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A MATHEMATICAL MODEL OF
PHOTOPOLYMERIZATION IN A BATCH REACTOR

BY
JYH-YAO LI

THESIS SUBMITTED TO THE FACULTY
OF THE GRADUATE SCHOOL
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ABSTRACT

Title of Thesis: A Mathematical Model of Photopolymerization
in a Batch Reactor

Jyh-yao Li, Master of Science in Chemical Engineering, 1987

Thesis directed by: Dr. C.R. Huang

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A mathematical model of a photo initiated addition-polymerization in a batch reactor was developed.

The model considered initiation, propagation and, termination to simulate the addition polymerization process, The model has the advantage that the concentration of any particular n-mer may be calculated without calculating all of its precursors. Other methods do not have this property. An analytical solution to the model for the photopolymerization of styrene was solved. The calculations were run on a VAX 8800 computer and the results were then compared with the experimental results. The calculated results fitted the experimental results to some extent. Effects from the variations of feed temperatures and light intensities were also discussed, the model predicted their influence very well.

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INTRODUCTION

It is well known that addition polymerization reactions involve three elementary stages, initiation, propagation and termination. Ideally, the overall process is one in which an infinite number of chemical reactions take place so that any kinetic analysis for a batchwise polymerization will require the solution of an infinite number of non-linear first-order ordinary differential equations. Liu and Amudson [4] solved a large number of differential equations on a computer and examined the effects of various reaction parameters and the termination step on the molecular-weight distribution and monomer-concentration history. It was found that if the degree of polymerization was very high the number of differential equations to be treated was so great that computers would not be able to produce the numerical solution by simultaneous solution of equations and other methods will be needed. Liu and Amudson suggested a way to reduce the infinite number of differential equations to two differential equations for thermal polymerization.

Addition polymerizations are usually initiated through the use of catalyst. Alternate means of initiation are available, including initiation by absorption of radiation (ionizing or ultraviolet). Both catalyst decomposition and radiation absorption lead to the production of free radicals

which initiate the polymerization reaction. However, there are differences between the initiation modes which can profoundly affect the case with which the reaction is carried out and the character of the product. Thus, in the case of radiation initiation, the rate of initiation is essentially independent of temperature, and because of the physical separation of radiation source and the reaction medium, the initiation rate may be changed very rapidly. By contrast, the rate of initiation with chemical initiators are usually strongly temperature dependent, and because the chemical initiator is in solution in the reaction medium, the initiation rate can not be changed rapidly. Because of these facts, radiation initiation may lead to greater reactor stability and greater ease of reactor control. An important consequence of greater stability and ease of reactor control should be less frequent instances of runaway reactions and explosive decompositions or the elimination of these events altogether. This consequence would result in greater safety of operation and less of product.

Polymerization process initiated by the thermal decomposition of a catalyst are well established. But very little work has been done on the engineering aspect of photopolymerizations (Yemin and Hill [6]; Jain et al. [7]; Chen and Hill [8,9]; Sandru and Smith [10]; Ibarra and Smith [11]; Mendiratta et al. [12]; Chen and Steenrod [13]). The

reason is because of incomplete exploration of their characteristics and advantages. Notice that a number of studies of the design and analysis of photochemical reactors have appeared in the literature during the past ten years, with outstanding contribution in this area being made by J.M. Smith and J.S. Dranoff and their coworkers [7]. The overall objectives of this thesis are to develop a mathematical model for the calculation of molecular-weight distribution for addition photopolymerization in an isothermal batch reactor. An analytical solution is worked out for the polymerization of styrene. Experimental measurements are also undertaken to compare with the theoretical results.

Mathematical Model

I: Light is on

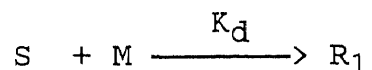
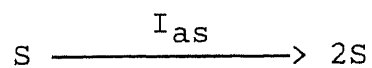
A method for the calculation of polymer concentration v.s. reaction time in a batch photopolymerization was developed in this study. A schematic diagram of the batch reactor is shown in Fig. 1. The light was turned on at time equals to zero and the light intensity kept constant as shown in Fig. 2. The method involves the use of a generating function which reduces the infinite number of differential equations to just one.

Reaction Mechanism :

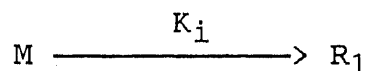
All of the reactor models developed in this investigation involve the following polymerization steps.

