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Fig. 1

Figure 1: Fig. 1

Abstract

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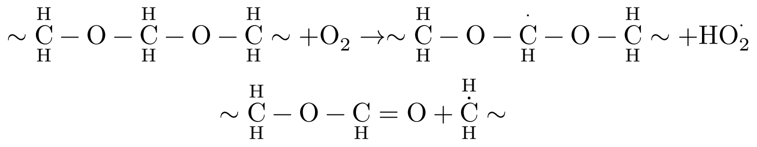
ON THE CHANGE OF MOLECULAR WEIGHT DURING THE OXIDATIVE DESTRUCTION OF POLYFORMALDEHYDE

(Presented by Academician N. N. Semenov, January 21, 1963)

In a previous communication (^{1}) we noted the distinctive features of the action of oxygen on the decomposition of polyformaldehyde (PFA), consisting in the initiation by it of depolymerization and in the absence of an oxidative direction of destruction proper. From the mechanism given there it follows that the act of initiation by oxygen is, with high probability, accompanied by random chain scission with the formation of a stable fragment and an active center according to the reaction:



$$\sim \underset{H}{\overset{H}{C}} - O - \underset{H}{\overset{H}{C}} - O - \underset{H}{\overset{H}{C}} \sim + O_2 \rightarrow \sim \underset{H}{\overset{H}{C}} - O - \underset{H}{\overset{\cdot}{C}} - O - \underset{H}{\overset{H}{C}} \sim + HO_2^{\cdot}$$
$$\sim \underset{H}{\overset{H}{C}} - O - \underset{H}{C} = O + \underset{H}{\overset{H}{\dot{C}}} \sim \qquad (1)$$

It could therefore be expected that the molecular weight of the polymer in the process of oxidative decomposition would change more sharply than in thermal destruction. As can be seen from Fig. 1, this supposition is confirmed experimentally*.

Fig. 1. Change in the molecular weight of polyformaldehyde with the degree of conversion during destruction in an oxygen atmosphere and in vacuum; **1** and **2** –in oxygen; **3** and **4** –in vacuum; **1** and **4** –nonacetylated PFA; **2** and **3** –acetylated PFA; **1**, **2**, and **4** –$T = 200°$, **3** –$T = 270°$.

However, it is necessary to establish whether reaction (1) can be fully responsible for the change in molecular weight observed during oxidative decomposition, or whether there exist additional processes leading to such a sharp decrease in it.

Let us consider how the number-average molecular weight depends on the amount of monomer evolved during destruction. We shall assume that destruction proceeds according to reaction (1), and that the active center formed depolymerizes to completion. Initiation occurs at any point of the chain, and any part of the decomposed molecule may be stable.

Denote by k the product of the rate constant of the reaction of oxygen with a bond and the oxygen concentration. Let, prior to destruction, the polymer have molecules with numbers of units from 2 to N, and let its number-average molecular weight be equal to $\overline{P}^0$. Then the rate of decrease in the number of molecules of length N (with number of units N) is

$$\frac{dP_N}{dt} = -k(N-1)P_N. \qquad \text{(2a)}$$

Molecules of length $N-i$ disappear according to an analogous law, but appear from molecules of length greater than $N-i$ only when one bond is hit. Therefore,

$$\frac{dP_i}{dt} = -k(i-1) + k\sum_{j=i+1}^{N} P_j, \quad \text{where } i = 2, \dots, N. \qquad \text{(2)}$$

Summing over i, we obtain a differential equation whose solution is

$$\sum_{j=2}^{N} P_j = \sum_{j=2}^{N} P_j^0 e^{-kt}. \qquad \text{(3)}$$

The amount of monomer liberated during time t is equal to the difference between the number of monomeric units contained in the polymer before destruction and at time t:

$$\Delta M = \sum_{j=2}^{N} jP_j^0 - \sum_{j=2}^{N} jP_j(t),$$

or the degree of conversion is

$$\alpha(t) = \frac{\Delta M}{\sum_{j=2}^{N} jP_j^0} = 1 - \frac{\sum_{j=2}^{N} jP_j(t)}{\sum_{j=2}^{N} jP_j^0}. \qquad \text{(4)}$$

From the definition of the number-average molecular weight,

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* For the decomposition of acetylated polymer in vacuum the curve of molecular-weight decrease at 270° is given, since at lower temperatures this polymer decomposes thermally at an insignificant rate.

$$M_0 \sum_{j=2}^{N} j P_j(t) = \overline{P}(t) \sum_{j=2}^{N} \overline{P}_j(t) \quad \text{and} \quad M_0 \sum_{j=2}^{N} j P_j^0 = \overline{P}^0 \sum_{j=2}^{N} P_j^0, \tag{5}$$

where M_0 is the molecular weight of the monomer.

