Average Degrees of Polymerizations of Macromolecules Built Up of Macromolecular Precursors

MARINO GUAITA* AND OSCAR CHIANTORE

Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Università di Torino, Via P. Giuria 7, 10125 Torino, Italy

Received April 9, 1991

In a previous paper[1] we derived the relations between the number- and weight-average degrees of polymerization (DPs) X_n and X_w of a population PX of molecules obtained by randomly linking in pairs the molecules of a population PY and the number- and weight-average DPs Y_n and Y_w of PY. Specifically, we showed that, independently of the molecular weight distribution, the following simple relations hold:

$$X_n = 2Y_n \quad (1)$$

$$X_w = Y_n + Y_w \quad (2)$$

An obvious extension of eqs 1 and 2 is to repeat the procedure on the molecules of the population PX, namely, by randomly coupling the molecules of PX, to obtain the molecules of a new population PZ whose number- and weight-average DPs Z_n and Z_w are

$$Z_n = 2X_n = 4Y_n$$

$$Z_w = X_n + X_w = 3Y_n + Y_w$$

and then to continue up to the generalized relations

$$Q_n = 2^m Y_n \quad (3)$$

$$Q_w = (2^m - 1)Y_n + Y_w \quad (4)$$

for the number- and weight-average DPs of a population PQ of molecules obtained after m coupling steps. The powers of 2 are clearly the consequence of the fact that the weight of the different populations is always the same, whereas the number of molecules is halved at each coupling step, so the number-average DP is doubled.

In the above discussion no hypothesis was made on the way the molecules are linked together and on the shape the coupled molecules take up. Therefore, eqs 3 and 4 hold when the molecules are successively linked either at their ends to yield linear structures or at some internal parts to yield branched structures. Particularly, let us imagine the case in which the molecules of population PY are linked in pairs at one end and subsequently the molecules of the population PX are repeatedly coupled to yield star-shaped molecules with 4, 8, 16, etc. arms. The resulting structures are the same as those which can be obtained by using a linking agent of suitable functionality f (say, 4, 8, 16, etc.) directly on the molecules of population PY. Kosmas and Hadjichristidis[2] have recently derived the number- and weight-average DPs of the star-branched molecules (Q_n and Q_w in the present notation) in terms of the number- and weight-average DPs of the precursor arms (Y_n and Y_w in the present notation) and the functionality f of the linking agent:

$$Q_n = fY_n \quad (5)$$

$$Q_w = (f - 1)Y_n + Y_w \quad (6)$$

Equations 5 and 6 are the same as eqs 3 and 4 when f is one power of 2; however, they are more general inasmuch as f can take any value. In the next section it will be shown that the method followed to obtain eqs 1 and 2 can be used to arrive at the more general eqs 5 and 6. A further generalization will be pursued by analyzing coupling of molecules of two different populations.

Linking More Than Two Molecules

Equation 1 is the simple consequence of the fact that the weight of populations PY and PX is the same, whereas the number of molecules in PX is half the number of molecules in PY. Of course, if the N molecules of PY are linked in groups of f, a population PQ results in which N/f molecules are present, whose number-average DP Q_n is given by

$$Q_n = fY_n$$

identical with eq 5.

Equation 2 is obtained by considering that the probability of finding in a population one molecule with a given DP coincides with the number fraction of molecules having that DP. Therefore, if n_i and n_j are the number fractions of molecules with DP Y_i and Y_j in population PY, $n_{ij} = n_i n_j$ is the number fraction of molecules in population PX with DP $X_{ij} = Y_i + Y_j$. Then the weight fraction w_{ij} can readily be written in the form

$$w_{ij} = \frac{n_{ij}X_{ij}}{X_n} = \frac{n_i n_j (Y_i + Y_j)}{2Y_n} \quad (7)$$

and the weight-average DP X_w in the form

$$X_w = \frac{1}{2Y_n}\sum_{i=1}^{N}\sum_{j=1}^{N} n_i n_j (Y_i + Y_j)^2 \quad (8)$$