(a) Initiation

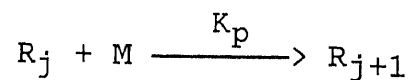
(i) Initiated by UV light



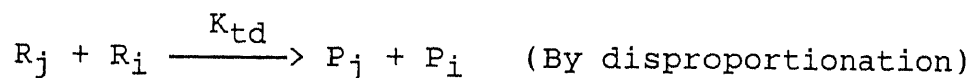
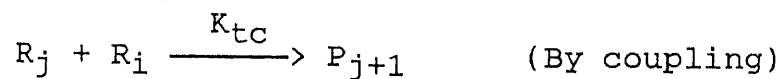
(ii) Initiated by thermal decomposition



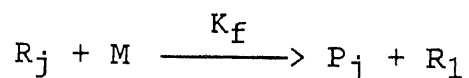
(b) Propagation



(c) Termination



(d) Chain transfer to the monomers



where R_j , P_j , S , and M are the concentrations of active polymer, polymer, sensitizer and monomer, respectively.

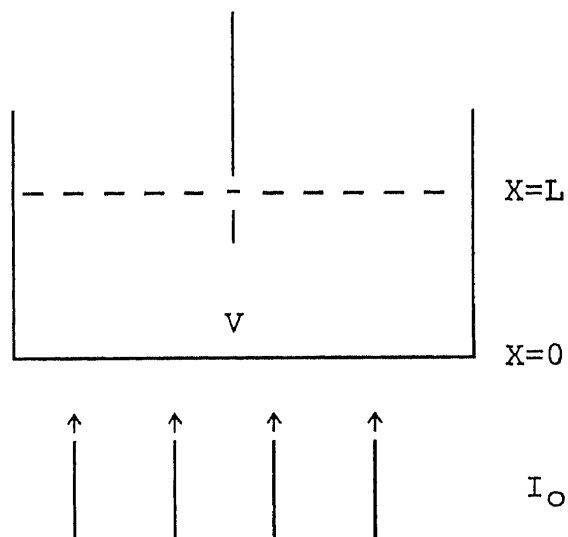


Fig.1. Schematic Diagram of Batch Reactor

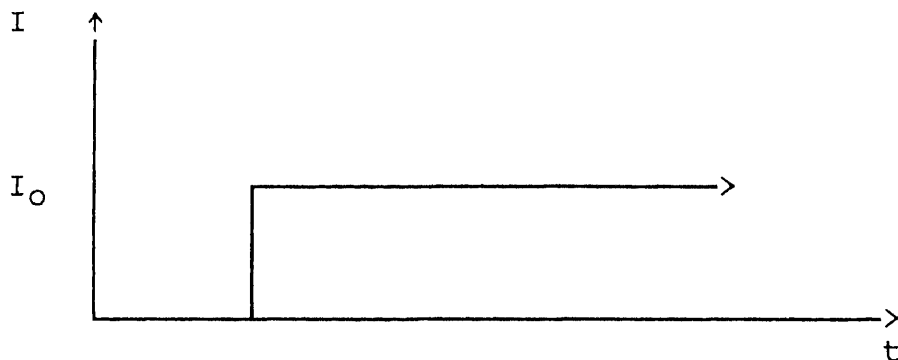


Fig.2. Polymerization Time v.s.
Light Intensity

It is found that in radical chain polymerization, the deactivation of radicals can occur by two distinct mechanisms, namely, combination and disproportionation. Termination by combination has been shown to be the predominant mechanism in styrene polymerization [1]. It implies that $K_t = K_{tc} + K_{td} \approx K_{tc}$, since K_{td} is much smaller than K_{tc} .

The Arrhenius equations for reaction constants in the polymerization of styrene are shown below [1] :

$$K_p = 1.051 \times 10^7 \text{ EXP}(-3557/T) \text{ liter / g-mole-sec}$$

$$K_t = 1.255 \times 10^9 \text{ EXP}(-844/T) \text{ liter / g-mole-sec}$$

$$K_f = 2.31 \times 10^6 \text{ EXP}(-6337/T) \text{ liter / g-mole-sec}$$

$$K_i = 2.19 \times 10^5 \text{ EXP}(-13810/T) \text{ liter / g-mole-sec}$$

As can be calculated that the chain transfer rate constant, K_f , is negligible due to a very small magnitude as compared to other rate constant. In this system the photosensitized initiation rate, i.e., Ω_i , is much larger than the thermal initiation rate the latter is therefore also negligible in this study.