Substituting (3) and (5) into (4), we obtain an expression for the degree of conversion:

$$\alpha = 1 - \frac{\overline{P}}{\overline{P}^0} e^{-kt}. \tag{6}$$

System (2) is solved successively, beginning with P_N. The solution of this system in general form is: $P_N = P_N^0 e^{-k(N-1)t}$,

$$P_i = \sum_{j=i}^{N} P_j^0 e^{-k(i-1)t} - \sum_{j=i+1}^{N} P_j^0 e^{-kit}, \quad \text{where } i = 2, \dots, N-1. \tag{7}$$

Equation (6), without taking into account the factor e^{-kt}, gives a straight line in the coordinates α and $\overline{P}/\overline{P}^0$.

Let us estimate what deviation from the straight line is obtained when the multiplier e^{-kt} is taken into account. Let us see what it is equal to when the destruction is already almost complete, for example, has proceeded to 90%. Let the initial molecular weight be 10,000, i.e., the number of monomeric units in a polyformaldehyde molecule is 300. Since, upon attack, one part of the polymer molecule is destroyed, it is clear that no less than 90% of the monomer will be liberated when all molecules longer than 30 units have disappeared.

From the solution of system (7) it is evident that the last of these molecules to disappear will be those having a length of 30 units. From (7),

$$P_{30} = \sum_{j=30}^{300} P_j^0 e^{-29kt} - \sum_{j=31}^{300} P_j^0 e^{-30kt}.$$

We shall assume that molecules of length 30 units have disappeared if

$$\frac{P_{30}}{\sum_{j=2}^{N} P_j^0} = 0.01.$$

Let us estimate the time when this will be valid:

$$P_{30} < \sum_{j=30}^{300} P_j^0 e^{-29kt} < \sum_{j=2}^{300} P_j^0 e^{-29kt},$$

$$e^{-29kt_{0.9}} = 10^{-2}, \qquad t_{0.9} \simeq \frac{1}{6k}.$$

The factor e^{-kt} at this instant of time will be equal to $e^{-kt_{0.9}} = e^{-1/6} \simeq 0.85$. Consequently, the deviation from a straight line at 90% conversion is, by the crudest estimate, no more than 0.15 of the value $\overline{P}/\overline{P^0}$. At smaller degrees of conversion this deviation is considerably weaker and, consequently, the dependence of the number-average molecular weight on the degree of conversion may be regarded as linear up to sufficiently large depths.

Having specified some initial distribution with respect to molecular weights, one can find the exact dependence of the number-average molecular weight on the degree of conversion. Let the initial distribution obey the law

$$P_j^0 = N_0 \frac{1-\beta}{\beta^2} \beta^j, \tag{8}$$

where

$$\beta = \frac{k_p MC}{k_p MC + k_n C + K_2 C}$$

is the probability of the addition reaction.

Then the number-average molecular weight is

$$\overline{P^0} = \frac{1}{N^0} \sum_2^\infty j P_j^0 = \frac{2-\beta}{1-\beta}.$$

To calculate the sum $\sum_2^N jP_j$, multiply each equation of system (7) by $N, N-1, \ldots, 2$, respectively, and add. As a result we obtain

$$\sum_2^N jP_j = \sum_{j=3}^N P_j^0 \sum_{i=3}^j e^{-k(i-1)t} + 2 \sum_{j=2}^N P_j^0 e^{-kt}, \tag{9}$$

substituting

$$\sum_{i=3}^j e^{-k(i-1)t} = \frac{e^{-2kt}\left(1 - e^{-k(j-2)t}\right)}{1 - e^{-kt}}$$

and passing to the limit as $N \to \infty$, we obtain

$$\sum_{2}^{\infty} jP_j = 2e^{-kt}\sum_{j=2}^{\infty} P_j^0 + \frac{e^{-2kt}}{1-e^{-kt}}\sum_{j=3}^{\infty} P_j^0 - \frac{1}{1-e^{-kt}}\sum_{j=3}^{\infty} P_j^0 e^{-kjt}. \tag{10}$$

Substituting (8) into the sums (10), let us calculate them.

