

## Changes in Molecular Weight During Autoxidation of Atactic Polypropylene in Solution

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### Synopsis

The authors had previously reported a general scheme with corresponding kinetic expressions for the uncatalyzed thermal autoxidation of polyolefins, such as atactic polybutene-1 (APB), in the bulk phase. Recently, Bawn and Chaudhri reported that similar kinetic expressions and scheme were also applicable to autoxidation of atactic polypropylene (APP) in solution. These workers did not attempt to correlate their results for the effect of oxidation on the molecular weight of APP as evidenced by intrinsic viscosity. In this paper, we have applied expressions, previously reported for changes in intrinsic viscosity as a function of time during the autoxidation of APB in the bulk phase, to the data provided by Bawn and Chaudhri for the autoxidation of APP in solution. The quantitative evidence obtained indicates that the intrinsic viscosity relationships which were found to be valid for the autoxidation of APB in the bulk phase are also valid for the autoxidation of APP in solution (at polymer concentrations of ca. 1.5M and above).

### Introduction

Recently, we presented a general scheme for the thermal oxidation, in the absence of additives, of isotactic polypropylene (PP)<sup>1-5</sup> and atactic poly(1-butene) (APB).<sup>5,6</sup> The thermal oxidation kinetics of films of these polyolefins were studied by using infrared spectroscopy, as a function of temperature and oxygen-to-nitrogen ratios, by observing rates of carbonyl and hydroperoxide formation. Activation energies were estimated for various steps in the scheme. We found that the scheme and the mathematical expressions derived therefrom satisfactorily explain the experimental results obtained. Furthermore, results obtained for PP and APB by other investigators, i.e., rate of formation of volatile products,<sup>3,5,7,8</sup> chemiluminescence,<sup>4,9,10</sup> oxygen absorption,<sup>4,9,10</sup> and changes in intrinsic viscosity as a function of time,<sup>11,12</sup> could also be accounted for by means of the scheme.

Recently, Bawn and Chaudhri<sup>13</sup> utilized a general scheme similar to ours in order to explain their experimental results for the autoxidation of atactic polypropylene (APP) in a solution of 1,2,4-trichlorobenzene. They found that the kinetic expressions obtained from this scheme satisfactorily accounted for their kinetic data. Thus, Bawn and Chaudhri were able to

explain the kinetic dependency of rate of oxygen absorption on polymer concentration and on oxygen pressure. However, they did not attempt to correlate their results for the effect of oxidation on the molecular weight of APP as evidenced by intrinsic viscosity (see Fig. 6 of ref. 13). In this paper, we will attempt this correlation using kinetic expressions previously reported<sup>11</sup> for changes in intrinsic viscosity as a function of time during the uncatalyzed thermal autoxidation of APB in the bulk phase.

### Theory

Based upon a general scheme for polyolefin autoxidation previously presented,<sup>1-6</sup> the following expression may readily be derived

$$\ln S = -At + \ln (A\rho_m/1 - e^{-At_m}) \quad (1)$$

where,  $S = d\rho/dt$ ;  $\rho$  and  $\rho_m$  denote oxidation rate during time  $t$  and at time  $t_m$ , respectively ( $t_m$  denotes the time at which oxidation rate approaches a maximum value).  $A$  denotes a kinetic parameter defined previously.<sup>1-6</sup> From eq. (1), it can be seen that a plot of  $\ln S$  versus  $t$  should give a linear relationship whose slope will afford a value of  $A$ . This value of  $A$  may be compared with another value of this parameter estimated from intrinsic viscosity data reported<sup>13</sup> as follows.