The content of the isothermal batch reactor is assumed to be perfectly mixed and fully illuminated during the photochemical reaction. If I_0 is the flux of radiation incident upon the reactor, and the total rate of light absorption is averaged over the path length of light [2] then

$$I_{as} = I_0 \left[\frac{\epsilon_S S}{\epsilon_S S + \epsilon_M M + \epsilon_{P_i} P_i} \right] \left[\frac{1 - e^{-(\epsilon_S S + \epsilon_M M + \epsilon_{P_i} P_i)L}}{L} \right] \quad (1)$$

where ϵ_M , ϵ_S , and ϵ_{P_i} are the molar absorptivities of monomer, sensitizer and polymer, respectively, and L is the total path length of light in the reactor. Quantum yield, ϕ_S , has been estimated to be 0.072 g-mole/Einstein for benzoin methyl ether, which is the sensitizer for the styrene polymerization, from measured polymerization rates at full

illumination and perfect mixing . The following assumptions were employed in equation (1) : axial nonuniformities due to light attenuation are negligible, the rates of reaction are uniform throughout the reactor and the fractions of light being absorbed by the monomer and the polymer are the same. In addition, for the present case, the following assumptions are also being made :

(1) The light absorbed by the monomer and the polymer are negligible, i.e., $\epsilon_S S \gg \epsilon_m^M + \epsilon_p P_i$.

(2) The light intensity absorbed by the sensitizer is assumed to be constant and of the magnitude of order 10. Hence, the exponential term in equation (1) may be neglected.

By applying the assumptions (1) and (2), the corresponding relationship between the total rate of light absorption and I_0 is insensitive to chemical compositions, i.e.,

$$I_{as} = \frac{I_0}{L} = \text{constant}$$

and the initiation rate via absorption of ultraviolet light is

$$\begin{aligned} \Omega_i &= 2 \phi_S I_{as} \\ &= \frac{2\phi_S I_0}{L} \end{aligned}$$

Derivation :

The derivation of the mathematical equations is accompanied by three assumptions for a bulk photopolymerization carried out in a batch reactor :

- (1) The reactor is perfectly mixed and isothermal.
- (2) The kinetic constants of the various reaction steps are independent from the chain length at low conversion; i.e., no gel effect.
- (3) No density variation occurs in the reactor; i.e., the reaction volume is constant.

Then the material balance for a batch reactor yields the equations as follows :

For monomer

$$\frac{dM}{dt} = - \Omega_i - K_p M \sum_{i=1}^{\infty} R_i \quad (2)$$

For radicals

$$\frac{dR_1}{dt} = \Omega_i - K_p M R_1 - K_t R_1 \sum_{i=1}^{\infty} R_i \quad (3)$$

$$\frac{dR_2}{dt} = K_p M R_1 - K_p M R_2 - K_t R_2 \sum_{i=1}^{\infty} R_i \quad (4)$$

$$\frac{dR_n}{dt} = K_p M R_{n-1} - K_p M R_n - K_t R_n \sum_{i=1}^{\infty} R_i \quad (5)$$

:

For terminated polymers

$$\frac{dP_2}{dt} = \frac{1}{2} K_t R_1 R_1 \quad (6)$$

$$\frac{dP_3}{dt} = K_t R_1 R_2 \quad (7)$$

$$\frac{dP_4}{dt} = K_t (R_1 R_3 + \frac{1}{2} R_2 R_2) \quad (8)$$

$$\frac{dP_5}{dt} = K_t (R_1 R_4 + R_2 R_3) \quad (9)$$

:

:

with initial conditions :

$$\text{I.C.1 At } t=0 \quad M = M_0$$

$$\text{I.C.2 At } t=0 \quad R_1 = R_2 = R_3 = \dots = 0$$

$$\text{I.C.3 At } t=0 \quad P_2 = P_3 = P_4 = \dots = 0$$

To add up equations (3), (4), (5) the following equation is obtained :

$$\frac{d \sum_{i=1}^{\infty} R_i}{dt} = \Omega_i - K_t \left(\sum_{i=1}^{\infty} R_i \right)^2 \quad (10)$$

Since $R_1=R_2=R_3= \dots =0$ at $t=0$, $\sum_{i=1}^{\infty} R_i$ must be also equal to zero.

$$t = 0 \qquad \sum_{i=1}^{\infty} R_i = 0$$

By using the initial condition above, the following equation can be derived from equation (10):

$$\sum_{i=1}^{\infty} R_i = \frac{\sqrt{\Omega_i/K_t} (e^{2\sqrt{\Omega_i K_t} t} - 1)}{e^{2\sqrt{\Omega_i K_t} t} + 1}$$

Since $e^{2\sqrt{\Omega_i K_t} t} \gg 1$ thus $\sum_{i=1}^{\infty} R_i(t)$ is approximately given by

$$\sum_{i=1}^{\infty} R_i(t) = \sqrt{\Omega_i/K_t} \qquad (11)$$

when t is larger than 1 second.