By developing the sums in eq 8, one obtains

$$\sum_{i=1}^{N}\sum_{j=1}^{N} n_i n_j (Y_i + Y_j)^2 = 2\sum_{i=1}^{N} n_i Y_i^2 + 2\sum_{i=1}^{N}\sum_{j=1}^{N} n_i n_j Y_i Y_j \quad (9)$$

and by introducing eq 9 into eq 8, taking into account that $\sum_i\sum_j n_i n_j Y_i Y_j = \sum_i n_i Y_i \sum_j n_j Y_j = Y_n^2$ and that $\sum_i n_i Y_i^2 = \langle Y^2 \rangle_n$ is the number-average-squared DP, one obtains eq 2.

The same procedure can be followed to obtain the relation between Y_n and Y_w and the weight-average DP U_w of a population PU of molecules obtained by linking in groups of three the molecules of PY. In this case the number fractions of PU and PY are related according to the equation $n_{ijk} = n_i n_j n_k$ and the DPs according to the equation $U_{ijk} = X_i + X_j + X_k$. Hence the weight fraction w_{ijk} and the weight-average degree of polymerization U_w take the form

$$w_{ijk} = \frac{n_{ijk}U_{ijk}}{U_n} = \frac{n_i n_j n_k (Y_i + Y_j + Y_k)}{3Y_n} \quad (10)$$

$$U_w = \frac{1}{3Y_n}\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{k=1}^{N} n_i n_j n_k (Y_i + Y_j + Y_k)^2 \quad (11)$$

to be compared with eqs 7 and 8. By developing the sums of eq 11, one obtains

$$\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{k=1}^{N} n_i n_j n_k (Y_i + Y_j + Y_k)^2 = 3\sum_{i=1}^{N} n_i Y_i^2 + 6\sum_{i=1}^{N}\sum_{j=1}^{N} n_i n_j Y_i Y_j \quad (12)$$

and since $\sum_i n_i Y_i^2$ and $\sum_i\sum_j n_i n_j$ are the same as those in eq 9, by introducing eq 12 into eq 11, one readily obtains

$$U_w = 2Y_n + Y_w \quad (13)$$

The comparison of eqs 13 and 2 allows one to conclude

0024-9297/91/2224-5881$02.50/0

that the weight-average DP of a population PQ of molecules obtained by linking together f molecules at a time of population PY is given by eq 6.

Linking Molecules of Two Populations

In the previous sections N molecules of one population PY were linked together in groups of f to form N/f larger molecules. Obviously, the same result would be obtained by dividing PY in f parts, each containing N/f molecules, and then linking together molecules taken one at a time from each part. If the f parts have been obtained by weighing equal amounts of the original PY, it is surely permissible (N and N/f are in general very large) to consider that each part has the same distribution of molecular species of PY. However, one might have prepared the f parts through some fractionation procedure, so they might contain the same number of molecules but weigh differently. More generally, the preparation of star- and comb-branched macromolecules from living polyanions and suitable linking agents[3] can involve the use of precursors with different average DPs as well as with different chemical composition. In the following it will be shown how eqs 5 and 6 can be generalized to cover these cases.

Let us consider the simplest case when $f = 2$, any generalization being straightforward. Given two populations PT and PV, each containing N molecules, their number- and weight-average DPs can be put in the form

$$T_n = \frac{1}{N}\sum_i T_i \qquad T_w = \frac{\sum_i T_i^2}{\sum_i T_i} \tag{14a}$$

$$V_n = \frac{1}{N}\sum_i V_i \qquad V_w = \frac{\sum_i V_i^2}{\sum_i V_i} \tag{14b}$$

where the sums are extended to all the molecules in the two populations. By linking the molecules of PT with those of PV, a population PX of N molecules is obtained, in which the ith molecule has DP $X_i = T_i + V_i$. The number-average DP X_n is immediately calculated

$$X_n = \frac{1}{N}\sum_i X_i = \frac{1}{N}(\sum_i T_i + \sum_i V_i) = T_n + V_n \tag{15}$$

and the weight-average DP X_w takes the form

$$X_w = \frac{\sum_i X_i^2}{\sum_i X_i} = \frac{\sum_i (T_i + V_i)^2}{\sum_i (T_i + V_i)} = \frac{\sum_i T_i^2 + \sum_i V_i^2 + 2\sum_i T_i V_i}{\sum_i T_i + \sum_i V_i} \tag{16}$$

