for case I

$$M_\mathrm{w} \simeq \left[1 + \left(\frac{2}{1 + T}\right)\left(\frac{\bar{f}_\mathrm{w} + 1 + P_\mathrm{B}}{1 - \bar{f}_\mathrm{w} - 1/P_\mathrm{B}}\right)\right]\sum M_i X_i \quad (25)$$

and case II

$$\overline{M}_\mathrm{w} \simeq [\sum M_i X_i/(T + 1)]\{8/[1 - P_\mathrm{A}(\bar{f}_\mathrm{w} - 1)] + T - 1\} \quad (26)$$

Similar equations for chains only are obtained by use of eq 19 and 22.

We have made this comparison using, as an illustrative case, the reaction of a difunctional B species whose molecular weight is 146. Mono-, bi-, and trifunctional A species considered here as possessing hydroxyl functionality were used with $M_1 = 50$, $M_2 = 1000$, $M_3 = 134$. In Table I, the ratio of molar amounts T and the values of P_B used for case I are indicated, along with $\overline{M}_\mathrm{w}$ from computer evaluation of Stockmayer's equation and from calculated results of eq 25. In Table II, similar comparisions are made for case II. Agreement is sufficiently close that the approximate method outlined above seems sufficient for practical situations.

IV. Effect of Polydispersity of Reactants

In the preceding treatments it has been assumed that the reactant species A_i and B_j were monodisperse with respect to functionality and molecular size. This has permitted the interchangeable use of the index i for the functionality f_i. It is important to consider the effect of two or more monomers of equal functionality and the extension of this degeneracy of f_i to the case of a distribution of molecular size within a monomer type, for example, a polymeric glycol with functionality precisely equal to 2.

The index i will still represent the type of monomer of functionality f_i, but A_i will include molecules of varying sizes or molecular weight represented by A_j and M_j. Thus $A_i = \Sigma_j A_j$. Using this notation, $\Sigma A_i = \Sigma_i\Sigma_j A_j = \Sigma_i A_i$. Similarly, $\Sigma f_i A_i = \Sigma_i f_i \Sigma_j A_j = \Sigma f_i A_i$. Thus, the summations involving molar amounts and functionality are unaffected by the polydispersity of reactants. In calculating the values $\bar{f}_\mathrm{n}$, $\bar{f}_\mathrm{w}$, P_A, P_B, one can use A_i as the total moles of all f_i functionality species.

The sum $\Sigma_i M_i A_i$ can be expanded for the case of $f_i = 2$ degeneracy to

$$\sum_i M_i A_i = M_1 A_1 + \sum M_{2,j} A_{2,j} + M_3 A_3 + \ldots \quad (27)$$

The number-average molecular weight of species $i = 2$ is

$$\overline{M}_{\mathrm{n}2} = \sum_j M_{2,j} A_{2,j}/\sum_j A_{2,j} \quad (28)$$

Then eq 27 is apparently

$$\sum_i M_i A_i = \sum \overline{M}_{\mathrm{n}i} A_i \quad (29)$$

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(3) A. W. Fogiel, *Macromolecules*, **2**, 581 (1969).

TABLE I

COMPARISON OF M_w BY VARIOUS METHODS

Diol/triol	T	P_B	DP_w All species	DP_w Chains only	ΣX_iM_i	M_w, g/mol All species	M_w, g/mol Chains only	M_w, g/mol Stockmayer
Case I: B in excess								
5:1	0.727	0.78787	122.0	125.18	444.8	54,260	55,680	52,530
	0.706	0.7647	61.89	63.93	439.6	27,210	28,100	26,790
	0.666	0.7222	31.94	33.32	429.9	13,730	14,320	13,910
	0.600	0.65	16.77	18.07	412.7	6,930	7,460	7,460
	0.480	0.52	8.32	9.67	376.7	3,110	3,640	3,830
	0.400	0.433	5.86	7.36	349.2	2,050	2,550	2,770
10:1	0.846	0.8846	177,887	179,240	501.3	89,174,000	89,853,000	62,387,000
	0.815	0.85185	101.9	103.2	494.1	50,350	50,970	49,750
	0.786	0.82143	51.9	52.83	487.1	25,280	25,730	25,420
	0.688	0.71875	18.49	19.35	466.8	8,540	9,030	9,210
	0.550	0.575	8.855	9.89	421.1	3,730	4,160	4,500
	0.367	0.3833	4.49	5.82	351.5	1,470	2,050	2,370
100:1	0.953	0.95755	138.67	138.79	558.5	77,450	77,510	78,020
	0.918	0.9227	61.09	60.68	550.7	33,640	33,410	34,060
	0.842	0.8458	26.62	26.35	532.4	14,170	14,040	14,680
	0.777	0.78077	17.06	17.51	515.6	8.800	9,030	9,650
	0.721	0.725	12.92	13.47	500.3	6,460	6,740	7,350
	0.631	0.6344	8.97	9.71	473.2	4,240	4.600	5,120
	0.505	0.5075	5.90	7.603	429.7	2,530	3,270	3,410
	0.337	0.3383	3.58	4.84	358.9	1.280	1.740	2,110