It has been previously reported<sup>11</sup> that the following expression is applicable to changes in molecular weight of APB during autoxidation in the bulk phase

$$F_n = Ct - (C/A) + (Ce^{-At}/A) \quad (2)$$

where,  $F_n = ([\eta]_0/[\eta])^{1/a} - 1$ ;  $a$  is the Mark-Houwink exponent (taken as 0.8 for APP);  $[\eta]_0$  and  $[\eta]$  denote initial value and value at time  $t$  respectively, of intrinsic viscosity; and  $C$  is a constant. Since Bawn and Chaudhri reported data for  $[\eta]$  versus per cent oxidation (PO), it is necessary to convert  $t$  in terms of PO before eq. (2) may be utilized. It can be shown<sup>13</sup> that

$$t = (\text{PO})^{1/2}/C' \quad (3)$$

where  $C' = 5K_A/[\text{RH}]_0^{1/2}$ ;  $K_A$  is a constant at constant temperature and oxygen pressure and  $[\text{RH}]_0$  is the initial polymer concentration. By substituting eq. (3) into (2) we obtain

$$F_n = (C/C') (\text{PO})^{1/2} - (C/A) + (C/A)e^{-A(\text{PO})^{1/2}/C'} \quad (4)$$

At relatively high values of  $(\text{PO})^{1/2}$ , eq. (4) may be written as

$$F_n \approx (C/C') (\text{PO})^{1/2} - C/A \quad (4a)$$

From eq. (4a), values of  $(C/C')$ ,  $(C/A)$ , and  $(A/C')$  may be initially estimated. These values can then be substituted into eq. (4b), and new values of these parameters are obtained and compared with the initial values

$$[F_n - (C/A)e^{-A(\text{PO})^{1/2}/C'}] \equiv \varphi = (C/C')(\text{PO})^{1/2} - C/A \quad (4b)$$

If the sets of values of the corresponding parameters are in good agreement, these values are adopted as the final values, otherwise this trial-and-error procedure can be continued until good agreement obtains.

### Results and Discussion

In Figure 1 is shown a plot of  $-\log S$  versus time. From the slope of the line drawn, a value of  $A = 8.5 \times 10^{-3} \text{ min}^{-1}$  was estimated at  $135^\circ\text{C}$ , according to eq. (1) (from this value of  $A$ , an intercept of 5.0 was estimated which compared favorably with the extrapolated value of 5.1). This value of  $A$  may be checked by means of eqs. (4a) and (4b) and the smoothed curve in Figure 6 of Bawn and Chaudhri.<sup>13</sup>

In Figure 2 are shown plots of  $F_n$  and  $\varphi$  versus  $(\text{PO})^{1/2}$  in accordance with eqs. (4a) and (4b), respectively. From the  $F_n$  plot, the following values of  $(C/C')$ ,  $(C/A)$ , and  $(A/C')$  were obtained respectively: 0.58, 0.43, and 0.74. From these values and eq. (4b), the following modified values of these parameters were obtained, respectively: 0.57, 0.48, and 0.83. These latter values were used in estimating the value of  $A$  at  $135^\circ\text{C}$ , as follows. From Figure 5, (eq. 18), and other data of Bawn and Chaudhri<sup>13</sup> a value of  $C' = 1.05 \times 10^{-2}$  was estimated. By using this value,  $A \approx 8.8 \times 10^{-3} \text{ min}^{-1}$ , which is in reasonably good agreement with that previously obtained from different experimental data. However, the two values of  $A$

