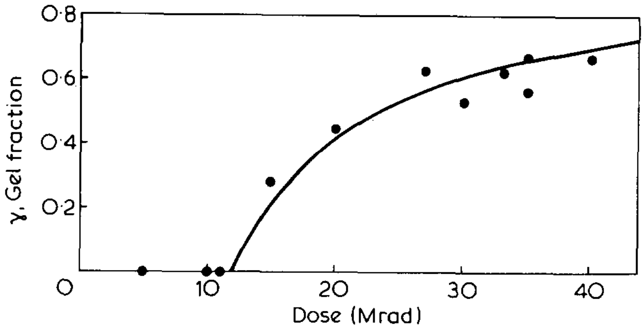

Figure 2 Determination of gelation dose D_g of γ-irradiated PAN using the gel fraction method

appearance of gels determined by this method gives nearly the same value as obtained by photometric method—12 Mrad.

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COMMENTS

Flory-Schulz distribution does hold for reversible polycondensation

Comments on the articles on reversible nylon-6 polymerization by S. K. Gupta *et al.*

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(*Received May* 27 1981)

Reading two articles[1,2] invites some comment (*Polymer* 1981, **22**, 387; *Polymer* 1981, **22**, 481).

FLORY-SCHULZ DISTRIBUTION

The general idea put forward in these articles is that the Flory-Schulz distribution in polycondensation holds only when the forward reaction is taken into consideration, whereas deviations should occur when the backward reaction is also included. To prove this hypothesis the authors borrow rate and equilibrium constants from the literature and by using rate equations for the monomer (S_1) and for a chain of length n (S_n) they calculate the number distribution during reaction. They find a maximum for $n=2$ if the backward reaction is also taken into consideration and thus conclude the distribution differs from a F.S. distribution. An F.S. distribution is found by the authors only in those cases where the backward reaction is neglected.

Flory in his book does not make any assumption about forward and backward reactions but only defines the probability for any functional end group to be free as p or to be connected as $(1-p)$, independent of chain length. As a consequence the result of the authors is in contradiction with their own and the identical assumption of equal reactivity. Therefore, there may be some errors in the authors' equations.

They define the rate constants k_1 and k_2 for condensation and hydrolysis, successively, based on concentrations of functional groups.

The equation for the monomer then becomes:

$$\frac{\mathrm{d}[S_1]}{\mathrm{d}t} = -2k_1[S_1]\sum_{n=1}^{\infty}[S_n] + 2k_2[W]\sum_{n=2}^{\infty}[S_n]$$

The factor 2 in the first term originates from the two possibilities of reacting an S_1 with an S_n (both having two end groups). The authors state, however, that for $S_n = S_1$, this factor should be unity and from their calculations it can be assumed that they indeed took that factor as equal to unity. However, also in that case the factor should have the value of 2.

The explanation is as follows: a factor 2 should be added because of the two end groups in one S_1 molecule

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and two in the other, giving two possibilities of the reaction leading to S_2.

$$S_1 + S_1 \underset{k_1}{\overset{\rightarrow}{\leftarrow}} S_2 + W$$

an extra factor 2 should be added because in any event of reaction, 2 monomers are converted. But as the authors rightly remark a factor $\frac{1}{2}$ should be added as in the case of equal molecules a double count is made by putting the rate equal to $[S_1]^2$.

So for equal molecules

$$\frac{\mathrm{d}[S_1]}{\mathrm{d}t} = -\underset{\text{end group}}{2}.\underset{\text{2 monomers are converted}}{2}.\overset{\text{double counting}}{\tfrac{1}{2}}k_1[S_1]^2 = -2k_1[S_1]^2 \qquad (1)$$

In case of unequal molecules

$$\frac{\mathrm{d}[S_1]}{\mathrm{d}t} = -\underset{\text{end group}}{2}k_1[S_1][S_n] \qquad (2)$$

only one factor 2 should be added for the two end groups of S_1 and S_n.

So for reaction of S_1 with all molecules

$$\frac{\mathrm{d}[S_1]}{\mathrm{d}t} = -2k_1[S_1]\sum_{n=1}^{\infty} S_n + 2k_2[W]\sum_{n=2}^{\infty}[S_n] \qquad (3)$$

So equation (3) in ref 1 is correct but without any restriction about reactions of S_1 with S_1. Also equation (4) in ref 2 is correct,

$$\frac{\mathrm{d}[S_n]}{\mathrm{d}t} = k_1\sum_{r=1}^{n-1} S_r S_{n-r} - 2k_1[S_n]\sum_{m=1}^{\infty}[S_m]$$

$$-(n-1)k_2[W][S_n]$$

$$+2k_2[W]\sum_{m=1}^{\infty} S_{n+m} \qquad (4)$$

but without the restriction $n \geqslant 2$.

