The molecular weight distribution of oligomers

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It is shown that the relation $P_w/P_n=2$ or the nonuniformity $U=1$ is only a limiting case for high degrees of polymerization, is no more valid for oligomers. Two new relations are derived, one including and one excluding monomers. For the oligomer part of cationically produced polystyrenes the second relation is in good agreement with experiments.

Keywords Oligomers; molecular weight distribution; random formation; polymerization; polystyrenes

In a previous publication[1] the molecular weight distribution (*MWD*) for polymers was derived assuming that average degree of polymerization is much greater than unity. In this communication it is shown that this distribution function is only a limiting one, no more applicable to oligomers. The nonuniformity

$$U=(P_w/P_n)-1 \tag{1}$$

equals unity only in the case $P \gg 1$ (without coupling[2]); in the range of oligomers—already at $P_n=30$—it drops to considerably lower values, and in a different way if the monomer is or is not included.

Firstly, we repeat the derivation made in the cited paper[1], but without the simplifications for higher degrees of polymerization. Let the probability of the addition of a monomer to the growing chain W_p for a termination or a transfer reaction be W_t. Then

$$W_p+W_t=1 \quad \text{and} \quad W_p/W_t=\kappa \tag{2}$$

giving

$$W_p=\frac{\kappa}{1+\kappa}=\alpha$$

Thus, as is shown in the footnote on page 384 of ref. 1, it follows for the mole number of polymers with the degree of polymerization P in one basic mole:

$$n_P=\alpha^{P-1}\Big/\sum_{P=1}^{\infty} P\alpha^{P-1}=\alpha^{P-1}(1-\alpha)^2 \tag{3}$$

The total number of polymers including the monomer is then:

$$n=\sum_{P=1}^{\infty}\alpha^{P-1}(1-\alpha)^2=1-\alpha$$

Since $P_n=1/n$, the number average of the *DP*

$$P_n=1/(1-\alpha) \tag{4}$$

follows.

The definition of the weight average

$$P_w=\frac{\sum\limits_{P=1}^{\infty}P^2n_P}{\sum\limits_{P=1}^{\infty}Pn_P}=\frac{\sum\limits_{P=1}^{\infty}P^2\alpha^{P-1}(1-\alpha)^2}{\sum\limits_{P=1}^{\infty}P\alpha^{P-1}(1-\alpha)^2} \tag{5a}$$

gives the expression

$$P_w=\frac{1+\alpha}{1-\alpha} \tag{5b}$$

Combining equations (1), (3) and (5b) one obtains the nonuniformity

$$U=\alpha \tag{6}$$

The function $U(P_n)$ as calculated from equations (1), (4) and (5b) is represented by the broken line in *Figure 2.*

If the summation is started by the dimer (because the monomer is lost during the evaporation or the precipitation) then

$$n=\sum_{P=2}^{\infty}\alpha^{P-1}\Big/\sum_{P=2}^{\infty}P\alpha^{P-1}=\frac{1-\alpha}{2-\alpha}$$

is valid, with the result

$$P_n=1/n=\frac{2-\alpha}{1-\alpha} \tag{7}$$

In analogy to the definition (5a) the weight average

$$P_w=\frac{\sum\limits_{P=2}^{\infty}P^2\alpha^{P-1}(1-\alpha)^2}{\sum\limits_{P=2}^{\infty}P\alpha^{P-1}(1-\alpha)^2}=\frac{\sum\limits_{P=1}^{\infty}P^2\alpha^{P-1}-1}{\sum\limits_{P=1}^{\infty}P\alpha^{P-1}-1}$$

or

$$P_w=\frac{1+\alpha-(1-\alpha)^3}{(1-\alpha)[1-(1-\alpha)^2]} \tag{8}$$

follows in this case. Hence the nonuniformity

$$U=\frac{\alpha}{(2-\alpha)^2} \tag{9}$$

results. *Table 1* contains the dependence of P_n, P_w and U on α for both types of calculation. One can see great difference, especially for lower oligomers.

It is well known that cationic polymers often have a bimodal *MWD*, the lower component of them lying in the

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Table 1 P_n, P_w and U as a function of α for oligomers. Summation started from $P = 1/P = 2$

α	P_n Equation (4)	P_w Equation (5b)	U Equation (6)	P_n Equation (7)	P_w Equation (8)	U Equation (9)
1/2	2	3	0.5	3	3.66	0.22
2/3	3	5	0.667	4	5.50	0.37
3/4	4	7	0.750	5	7.39	0.48
5/6	6	11	0.833	7	11.27	0.61
9/10	10	19	0.90	11	19.45	0.74
15/16	16	31	0.94	17	31.17	0.83
19/20	20	39	0.95	21	39	0.86
29/30	30	59	0.967	31	59	0.90
49/50	50	99	0.98	51	99	0.94
99/100	100	199	0.99	101	199	0.97

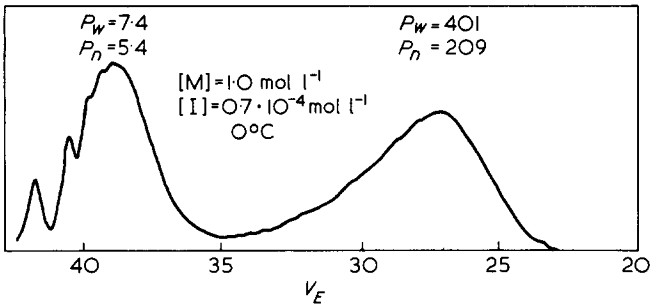

Figure 1 Typical bimodal g.p.c. plot of a cationically synthesized polystyrene. [I] is the concentration of the catalyst[5]

oligomer range (Higashimura[3], Pepper[4]). In *Figure 1* a g.p.c.-curve of a cationically prepared polystyrene is shown, obtained with a column especially suitable for oligomers with a negligible axial dispersion[5]. One can see that the two components are easily separable.

From *Figure 2* it can be clearly seen that the summation beginning from dimer is in good agreement with the theory. One can assume that whenever oligomers are formed in a random manner, the relations developed in this paper are valid.

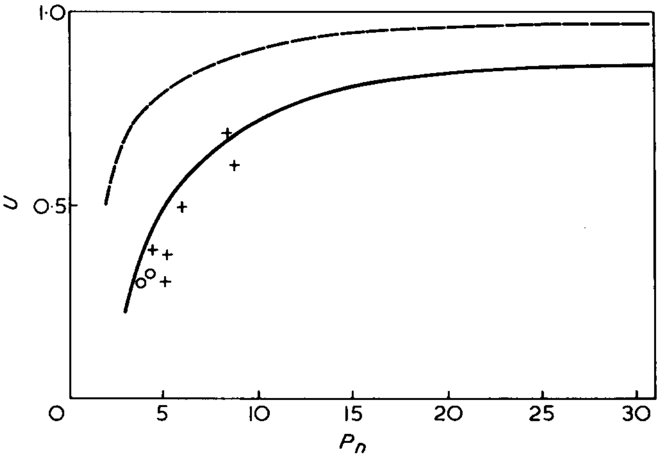

Figure 2 The function $U(P_n)$ as calculated including monomer (broken line) and excluded monomer (solid line). Measuring points correspond to the oligomer part of the distribution curves of cationically synthesized polystyrenes under different conditions. Catalyst: trifluormethanesulphuric acid; solvent: CCl_2H_2; + 15°C > T > −15°C; $[M]$ = 1.0 bzw. 0.3 mol l^{-1}; [I] = 1.5/0.7: 10^{-4} mol l^{-1} [5]

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