equations to get distributions at real times instead of time free distributions cannot possibly cause deviations from the F.S. distribution which is an inner result of correct kinetic equations.

CYCLIC OLIGOMERS

The second article[2] in Polymer contains the same type of statements as mentioned above. The same holds for different rates for $n \neq m$ and $n = m$ and for $(n+m)$ even and $(n+m)$ odd in *Table 1* and for the resulting errors in *Table 2*. Apart from that the authors make statements about oligomers in *Figures 9* and *10*, which are not compared with data from themselves or other authors.

For instance the cyclic dimer concentration is (*Figure 9*) of the order of 1.2 10^{-2} g/kg mix according to their calculations.

Experimental values of Hermans[3] and other authors are 9 g/kg (a factor of 100 larger). All cyclic oligomers (*Figure 8*) together are at equilibrium at about 1–2 g/kg, whereas the sum of the values for the first oligomers dimer, trimer, tetramer are experimentally already of the order of 25 g/kg [3].

Moreover, according to *Table 3* the experiments cited indicate K_{5m} $(m=2)=0.0553$, which with equation (4) means that the concentration of the cyclic dimer is about 0.0553 mol kg^{-1} and in total mass in g/kg $C_2 = 0.0553 \times 226$ g/kg $\sim$ 12,5 g/kg, which seems to be in accord with the Hermans figures given above, but 100 times larger than that of the author in *Figure 9* $\sim 10^{-1}$ g/kg. The authors write (last sentence of the first column of page 487): it is interesting that the total oligomers (*Figure 8*) are 100 times that of C_2. Stating otherwise: as we know from *Table 3* that experimentally $C_2 \sim 12{,}5$ g/kg, the total oligomers should be 1250 g/kg according to theory *e.g.* there is no linear polymer any more, only cyclic oligomer! Without going into too much detail it seems that this internal difficulty in the published paper must rest upon some wrong assumptions.

REFERENCES

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3 van Velden, P. F., van der Want, G. M., Heikens, D., Kruissink, Ch. A., Hermans, P. H., and Staverman, A. J. *Rec. Trav. Chim. Pays-Bas* 1955, **74**, 1376; Heikens, D. *Rec. Trav. Chim. Oays-Bas* 1956, **75**, 1199

Response to Professor Heiken's letter:

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Polymer paper published March 1981 (1981, **22**, 387):

We have gone through the paper carefully and we find that at no time do we attribute the effect observed in *Figure 1* to reversibility alone. Our work as reported is correct and we respond to Professor Heikens comments pointwise as follows:

(1) *The factor of two*:

(a) For the reaction

$$S_m + S_m \underset{k_2}{\overset{k_1}{\rightleftarrows}} S_{2m} + W$$

the forward rate constant has been put as k_1 {2 possibilities of end groups reacting $\times \frac{1}{2}$ to prevent double counting of molecules and the corresponding term for $d[S_m]/dt$ is $-2k_1[S_m^2]$ because two molecules of S_m are disappearing simultaneously}. This is consistent with the convention followed by R. Aris, 'Introduction to the analysis of Chemical Reactors' (equations 2.9.8 giving the mass balance for batch reactors with the general expression for the intrinsic rate stated in equations 4.2.4), [Prentice Hall, (1965)] and other workers in the field who write for the reaction $2A \xrightarrow{k}$ products: $d[A]/dt = -2k[A]^2$.

Prof. Heikens, however, suggests that we write

$$S_m + S_m \xrightarrow{2k_t} S_{2m} + W$$

with $d[S_m]/dt = -2k_1[S_m]^2$. The end results are identical, though he deviates from convention. This is exactly why, even though Professor Heikens feels that we have made an error, he gets the same equations as we have.

The same is true for our second paper (April '81) and Professor Heikens can easily confirm that he would get the same mass-balance equations even by his method. In fact, if we neglect cyclization and monofunctional groups, our results are identical to those published by Tai *et al.* (*J. Appl. Polym. Sci.* 1980, **25**, 2789), which appeared only after we had submitted our papers.

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Thus we feel we have made no errors in the two papers.

(b) When one substitutes $n=1$ in equation (4) a term like

$$\sum_{r=1}^{0} [P_r][P_{1-r}]$$

is obtained. Since this expression has no meaning on a computer, a different balance equation for S_1 has been written. There is also no species called S_0 in the system and Professor Heikens puts $[S_0]=0$ which is once again a matter of convention.

(2) *Reversible polymerization with* k_1 *and* k_2 *as function of* [W]:

We have obtained the Flory distribution under

(i) irreversible polymerization with k_1 constant;
(ii) irreversible polymerization with varying k_1; and
(iii) reversible polymerization with constant k_1 and k_2.

However when k_1 and k_2 are allowed to vary as given in *Table 1* of the paper, we obtain the deviation and this can be easily seen as follows.

Professor Heikens gives in equation (5): the Flory distribution is characterized by

$$[S_n]=p[S_{n-1}]$$

For a given p independent of chain length

$$[S_n]=p^{n-1}[S_1]. \tag{2}$$

For irreversible polymerization, one has

$$\sum_{n=1}^{\infty} [S_n]/[S_1]_0=\frac{1}{[S_1]_0\tau+1}=(1-p) \tag{3}$$

where $[S_1]_0$ as the initial concentration of monomer, p is the conversion and

$$\tau=\sum_0^t k_1 \mathrm{d}t \tag{4}$$

It can be shown that

$$[S_1]/[S_1]_0=\frac{1}{([S_1]_0\tau+1)^2}=(1-p)^2 \tag{5}$$

Thus the distribution is given by equation (2) as

$$[S_n]=[S_1]_0(1-p)^2p^{n-1} \tag{6}$$

To find $[S_1]$ as a function of time kinetically for reversible polymerization for constant k_1 and k_2 is not easy algebraically but it has been shown that the Flory distribution still holds. Our own numerical calculations also testify to that.

However, with k_1 and k_2 as a function of $[W]$, it is a different matter. One would have to find $[S_1]$ as a function of p and substitute in equation (2). For an arbitrary functional dependence, $[S_1]$ will not be expected to be governed by equation (5) and therefore equation (6) would not hold good. We believe this is what we are observing.

Polymer paper published April 1981 (1981, **22**, 481):

1 Comment on factor of 2 — as above.

2 As the reviewer has correctly pointed out, our work on oligomer formation in nylon-6 is a sensitivity study. In fact, in our more recent paper (*J. App. Polym. Sci.*, in press) we have improved the kinetic scheme along the lines of what we have already suggested in the *Polymer* paper, and have found much higher oligomer concentrations. The main object of our nylon-6 paper was to present a technique to obtain the *MWD*s, which was being done for the first time (we had also emphasized this in our reply to the reviewer's comments) and modelling cyclic oligomer formation is only one of the several aspects studied. The only other kinetic model on cyclic oligomer formation was that of Ito and Mochizuki and who presented incomplete information for proprietary reasons. We have tried to model oligomer formation in a more fundamental manner and have admitted in the paper itself that improvements are required.

(3) After our two papers were submitted, Tai *et al.* [*J. Appl. Polym. Sci.*, 1980, **25**, 1789] published results on the polydispersity index, ρ, calculated from the experimental *MWD* obtained by g.p.c. Since their theoretical model yielded ρ only and not the complete *MWD*, they compare ρ only. Now with our model, it is possible for them to compare their experimental *MWD*s. This would be a better approach since in obtaining the moments from experimental results, there is a loss of sensitivity.