It can be seen that this last equation also describes the reaction between equal molecules, since the rate constants contain the given factors according to analogous reasoning as for equation (3).

Comparing equations (3) and (4) it becomes evident that equation (4) does hold for $n = 1, 2, \ldots \infty$ and not only for $n = 2, 3, \ldots \infty$ as stated in ref 2 ($[S_{n-r}] = [S_0] = 0$ for $(n-1) = 0$, $n = 1$). As equation (4) assumes equal reactivity it must be in accordance with the F.S. distribution.

A F.S. distribution is characterized by:

$$[S_n] = p[S_{n-1}], \qquad (5)$$

or, during reaction:

$$\frac{\mathrm{d}[S_n]}{\mathrm{d}t} = p\frac{\mathrm{d}[S_{n-1}]}{\mathrm{d}t} + [S_{n-1}]\frac{\mathrm{d}p}{\mathrm{d}t} \qquad (6)$$

where $\mathrm{d}p/\mathrm{d}t$ should be a function of time and not of chain length n. Assuming an F.S. distribution throughout the reaction (in general $S_n = pS_{n-1}$) equation (4) can be rewritten as

$$\frac{\mathrm{d}[S_n]}{\mathrm{d}t} = pk_1\sum_{r=1}^{n-2}[S_r][S_{n-1-r}]$$

$$-p2k_1[S_{n-1}]\sum_{m=1}^{\infty}[S_m]$$

$$+p(n-2)k_2[W][S_{n-1}]$$

$$+p2k_2[W]\sum_{m=1}^{\infty}[S_{n-1+m}]$$

$$+k_1[S_{n-1}]\left[[S_1] - p\frac{k_2}{k_1}[W]\right]$$

$$\frac{\mathrm{d}[S_n]}{\mathrm{d}t} = p\frac{\mathrm{d}[S_{n-1}]}{\mathrm{d}t} + [S_{n-1}]k_1\left[[S_1] - \frac{p[W]}{K}\right] \qquad (7)$$

Comparing equation (7) with equation (6) shows that the F.S. distribution is the relevant distribution, also valid when backward reactions are included.

Moreover it can be shown that:

$$\frac{\mathrm{d}p}{\mathrm{d}t} = k_1\left[[S_1] - p\frac{[W]}{K}\right] \qquad (8)$$

Taking $S_1 = S_1^0(1-p)^2$

$$\frac{\mathrm{d}p}{\mathrm{d}t} = k_1[S_1^0]\left[(1-p)^2 - p\frac{[W]}{K}\right] \qquad (9)$$

Starting at $t = 0$, $S_1 = S_1^0$ and $[W] = 0$, at time t, $[W] = pS_1^0$ and

$$\frac{\mathrm{d}p}{\mathrm{d}t} = k_1 S_1^0\left[(1-p)^2 - \frac{p^2}{K}\right]$$

$$= \frac{k_1[\mathrm{NH_2}][\mathrm{CO_2H}] - k_2[W][\mathrm{NHCO}]}{[S_1^0]} \qquad (10)$$

as $[\mathrm{NHCO}] = p[S_1^0]$ and $[\mathrm{CO_2H}] = [\mathrm{NH_2}] = (1-p)[S_1^0]$. Taking

$$\frac{\mathrm{d}p}{\mathrm{d}t} = \frac{1}{[S_1^0]}\frac{\mathrm{d}[\mathrm{NH_2}]}{\mathrm{d}t},$$

equation (10) becomes

$$\frac{\mathrm{d}[\mathrm{NH_2}]}{\mathrm{d}t} = k_1[\mathrm{NH_2}][\mathrm{CO_2H}] - k_2[W][\mathrm{NHCO}] \qquad (11)$$

which proves equation (7) has the correct form. Therefore, it may be concluded that the maximum for $n \sim 2$ in the F.S. distribution calculated by the authors may very well originate from using the incorrect factors in equation (3) for $\mathrm{d}[S_1]/\mathrm{d}t$.

Furthermore, introduction of experimental values of k_1 and K independent of chain length in the kinetic 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.

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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 $\mathrm{d}[S_m]/\mathrm{d}t$ 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: $\mathrm{d}[A]/\mathrm{d}t = -2k[A]^2$.

Prof. Heikens, however, suggests that we write

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

with $\mathrm{d}[S_m]/\mathrm{d}t = -2k_1[S_m]^2$. 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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