To substitute equation (10) into equation (1) and let $M(t) = M_0$ at $t = 0$ then

$$M = (M_0 + \frac{\sqrt{K_t \Omega_i}}{K_p}) e^{-K_p \sqrt{\Omega_i/K_t} t} - \frac{\sqrt{K_t \Omega_i}}{K_p} \qquad (12)$$

In order to find the concentration of radical R_j , the

generating function for this system is defined as [3], [4]

$$\varphi(w, t) = \sum_{j=1}^{\infty} R_j(t) W^j \quad (13)$$

where w is a parameter.

Equation (14) is the result of partial differentiation of equation (11) with time.

$$\frac{\partial \varphi}{\partial t} = \sum_{j=1}^{\infty} \frac{dR_j}{dt} \times W^j \quad (14)$$

To substitute equation (3), (4), and (5) to equation (14) above yields

$$\frac{\partial \varphi}{\partial t} + (K_p M - K_p M W + K_t \sum_{i=1}^{\infty} R_i) \varphi = \Omega_i W \quad (15)$$

By letting

$$q_1 = K_p M - K_p M W + K_t \sum_{i=1}^{\infty} R_i$$

$$q_2 = \Omega_i W$$

equation (15) becomes

$$\frac{\partial \varphi}{\partial t} + q_1 \varphi = q_2$$

When it is multiplied by integrating factor, $Q = \exp\left(\int_0^t q_1 dt_2\right)$

the following relationships are obtained :

$$\frac{dQ\phi}{dt} = q_2 Q$$

$$(Q\phi)_{t=t} - (Q\phi)_{t=0} = \int_0^t q_2 Q dt_1$$

From initiation condition (2) and the definition of the generating function, , it is very easy to find $Q = 0$ at $t=0$ since there is no active polymer being generated before light is turned on. Therefore

$$\phi = Q^{-1} \int_0^t q_2 Q dt_1$$

$$\begin{aligned} \phi &= \int_0^t q_2 \times \exp\left(-\int_0^t q_1 dt_2 + \int_0^{t_1} q_1 dt_2\right) dt_1 \\ &= \int_0^t q_2 \times \exp\left(-\int_{t_1}^t q_1 dt_2\right) dt_1 \end{aligned}$$

By inserting q_1 and q_2 into the equation above, then it can be rewritten as

$$\phi(t) = \int_0^t \Omega_i \times e^{-\int_{t_1}^t (K_p M + K_t \sum_{i=1}^{\infty} R_i) dt_2} \times \underbrace{we^{\int_{t_1}^t K_p M_w dt_1}}_{(A)}$$

Using Taylor's series to expand term (A) above, the following is obtained :

$$we \int_{t_1}^t K_p M w dt_2 = \sum_{j=1}^{\infty} \frac{1}{(j-1)!} \left(\int_{t_1}^t K_p M dt_2 \right)^{j-1} w^j$$

and $\varphi(t)$ becomes

$$\varphi(t) = \int_0^t \Omega_i \times e^{-\int_{t_1}^t (K_p M + K_t \sum_{i=1}^{\infty} R_i) dt_2} \times \sum_{j=1}^{\infty} \frac{1}{(j-1)!} \\ \times \left(\int_0^t K_p M dt_2 \right)^{j-1} w^j dt_1$$

Thus, by comparing with the defined generating function (13), it follows that

$$R_j(t) = \int_0^t \Omega_i e^{-\int_{t_1}^t (K_p M + K_t \sum_{i=1}^{\infty} R_i) dt_2} \times \frac{1}{(j-1)!} \\ \times \left(\int_0^t K_p M dt_2 \right)^{j-1} dt_1 \quad (16)$$

