On the High Pressure Polymerization of Ethylene

In a recent paper Kodama et al.,[1] by inspection of their Figure 9, state that the rate of polymerization of ethylene with di-*tert*-butyl peroxide in water at 150°C proceeds according to the equation

$$R = 5.3 \times 10^{-5}[I_0] \exp\{-1.38 \times 10^{-2}t\}P^{1.9} \tag{1}$$

where I_0 is the initial peroxide concentration in g-moles, P is the pressure in kg/cm^2, and R is the polymerization rate in g-moles of ethylene/l-min. from careful numerical examination of Figure 9, eq. (1) is in error. The slope of the $P = 400$ kg/cm^2 curve is -1.54×10^{-2} and that of the $P = 600$ kg/cm^2 curve is -1.58×10^{-2}, instead of -1.38×10^{-2}. Furthermore, the pressure exponent is very nearly 2.0. Consequently, the correct expression is

$$R = 8.15 \times 10^{-5}[I_0] \exp\{-1.58 \times 10^{-2}t\}P^{2.0} \tag{2}$$

When the reported value of $R = 0.008$ in Figure 9 at 600 kg/cm^2, $t = 100$ min, e.g., is recalculated, eq. (2) correctly yields 0.008 whereas eq. (1) yields 0.00545 which is 30% in error. In view of the inadequacy of eq. (1) the numerical accuracy of eq. (5) and eq. (6) and indeed, of the entire analysis is in doubt.

Reference

1. S. Kodama, T. Shimidzu, S. Yuasa, T. Kagiya, and K. Fukui, *J. Polym. Sci.*, **55**, 285 (1961).

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