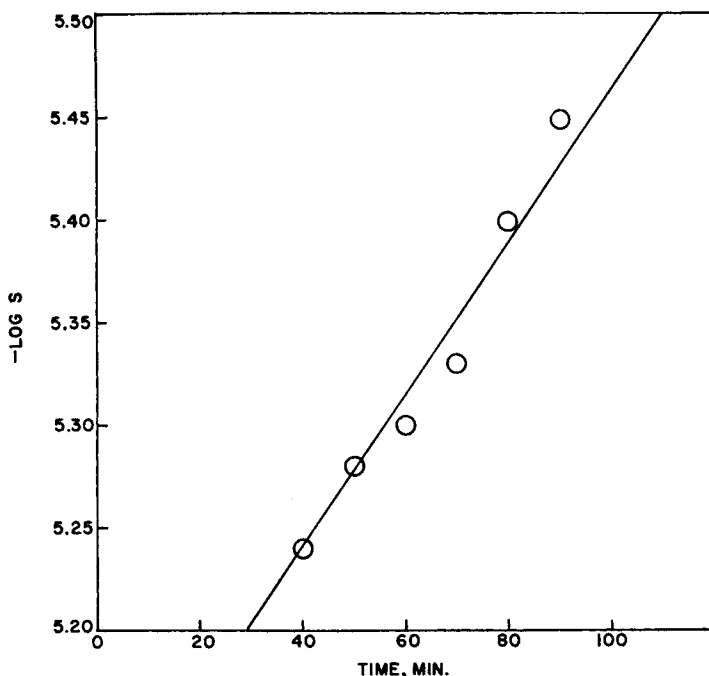


Fig. 1. Plot of  $-\log S$  vs. time for the autoxidation of atactic polypropylene in solution at  $135^\circ\text{C}$ ,  $[\text{RH}] = 1.63M$ .

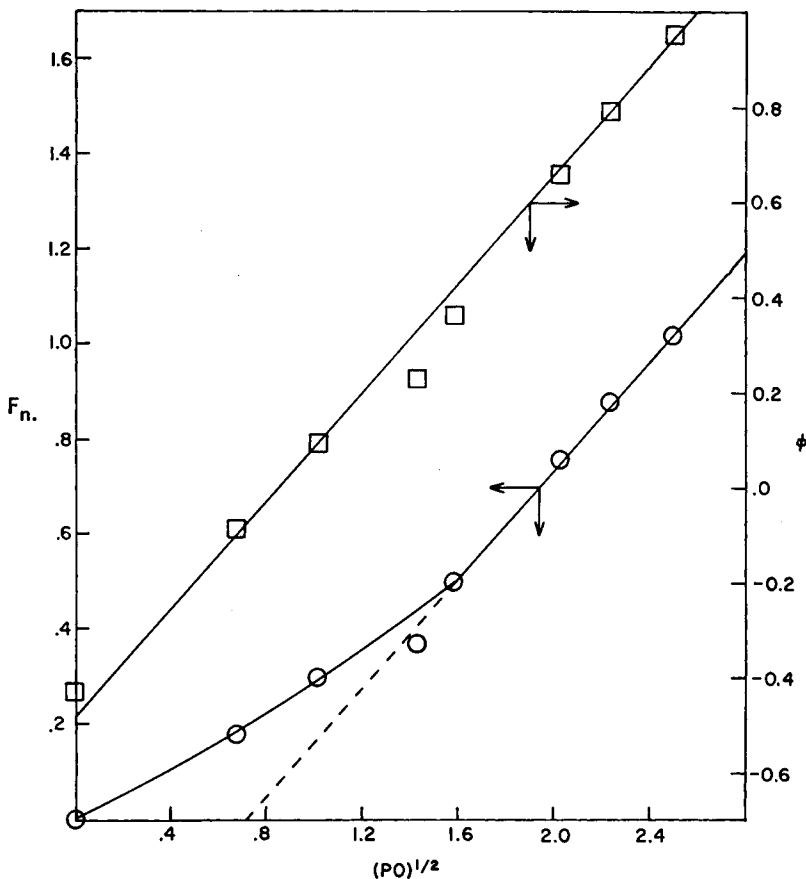


Fig. 2.  $F_n$  and  $\phi$  vs.  $(PO)^{1/2}$  for atactic polypropylene autoxidation at 135°C in 1,2,4-trichlorobenzene solution,  $RH = 1.82M$ .

obtained would not be expected ever to be identical, since the values of  $[RH]$  were a little different in the two sets of experimental data employed and furthermore, there may have been some variation in the oxygen pressure for these sets of data. At any rate, the above treatment lends strong support to the validity of expressions developed by us relating intrinsic viscosity as a function of time during polyolefin autoxidation both in the bulk phase and at relatively high polymer concentrations (ca. 1.5M and above).

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