Substitute the derived equation (11) and (12) into equation (16) above and let

$$\alpha = K_p M_0 + \sqrt{K_t \Omega_i}$$

$$\beta = K_p \sqrt{\Omega_i / K_t}$$

$$\gamma = \sqrt{K_t \Omega_i}$$

Then $R_j(t)$ becomes

$$\begin{aligned} R_j(t) &= \int_0^t \Omega_i \times e^{-\alpha x} \times \int_{t_1}^t e^{-\beta t_2} dt_2 \times \frac{1}{(j-1)!} \\ &\quad \times \left[\int_{t_1}^t (e^{-\beta t_2} - \gamma) dt_2 \right]^{j-1} dt_1 \\ &= \Omega_i \int_0^t e^{-\beta t} \frac{\alpha}{\beta} (e^{-\beta t} - e^{-\beta t_1}) \times \frac{1}{(j-1)!} \left[-\frac{\alpha}{\beta} \right. \\ &\quad \left. (e^{-\beta t} - e^{-\beta t_1}) - \gamma(t-t_1) \right]^{j-1} dt_1 \end{aligned}$$

For $\beta \ll 1$, $e^{-\beta t}$ is approximately equal to $1 - \beta t$ by truncating the terms after βt .

Then

$$R_j(t) = \frac{\Omega_i}{(j-1)!} \times (\alpha - \gamma)^{j-1} \times \int_0^t e^{-\alpha(t-t_1)} (t-t_1)^{j-1} dt_1$$

Now let

$$Y = t - t_1$$

$$dY = -dt_1$$

$R_j(t)$ becomes

$$R_j(t) = \frac{\Omega_i}{(j-1)!} \times (\alpha - \gamma)^{j-1} \times \int_0^t e^{-\alpha Y} Y^{j-1} dY$$

$$= \Omega_i (\alpha - \gamma)^{j-1} \times \left[\frac{1}{\alpha^j} - e^{-\alpha t} \sum_{p=0}^{j-1} \frac{t^{j-1-p}}{\alpha^{p+1} (j-1-p)!} \right] \quad (17)$$

From equation (6), (7), (8), and (9), a generalized expression for any degree of terminated polymer can be derived as follows :

$$\frac{dP_r}{dt} = \frac{1}{2} K_t \sum_{j=1}^{r-1} R_j R_{r-j} \quad (18)$$

To substitute equation (17) into equation (18) above and integrate from 0 to t

$$P_r = \frac{K_t \Omega_i}{2} (\alpha - \gamma)^{r-2} \sum_{j=1}^{r-1} \left[\frac{t}{\alpha^r} - \frac{1}{\alpha^j} \sum_{q=0}^{r-j-1} \left(\frac{e^{-\alpha t}}{-\alpha^{q+2}} \sum_{s=0}^{r-j-1-q} \frac{t^{r-j-1-q-s}}{\alpha^s (r-j-1-q-s)!} + \frac{1}{r-j+1} \right) \right. \\ \left. - \frac{1}{\alpha^{r-j}} \sum_{p=0}^{j-1} \left(\frac{e^{-\alpha t}}{-\alpha^{p+2}} \sum_{u=0}^{j-1-p} \frac{t^{j-1-p-u}}{\alpha^u (j-1-p-u)!} + \frac{1}{\alpha^{j+1}} \right) \right]$$

(A)
(B)

(C)
(D)

calculating the concentrations of all of its precursors.

The accuracy of the approximation depends on the number of exponential terms used in equation (17). At higher temperature the inaccuracy induced by the approximation becomes greater and needs maybe one or two more terms. But normally, the approximation is accurate for proceeding time below five hours.

II: Light is on and then off

The variation of polymer molecular weight distribution when the UV light is turned off after a small period of illumination time as shown in Fig.3 will be discussed next.

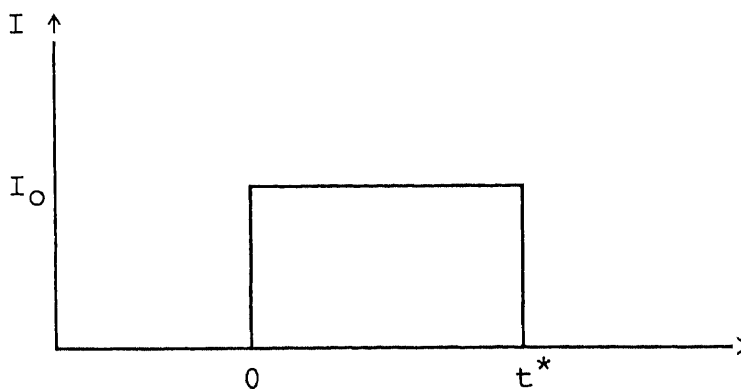


Figure 3. Polymerization time v.s. Light Intensity
in Case II

Theoretically, since the rate of termination is a second-order reaction of radicals and the rate of propagation is a first-order reaction of radicals, the decrease of radicals by shutting the light source off should favor the radical propagation process. Higher degree of polymerization should then be expected.

