

**Comments on the Paper by J. B. Lawrence and N. A. Weir, "The Kinetics of Atactic Polystyrene Oxidation in Solution," *J. Appl. Polym. Sci.*, 18, 1821 (1974)**

The problem of free-valency intramolecular transfer in polymers is widely discussed in the literature. There is some experimental proof of this fact in the appearance of neighboring hydroperoxide groups in polystyrene at low temperature oxidation<sup>1</sup>; dependence of destruction velocity of macromolecules on their molecular weight,<sup>2</sup> followed by a decrease in molecular weight distribution width, and so on. This problem is the concern of the paper by J. B. Lawrence and N. A. Weir.

The paper presents the results of polystyrene oxidation in solution initiated by photolysis of azoisobutyrodinitrile at 25°C. Oxidation of the model hydrocarbons cumene and three diphenylalkanes was also investigated.

One could have expected that in view of the commonly adopted oxidation mechanism, the effective order of oxygen absorption rate would be near  $\frac{1}{2}$  to the light intensity  $I$  and initiator concentration  $[A]$  and near unity in the oxidized substance concentration  $[RH]$ . Such regularity was observed for cumene and 1,3-diphenylpropane. However, an alternative dependence was observed in the case of diphenylalkanes with longer hydrocarbon chain and for various molecular weight polystyrenes: the order in  $I$  and  $[A]$  was near unity, while that to  $[RH]$  was essentially smaller than unity.

From the analysis of the equation of the general oxidation rate  $R$ ,

$$R_0 = \frac{K_3[PH](2\xi I_0[A]\epsilon)^{1/2}}{K_6^{1/2}} + 3\xi I_0[A]\epsilon$$

and the authors' experimental results, they have concluded that in the case of hydrocarbons with the longer hydrocarbon chains and especially for the polymers, the second term in this equation contributes quite essentially to the total reaction rate. The authors have assumed that the second term is responsible for an intramolecular chain propagation and concluded that this process plays a significant role in the polymer oxidation.

However, it should be noted that the second term in the kinetic equation does not relate to the intramolecular chain propagation at all. It accounts quantitatively for both oxygen absorption by initiator and polymer radical generated with the first step of hydrogen abstraction from the polymer molecule, and the oxygen evolution by recombination of two polymeric peroxide radicals. Thus, the second term describes reaction conditions when no intramolecular chain propagation takes place. In this case, the chain length per the unit of initiation rate is equal to  $\nu = 3$ . The rate corresponding to this chain length should be subtracted from the total oxidation rate and the resulting value would be characteristic of chain propagation in the polymer.

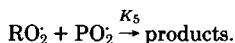
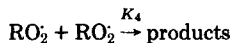
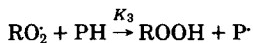
Oxidation of four (from six) compounds studied in the work occurs with a chain length less than 6 and for the polymers  $\nu < 3$ . Obviously, in these cases the treatment of experimental data should be performed in view of the concepts mentioned above. This probably has not been done by the authors. As a result, the kinetic parameters obtained and discussed in the paper apparently have no clear physical meaning. Probably, the high apparent activation energies of the polymer oxidation correspond to a considerable decrease in viscosity and increase in the coefficient of cage yield with increasing temperature.

One may draw the following conclusions:

1. The authors present the kinetic scheme involving the reactions of recombination of the peroxide initiator radicals and cross recombination of the initiator and polymer peroxide radicals. However, these reactions have not been taken into account in the computation. In the final formula eqs. 2, 6, and 7, one may find the following error: the constant  $K'_3$  (reaction  $PO_2 + PH$ ) should be used instead of  $K_3$  (reaction  $RO_2 + PH$ ).

2. The reaction order to  $[PH]$  could be the first as well. As can be seen from Figure 4, the initial part of curve A is almost linear. But in curve B, this part was not measured since such measurement would require lower concentrations. In the method adopted by the authors, any order (from 0 to 1) can be obtained with curve A depending on which part is drawn in logarithmic coordinates.

3. A decrease of rate with [PH] (Fig. 4) observed by the authors may be explained by the following competing reaction:



The recombination of  $\text{PO}_2$  radicals is neglected since, according to the authors' data, the chains are short in the polymer. Computation of such a scheme shows that at sufficiently high [PH] (i.e., when  $K_3[\text{PH}] \gg K_4[\text{RO}_2]$ ),  $d\text{O}_2/dt \neq f[\text{PH}]$ . Thus, the authors' explanation of this phenomenon is not unequivocal.

4. The reaction order to [PH] should be increased over 1 since the rate of  $\text{O}_2$  absorption, usually measured in moles/l.-sec, has been related by the authors to [PH] concentration and is expressed in moles  $\text{O}_2/\text{mol PH}\cdot\text{sec}$ . In the light of remarks 2 and 3, it is quite obvious that according to the authors' data, there are certain inconsistencies in this problem.

5. Equation (11),

$$\frac{1}{1 - \epsilon} = \alpha + \frac{\beta}{\eta}$$

is not even a qualitative explanation of the observed reaction rate dependence versus solution viscosity. According to eq. (11), the greatest effect on the coefficient of radical cage yield is observed at small viscosity values, and when  $\eta \rightarrow \infty$ ,  $\epsilon \rightarrow \text{const}$ . However, an opposite pattern is seen from Figure 5: it is at the lower viscosity that the reaction rate is practically independent of  $\eta$ .

For these reasons, the very interesting experimental material of this paper has to be viewed with some limitations.

### References

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