Using

$$\sum_{2}^{\infty} jP_j = (1-\alpha)N_0\overline{P^0} = (1-\alpha)\frac{2-\beta}{1-\beta}N_0,$$

we obtain an equation for e^{-kt}:

$$(1-\alpha)\frac{2-\beta}{1-\beta} = 2e^{-kt} + \beta\frac{e^{-2kt}}{1-e^{-kt}} - \beta(1-\beta)\frac{e^{-3kt}}{\left(1-e^{-kt}\right)\left(1-\beta e^{-kt}\right)},$$

which after transformation takes the form

$$(1-\alpha)\frac{2-\beta}{1-\beta} = \frac{2x-\beta x^2}{1-\beta x}, \qquad \text{where } x = e^{-kt}.$$

This quadratic equation has two solutions, one of which is greater than unity, and the other

$$x = \frac{1}{\beta} + \frac{1-\alpha}{2}\frac{2-\beta}{1-\beta} - \sqrt{\left(\frac{1}{\beta} + \frac{1-\alpha}{2}\frac{2-\beta}{1-\beta}\right)^2 - \frac{1-\alpha}{\beta}\frac{2-\beta}{1-\beta}}.$$

Since $\beta \simeq 1$, and

$$\frac{2-\beta}{1-\beta} = \overline{P^0},$$

we obtain

$$x = 1 + \frac{1-\alpha}{2}\overline{P^0} - \frac{1-\alpha}{2}\overline{P^0}\sqrt{1 + \left(\frac{2}{(1-\alpha)\overline{P^0}}\right)^2}.$$

For

$$\left(\frac{2}{\bar{P}^0(1-\alpha)}\right)^2 \ll 1$$

the factor

$$\sqrt{1+\left(\frac{2}{(1-\alpha)\bar{P}^0}\right)^2}$$

can be expanded in a series in powers of

$$\left(\frac{2}{\bar{P}^0(1-\alpha)}\right)^2$$

and the first two terms of the expansion taken. Then we obtain

$$e^{-kt} \simeq 1+\frac{1-\alpha}{2}\bar{P}^0-\frac{1-\alpha}{2}\bar{P}^0\left[1+\frac{1}{2}\left(\frac{2}{(1-\alpha)\bar{P}^0}\right)^2\right] \simeq 1-\frac{1}{(1-\alpha)\bar{P}^0}$$

or

$$e^{kt} \simeq 1+\frac{1}{(1-\alpha)\bar{P}^0}.$$

Substituting the expression for e^{kt} into (6), we finally obtain

$$\frac{\bar{P}}{\bar{P}^0}=(1-\alpha)\left(1+\frac{1}{(1-\alpha)P^0}\right).$$

For the case $\bar{P}^0 = 300$ and $\alpha = 0.9$, the deviation from the straight line is equal to 1/30, or 3%.

All calculations have been carried out by us for the number-average molecular weight. Let us consider how the weight-average molecular weight will change under the adopted destruction mechanism. With the initial distribution

$$P_j^0 = N_0\frac{1-\beta}{\beta^2}\beta^j$$

we have

$$\frac{M_w^0}{\bar{P}^0}=2.$$

Multiplying equations (7) by $N^2, (N-1)^2, \ldots, 4$, respectively, and adding them, we obtain:

$$\sum_{j}^{N} j^2 P_j = \sum_{j=3}^{N} P_j^0 \sum_{i=3}^{j} (2i-1) e^{-k(i-1)t} + 4e^{-kt} \sum_{j=2}^{N} P_j^0.$$

Passing to the limit as $N \to \infty$, neglecting terms containing $(1-\beta)$, and taking $\beta = 1$, we obtain

$$\sum_{j=2}^{\infty} j^2 P_j \simeq \frac{4e^{-kt} - 3e^{-2kt} + e^{-3kt}}{(1-e^{-kt})^2} N_0. \tag{11}$$

Since $e^{-kt} \simeq 1$, from (10) one can find an expression for

$$1 - e^{-kt} \simeq \frac{1}{\bar{P}-1} \simeq \frac{1}{\bar{P}},$$

which, substituting into (11), gives:

$$\sum_{j=2}^{\infty} j^2 P_j \simeq N_0 e^{-kt} 2\bar{P}^2, \qquad M_w = \frac{\sum_2^\infty j^2 P_j}{\sum_2^\infty j P_j} \simeq \frac{N_0 e^{-kt} 2\bar{P}^2}{N_0 e^{-kt} \bar{P}} \simeq 2\bar{P}.$$

Consequently, the calculation carried out for the number-average molecular weight is also valid for the weight-average molecular weight, which will likewise decrease linearly with the depth of destruction.

It is clear from the calculation that reaction (1) cannot lead to as sharp a decrease in molecular weight as is observed experimentally. The experimentally obtained dependence of molecular weight on the degree of conversion is characteristic of the case in which, as a result of the decomposition of a molecule, two stable fragments are formed (^{2}). The latter may arise either because oxygen, along with initiating destruction, inhibits the decomposition of the active center, or as a consequence of acidolysis of the polymer by an acid formed in the process of "oxidation."

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CITED LITERATURE

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