Greek Letters

α = dimensionless diffusion parameter = a/k
γ = dimensionless film thickness = $d(k/D)^{1/2}$
ϵ = eddy diffusion coefficient
θ = dimensionless inlet concentration = $\dfrac{c_0 - c_e}{c_s - c_e}$
ν = kinematic viscosity, cm^2/s

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Induction-Period Kinetics in Acrylamide Photopolymerization

MIGUEL IBARRA and J. M. SMITH

Department of Chemical Engineering
University of California, Davis, California

In a recent study of photopolymerization of acrylamide (Sandru and Smith, 1973) the induction period was observed to depend upon monomer concentration as well as light intensity and initiator concentration. This note reports the results of a careful quantitative study of the kinetics of the induction period during which dissolved oxygen in the aqueous solution is consumed. Of specific interest was the effect of monomer concentration.

Induction times were measured at 25°C, in the same batch-recycle photoreactor as employed by Sandru and Smith (1973), for aqueous solutions of various concentrations of monomer (0.05 to 0.5 g mole/liter), initiator (1×10^{-3} to 6.5×10^{-3} g mole/liter of potassium persulfate) and dissolved oxygen. Since the polymer of acrylamide is insoluble in methanol, the induction time was determined by noting the onset of turbidity with a Hach turbidimeter, when a 4-cm^3 sample of the reaction mixture was added to 10-cm^3 of methanol. Induction times, and hence rates of reaction were reproducible within 4%. The annular reactor had an inside radius of 33.5 mm and an outer radius of 45 mm and an irradiated length of 8.2 cm. Radiation was from a high-pressure mercury lamp (Hanovia 679A-36, 450 watts) placed at the axis of the annulus. There was significant radiation from this lamp in the range 2224 to 4358 Å. The volumes of reactor and reservoir and the circulation rate of the recycle system were such that the reactor operated at close to differential conditions as long as the conversion of oxygen (the limiting reactant) per pass was less than 20%. That is, the error in assuming a constant rate through the reactor was less than 10% if conversions per pass of oxygen were 20% or less. Complete descriptions of these factors and the apparatus are available (Ibarra, 1973).

Different initial oxygen concentrations were obtained by varying the severity of stripping of the solution with helium. Initial concentrations ranged from about 0.2×10^{-4} to 2.4×10^{-4} g mole/liter and were measured by the Winkler optical method (Procedures Manual, Delta Scientific Company, 1968). In all runs the oxygen concentration was less than one-tenth of that of initiator.

Light intensity was varied by circulating a solution of $FeCl_3 \cdot 6H_2O$ and HCl, of different concentrations, through an annular jacket between the reactor and the lamp. Such filter solutions absorb about the same fraction of radiation regardless of the wave length so that the spectral distribution of the light reaching the reactor remains approximately the same. A Corex filter directly adjacent to the lamp also was employed to reduce the level of intensity. This was necessary because preliminary experiments with a higher intensity lamp (Hanovia LL 189A, 1200 watts) resulted in formation of a film of insoluble (in water and common solvents) polymer on the inner-wall surface of the reactor. The Corex filter transmitted no radiation at wave lengths shorter than 2482 Å and the absorptivities of initiator and monomer were negligible beyond 3660 Å. Hence, the effective range of radiation was from 2482 to 3660 Å.

The total light intensity $I_{b,t}$ at the inside wall surface of the reactor was determined using the uranyl oxalate actinometer (Sandru and Smith, 1973). Results for $I_{b,t}$ as a function of lamp operating time are shown in Table 1. Since the final induction runs were made after the second actinometer run, $I_{b,t} = 1.61 \times 10^{-6}$ Einsteins/cm²-s was used in evaluating the kinetics for the induction period.