TABLE II

COMPARISON OF M_w BY VARIOUS METHODS

Diol/triol	T	P_A	DP_w All species	DP_w Chains only	ΣM_iX_i	M_w, g/mol All species	M_w, g/mol Chains only	M_w, g/mol Stockmayer
Case II: A in excess								
5:1	1.143	0.8077	621.4	632.1	524.5		331,540	270,510
	1.165	0.7923	145.75	148.7	527.9	76,940	78,500	63,850
	1.200	0.7692	66.61	68.33	533.1	35,510	36,430	29,480
	1.333	0.6923	22.21	23.32	551.5	12,250	12,860	10,250
	1.500	0.6153	12.324	13.39	571.8	7,050	7,660	6,020
	2.00	0.4615	5.37	6.506	619.1	3,320	4,030	3,120
10:1	1.089	0.87826	529.0	532.7	550.2	291,050	293,090	263,750
	1.100	0.8696	222.8	224.4	552.1	123,000	123,890	110,740
	1.158	0.82609	55.26	56.11	562.0	31,060	31,530	27,450
	1.222	0.7826	30.597	31.32	572.4	17,510	17,930	15,410
	1.375	0.69565	15.117	15.93	594.8	8,990	9,470	7,940
	1.833	0.52174	6.16	7.18	647.6	3,990	4,650	3,780
100:1	1.020	0.97537	387.6	387.7	572.9	222,060	222,110	217,970
	1.031	0.9655	194.6	194.76	575.1	111,940	112,000	109,570
	1.063	0.93596	77.1	77.26	581.65	44,850	44,940	43,490
	1.122	0.8867	37.42	37.81	597.6	22,360	22,600	21,270
	1.263	0.78818	17.325	17.78	617.75	10,700	10,980	10,060
	1.443	0.68966	10.445	11.09	645.3	6,740	7,160	6,320
	1.683	0.59113	6.883	7.71	676.4	4,660	5,220	4,440
	3.367	0.29556	2.609	3.16	797.8	2,080	2,520	2,000

Similarly, for $f_i = 2$ degeneracy

$$\sum_i M_i^2A_i = M_1^2A_1 + \sum M_{2,j}^2A_{2,j} + M_3^2A_3 + \ldots \qquad (30)$$

Since $\overline{M}_{w2} = \Sigma_j M_{2,j}^2A_{2,j}/\Sigma M_{2,j}A_{2,j}$ and from eq 28

$$\sum_i M_{2,j}A_{2,j} = \overline{M}_{n2}\sum_i A_{2,j}$$

we find

$$\sum_i M_i^2A_i = \sum \overline{M}_{n_i}\overline{M}_{w_i}A_i \qquad (31)$$

Also

$$\sum_i f_iM_iA_i = \sum_i f_i\overline{M}_{n_i}A_i \qquad (32)$$

The implication of these arguments can be seen by writing Stockmayer's equation in terms of these summations, *i.e.*

$$(M_w)_I = \frac{\sum_R \overline{M}_{n_k}\overline{M}_{w_k}C_k + \dfrac{\sum f_iA_i(f_w - 1)M_b^2 + P_B(g_w - 1)M_a^2 + 2M_aM_b}{1 - P_B(f_w - 1)(g_w - 1)}}{\sum_k \overline{M}_{n_k}C_k} \qquad (33)$$

where C_k is the molar concentration of each species (A and B types) of a given functionality. The values M_a and M_b can be considered to be the "functional-average molecular weights" and are derived from the number-average molecular weight of each species. It is apparent that the effect of polydispersity of reactant species is to increase $\overline{M}_w$ since $\overline{M}_w\overline{M}_n$ for a given species is always greater than $\overline{M}_n^2$ if the species is polydisperse.