The sums in the denominator of the right member of eq 16 can be evaluated from eqs 14. The exact relations $\sum_i T_i^2 = NT_nT_w$ and $\sum_i V_i^2 = NV_nV_w$ hold and, if N is large, it is permissible to substitute in $\sum_i T_iV_i$ the products T_iV_i with the product T_nV_n of the average values. By introducing the number fractions

$$n_T = \frac{T_n}{T_n + V_n} \qquad n_V = \frac{V_n}{T_n + V_n}$$

of the two precursors in population PX, one obtains from eq 16

$$X_w = n_T T_w + n_V V_w + 2n_T n_V(T_n + V_n) \tag{17}$$

Equations 15 and 17 are reduced to eqs 1 and 2, respectively, when the populations PT and PV are identical. To show the differences and the analogies between eqs 15 and 17 on one side and eqs 1 and 2 on the other, let us assume $T_n/V_n = \sigma$, which implies $n_T = \sigma/(\sigma + 1)$ and $n_V = 1/(\sigma + 1)$. From eqs 15 and 17 one obtains

$$X_n = (\sigma + 1)V_n \tag{18}$$

$$X_w = \frac{\sigma}{\sigma + 1}T_w + \frac{1}{\sigma + 1}V_w + \frac{2\sigma}{\sigma + 1}V_n \tag{19}$$

By mixing (without linking molecules) populations PT and PV, a population PY is obtained, for which

$$Y_n = \frac{\sigma + 1}{2}V_n \tag{20}$$

$$Y_w = \frac{\sigma}{\sigma + 1}T_w + \frac{1}{\sigma + 1}V_w \tag{21}$$

By introducing eqs 20 and 21 into eqs 18 and 19, one obtains

$$X_n = 2Y_n \tag{22}$$

$$X_w = Y_w + \frac{4\sigma}{(\sigma + 1)^2}Y_n \tag{23}$$

to be compared with eqs 1 and 2. The more σ differs from 1, the more eq 23 differs from eq 2. Such a difference arises from the fact that, in obtaining eq 2, the molecules of PY are supposed to be randomly linked in pairs whereas, in obtaining eq 23, only linkages between molecules which were initially in the different populations PT and PV are considered.

The process of linking the molecules of two different populations can obviously be repeated, so eqs 15 and 17 can be used to calculate the average DPs of a population of molecules of any desired architecture. As an example, for three-arm star molecules with different average length (and possibly different chemical structure) of the arms, letting A_n, B_n, and C_n be the number-average DPs of the arms and A_w, B_w, and C_w be the corresponding weight-average DPs, one obtains

$$X_n = A_n + B_n + C_n$$

$$X_w = n_A A_w + n_B B_w + n_C C_w + 2(n_A n_B + n_A n_C + n_B n_C)(A_n + B_n + C_n)$$

where $n_A = A_n/X_n$, $n_B = B_n/X_n$, and $n_C = C_n/X_n$. Needless to say, when different parts of the molecules have the same average length, these can be grouped and the resulting number- and weight-average DPs can be conveniently calculated according to eqs 5 and 6.

In conclusion, eqs 6 and 17 allow one to predict the weight-average DP of macromolecules built up by linking together several precursors of either equal or different average DPs and/or chemical structure, thus giving a further possibility, beyond the prediction of the number-average DP, of testing the synthesis procedure. In this sense, they fill a gap already pointed out by Bywater.[3]

Acknowledgment. This work has been supported by C.N.R., Progetto Finalizzato Chimica Fine II.

References and Notes

(1) Guaita, M.; Chiantore, O.; Luda, M. P. *Macromolecules* **1990**, *23*, 2087.
(2) Kosmas, M.; Hadjichristidis, N. *Macromolecules*, in press.
(3) Bywater, S. *Adv. Polym. Sci.* **1979**, *30*, 89.