TABLE 1. ACTINOMETER RESULTS

Run	Lamp operating time, hr.	$I_{b,t}$ Einsteins/cm²-s
1	84	1.80×10^{-6}
2	90	1.61×10^{-6}
3	115	1.57×10^{-6}

These intensities were calculated by assuming a radial light model for the lamp-reactor geometry. Because of the finite radius of the tubular lamp and because of end effects, the absolute values of $I_{b,t}$ are of uncertain accuracy. However, the same light model is used with these $I_{b,t}$ values to evaluate kinetic constants for the induction period. Therefore, this dual use of the model should reduce the error in absolute value of the kinetic constants even though errors may exist in $I_{b,t}$. Also errors in the light model should have no effect on the order of the rate with respect to concentrations of monomer and initiator.

RESULTS

The average rate, over the reactor volume, for the removal of dissolved oxygen in the batch-recycle system is given by the mass balance

$$-\overline{\Omega}_{O_2} = \frac{V_S}{V_R}\frac{d[O_2]}{dt} \tag{1}$$

Since the initiator and monomer concentrations are much greater than that of oxygen in any run, $\overline{\Omega}_{O_2}$ at a fixed temperature can depend only on $[O_2]$ and the intensity and spectral distribution of the radiation. If the rate is assumed to be independent of oxygen concentration, Equation (1) can be integrated to give

$$\overline{\Omega}_{O_2} = \frac{V_S}{V_R}\frac{[O_2]_0}{T} \tag{2}$$

This expression was used to calculate the rate for each run from measurements of the initial oxygen concentration and the induction time T. Figure 1 shows the results of runs made over a 10-fold range of initial oxygen concentrations at the same initiator $[In]$ and monomer concentrations and for the same radiation conditions. The constancy of the rate provides experimental verification for the assumption that $\overline{\Omega}_{O_2}$ is zero order in oxygen concentration as $[O_2]$ is reduced from $[O_2]_0$ to zero. This assumption is the basis for all studies of the kinetics of the induction period in polymerization and is based on free-radical reactions of the form (Flory, 1969)

$$S_2O_8^{=} + h\nu \xrightarrow{\phi_{In}} 2\,SO_4^{*} \tag{3}$$

$$SO_4^{*} + M \xrightarrow{k_1} M^{*} \tag{4}$$

$$M^{*} + O_2 \xrightarrow{k_2} M\text{—}O\text{—}O^{*} \tag{5}$$

The data points in Figures 2 to 4 present the experimental results for the influence of light intensity and initiator and monomer concentrations on the rate of oxygen removal. The abscissa in Figure 2 is the volumetric rate of energy absorption. Note that $I_{b,t}$ is constant in all the runs, but the intensity at the inner wall surface of the reactor varied because the transmission $T_{f,\lambda}$ of the filter solution was changed from run to run. The data show that the rate is directly proportional to the intensity of the light absorbed. Values of the absorptivities $\alpha_{In,\lambda}$ and $\alpha_{M,\lambda}$ and transmissions $T_{c,\lambda}$ and $T_{f,\lambda}$, were measured in a spectrophotometer and are tabulated elsewhere (Ibarra, 1973). The energy distribution F_λ/F_t and $T_{c,\lambda}$ were available from the lamp manufacturer (Hanovia Lamp Division 1968). The total attenuation factor μ_λ is related to $\alpha_{In,\lambda}$ and $\alpha_{M,\lambda}$ by the expression

$$\mu_\lambda = \alpha_{In,\lambda}\,[In] + \alpha_{M,\lambda}\,[M] \tag{6}$$

and includes the effect of both monomer and initiator.

The relation between initiator concentration and rate is complex. For $[M] \geqq 0.2$ g mole/liter, $\overline{\Omega}_{O_2}$ is proportional to $[In]^{3/2}$ but at lower $[M]$ the effect of $[In]$ is less. A logarithmic form of Figure 3 demonstrates this relation. On the other hand, Figure 4 indicates that the rate is directly proportional to monomer concentration over the entire range of $[In]$. The data in Figures 3 and 4 were obtained with distilled water flowing through the filter solution jacket so that $T_{f,\lambda} = 1.0$.

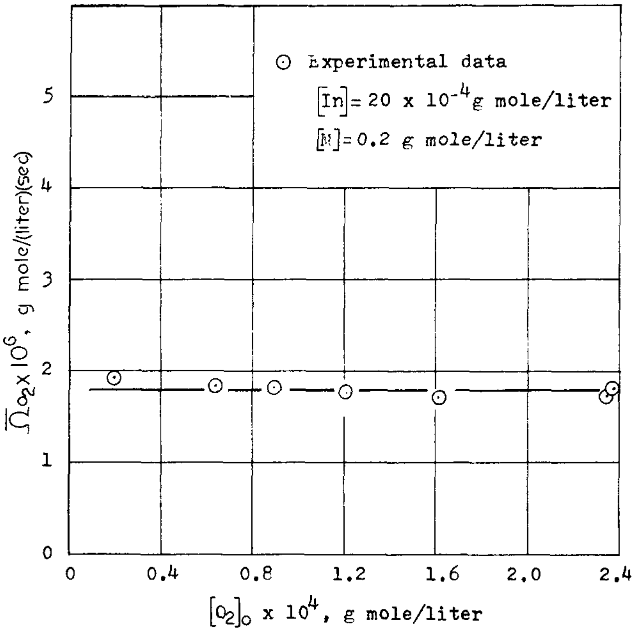

Fig. 1. Effect of oxygen on rate.

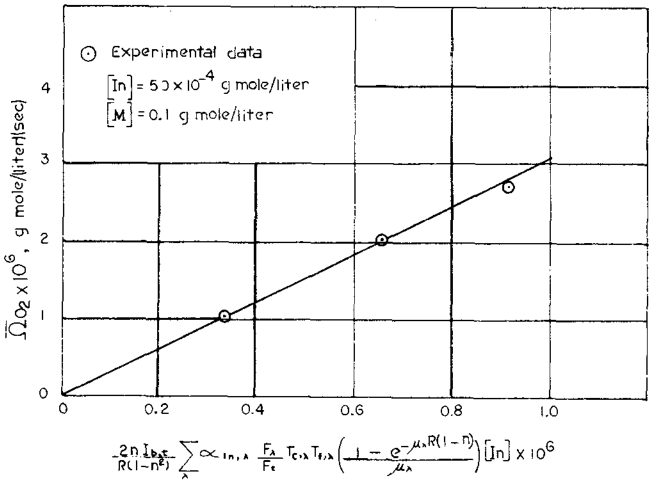

Fig. 2. Effect of intensity on the experimental rate.

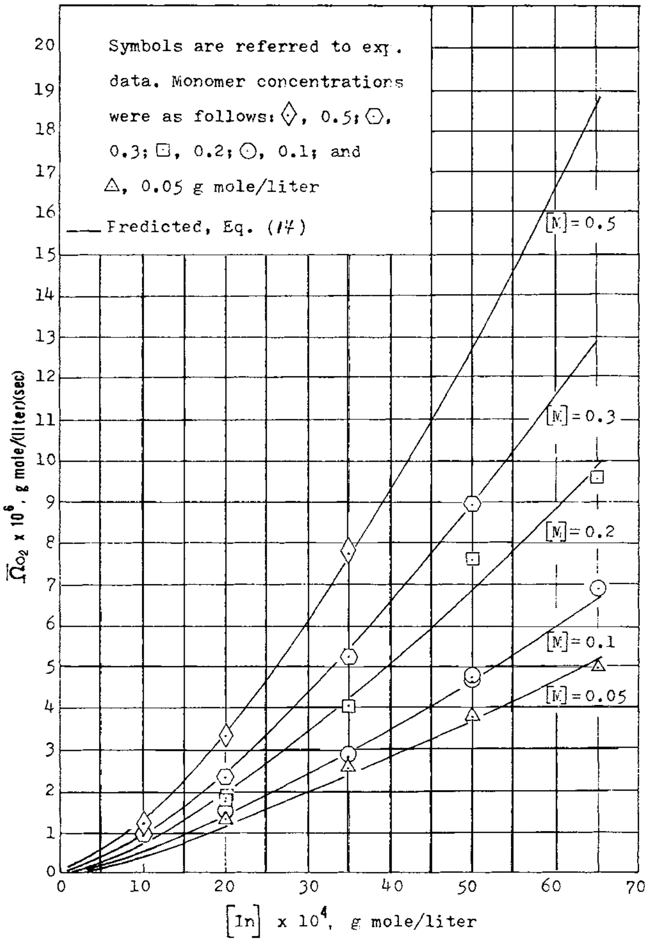

Fig. 3. Reaction rate vs. initiator concentration.

KINETICS OF INDUCTION PERIOD

The data show that the mechanism of oxygen removal must lead to an equation for the rate that shows direct proportionality to the intensity of absorbed light, and to monomer concentration, and a complex effect of $[In]$.

Equation (3) has been observed (Tsao and Wilmarth, 1959) for the photolytic decomposition at 32°C in aqueous solution with radiation of 2537 Å. The rate equation $\Omega = 2\phi_{In,\lambda}\,(Ia)_{In,\lambda}$ indicated a quantum yield of $\phi_{In,\lambda} = 0.79$. Also, Equation (4) has been verified in free radical polymerization (Flory, 1969). Flory (1969) has proposed a complete mechanism for consumption of oxygen by adding the following propagation and termination steps to reactions (3) to (5):

$$M\text{—O—O}^* + M \xrightarrow{k_3} M^* \tag{7}$$

$$2M\text{—O—O}^* \xrightarrow{k_4} \text{non-radical products} \tag{8}$$

If the stationary state hypothesis is applied to the free-radicals in Equations (3) to (5), (7), and (8), the local rate of disappearance of oxygen at wave length λ is

$$\Omega_{O_2,\lambda} = 2\,\phi_{In,\lambda}\,(Ia)_{In,\lambda} + k_3\left[\phi_{In,\lambda}\,(Ia)_{In,\lambda}\,\frac{1}{k_4}\right]^{1/2}\,[M] \tag{9}$$

This equation shows a complex effect of $[In]$, since

$$(Ia)_{In,\lambda} = \alpha_{In,\lambda}\,[In]\,I_{r,\lambda} \tag{10}$$

However, the rate becomes proportional to $[In]^{1/2}$ at high $[M]$ which is not in accord with the experimental data.

Bartlett and Cotman (1949) substituted the reaction

$$M\text{—O—O}^* + S_2O_8^{=} \xrightarrow{k_5} SO_4^* \tag{11}$$

for Equation (7). This modified reaction sequence also leads, via the stationary state hypothesis, to a two-term expression for the rate

$$\Omega_{O_2,\lambda} = 2\phi_{In,\lambda}\,(Ia)_{In,\lambda} + k_5\left[\phi_{In,\lambda}\,(Ia)_{In,\lambda}\,\frac{1}{k_4}\right]^{1/2}\,[In] \tag{12}$$

Equation (12) predicts well the observed effect of initiator concentration on the rate but does not account for the effect of monomer concentration.

No other sequence of reasonable reactions could be devised which would approach agreement with the observations. However, the following empirical expression agreed well with the data:

$$\Omega_{O_2,\lambda} = k_I\,\phi_{In,\lambda}\,(Ia)_{In,\lambda} + k_{II}\,\phi_{In,\lambda}\,[In]^{1/2}\,[M]\,(Ia)_{In,\lambda} \tag{13}$$

To compare Equation (13) with $\bar{\Omega}_{O_2}$ obtained from the data, the equation must be summed over the wave length range and integrated through the reactor volume. In the summation it is assumed that an average value of the quantum yield ϕ_{In} can be used. Since the concentrations of initiator and monomer are nearly constant throughout the reactor, due to the near-differential operation of the reactor, the only variable in Equation (13) is $(Ia)_{In,\lambda}$, or the intensity $I_{r,\lambda}$ according to Equation (10). The radial model for the intensity distribution $I_{r,\lambda}$ in the annular reactor and the details of this kind of summation and integration have been published elsewhere (Sandru and Smith, 1973; Ibarra, 1973). The result is

$$\bar{\Omega}_{O_2} = k_I\phi_{In}\,\frac{2n\,I_{b,t}}{R(1-n^2)}\sum_{\lambda}\alpha_{In,\lambda}\,\frac{F_\lambda}{F_t}\,T_{c,\lambda}\,T_{f,\lambda}\left[\frac{1-\exp[-\mu_\lambda R(1-n)]}{\mu_\lambda}\right][In]$$
$$+\,k_{II}\phi_{In}\,\frac{2n\,I_{b,t}}{R(1-n^2)}\sum_{\lambda}(\alpha_{In,\lambda})\,\frac{F_\lambda}{F_t}\,T_{c,\lambda}\,T_{f,\lambda}\left[\frac{1-\exp[-\mu_\lambda R(1-n)]}{\mu_\lambda}\right][In]^{3/2}\,[M] \tag{14}$$

where μ_λ represents the attenuation of the light intensity due to both initiator and monomer, as given by Equation (6).

The two unknown constants $(k_I\,\phi_{In})$ and $(k_{II}\,\phi_{In})$ in Equation (14) were evaluated using a multiple regression analysis applicable for the case of two independent variables (Volk, 1969). The values so determined for the constants are

$$k_I\,\phi_{In} = 1.56 \text{ g mole/Einstein}$$

$$k_{II}\,\phi_{In} = 339\left(\frac{\text{liter}}{\text{g mole}}\right)^{3/2}\left(\frac{\text{g mole}}{\text{Einstein}}\right)$$

The curves shown in Figures 3 and 4, which are based upon predictions from Equation (14), agree well with the data points. Thus Equation (13) is a satisfactory expression for the local rate for the conditions of this study. Note that Equation (13) predicts that the rate of oxygen removal would be zero in the absence of initiator, since $(Ia)_{In,\lambda}$ would be zero.

The mechanism of Equations (3) to (5) and (7) and (8) or (11), as well as Equation (13), presuppose that only radiation absorbed by initiator causes removal of

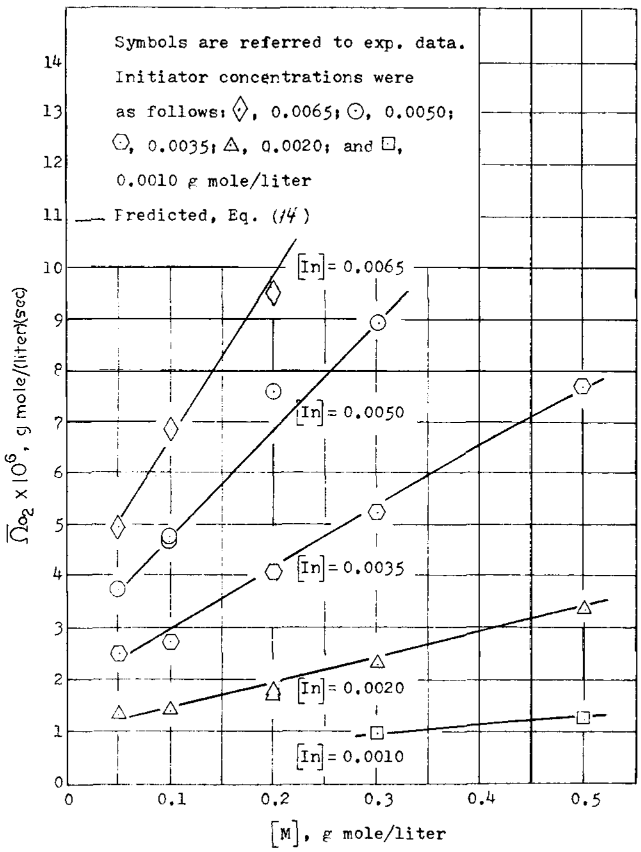

Fig. 4. Reaction rate vs. monomer concentration.

oxygen. Since absorptivities of aqueous solutions of acrylamide monomer are larger than those of initiator solutions (Ibarra, 1973), it was necessary to verify that activation of monomer by light was insignificant. For this purpose an experimental run was made in which no initiator was present and for which the initial oxygen concentration was reduced to as low a value as possible by stripping with helium. After 6 hours of run time there was no evidence of polymerization in the reaction mixture. From this experiment it was concluded that activation of monomer was very slow. Induction times for the data shown in Figures 2 to 4 varied from about 5 to 120 min.

These results indicate that a scheme of radical formation from initiator and monomer molecules, such as suggested by Equations (3) to (5) and (7), can demonstrate that monomer concentration can affect the induction time. However, it was necessary to use an empirical equation [Equation (13)] rather than a logical sequence of reactions in order to obtain quantitative agreement with the observed data. While Equations (3) to (5) appear to be involved, there are many potential reactions of persulfate ion with other substances in aqueous solutions (Wilmarth and Haim, 1962). It is likely that additional reactions occur to give the overall kinetic result correlated by Equation (13).

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NOTATION

F_λ = energy output of lamp at wave length λ, watts
F_t = total energy output of lamp, watts
$(Ia)_{In,\lambda}$ = absorbed light intensity by initiator at wave length λ, Einsteins/cm^3-s
$I_{b,t}$ = total intensity for polychromatic radiation at inner reactor wall, without filter solution, Einsteins/cm^2-s
$[In]$ = initiator concentration, g mole/liter
$I_{r,\lambda}$ = local intensity at radius r of annular reactor and for wave length λ, Einsteins/cm^2-s
k_I = constant defined by Equation (13), dimensionless
k_{II} = constant defined by Equation (13), $\left(\frac{\text{liter}}{\text{g mole}}\right)^{3/2}$
$[M]$ = monomer concentration, g mole/liter
n = ratio of inner and outer radii of the annular reactor, cm
nR = inner radius of annular reactor, cm
$[O_2]$ = dissolved oxygen concentration, g mole/liter
$[O_2]_0$ = initial concentration of dissolved oxygen, g mole/liter
r = radial coordinate in annulus measured from the axis, cm
R = outer radius of annular reactor, cm
t = reaction time, s
T = induction time, s
$T_{c,\lambda}$ = transmittance (fraction of light transmitted) of Corex filter at wave length λ
$T_{f,\lambda}$ = transmittance of filter solution at wave length λ
V_R = irradiated volume of reactor, cm^3
V_s = total volume of solution in reactor system, cm^3

Greek Letters

α_λ = absorptivity at wave length λ, liter/(g mole)(cm); based upon log to base e
$\Omega_{O_2,\lambda}$ = local rate of disappearance of oxygen at radius r and wave length λ in annular reactor, g mole/liter-s
$\overline{\Omega}_{O_2}$ = average rate over reactor volume, g mole/liter-s
$\phi_{In,\lambda}$ = quantum yield at wave length λ, of reaction (3), g mole/Einstein
ϕ_{In} = average quantum yield for all wave lengths of absorbed radiation for reaction (3), g mole/Einstein
λ = wave length, Å
μ_λ = total attenuation coefficient at wave length λ, cm^{-1}

Subscripts

In = initiator (potassium persulfate)
M = monomer (acrylamide)
O_2 = oxygen

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