It is assumed that the thermal initiation is very small in the temperature range interested and can be neglected. And all three assumptions made for the derivation of the mathematical equations in Part I are held. Using the same procedures as being discussed in Part I, equations for a batch reactor after the light is turned off can be derived. All the terms are similar, except that there are no more initiation terms and the initial values are what calculated from Part I. If t^* is the instant moment when the UV light is turned off, and let $t'=t-t^*$, the material balance of monomer becomes

$$\frac{dM}{dt'} = - K_p M \sum_{i=1}^{\infty} R_i \quad (1)$$

and that of radicals become

$$\frac{dR_1}{dt'} = -K_p MR_1 - K_t R_1 \sum_{i=1}^{\infty} R_i \quad (2)$$

$$\frac{dR_2}{dt'} = K_p MR_1 - K_p MR_2 - K_t R_2 \sum_{i=1}^{\infty} R_i \quad (3)$$

$$\begin{aligned} & \vdots \\ & \vdots \\ \frac{dR_n}{dt'} &= K_p MR_{n-1} - K_p MR_n - K_t R_n \sum_{i=1}^{\infty} R_i \end{aligned} \quad (4)$$

Which can be added together to yield

$$\frac{d \sum_{i=1}^{\infty} R_i}{dt'} = -K_t \left(\sum_{i=1}^{\infty} R_i \right)^2 \quad (5)$$

For dead polymer, the relationship is as follows :

$$\frac{dP_r}{dt'} = \frac{1}{2} K_t \sum_{i=1}^{r-1} R_i R_{r-i} \quad (6)$$

The initiation conditions are as follows :

$$\begin{aligned} \text{At } t'=0 & \quad M = M^* \\ \text{At } t'=0 & \quad R_1 = R_1^* \\ & \quad R_2 = R_2^* \\ & \quad \vdots \\ & \quad \vdots \\ & \quad R_n = R_n^* \\ & \quad \vdots \\ & \quad \vdots \end{aligned}$$

$$\begin{array}{ll}
 \text{At } t' = 0 & P_1 = P_1^* \\
 & P_2 = P_2^* \\
 & : \\
 & : \\
 & P_n = P_n^* \\
 & : \\
 & :
 \end{array}$$

From equation (5), it can be derived that

$$\sum_{i=1}^{\infty} R_i = \frac{R^*}{K_t R^* t' + 1} \quad (7)$$

$$\text{where } R^* = R_1^* + R_2^* + R_3^* + \dots$$

To replace equation (7) into equation (1) and use $M(t) = M^*$ at $t' = 0$ then we have

$$\ln M - \ln M^* = \frac{-K_p}{K_t} \ln(K_t R^* t' + 1) \quad (8)$$

Since $\frac{K_p}{K_t}$ is very small, i.e. in the order of 10^{-6}

the approximation solution for $M(t')$ is

$$M(t') \approx M^*$$

Now the same as in Part I, a generating function is defined as :

$$\phi(w, t') = \sum_{j=1}^{\infty} R_j(t') W^j \quad (9)$$

and

$$\frac{\partial \phi}{\partial t'} = \frac{dR_1}{dt'} W + \frac{dR_2}{dt'} W^2 + \frac{dR_3}{dt'} W^3 + \dots$$

Then substituting equations (2), (3), and (4) into the equation above the following result yields

$$\frac{d\phi}{dt} = (-K_p M + K_p M W - K_t \sum_{i=1}^{\infty} R_i) \phi \quad (10)$$

with the initial condition being that at $t'=0$, $\phi = \phi^*$ where $\phi^* = W^1 R_1^* + W^2 R_2^* + W^3 R_3^* \dots$. To replace equations (6) and (7) into above equation and integrate, the following is obtained.

$$\phi = \frac{K_t R^* C}{K_t R^* t' + 1} e^{-K_p M^* t'} \times e^{K_p M^* W t}$$

$$\text{with } C = \frac{\phi^*}{K_t R^*}$$

By using Taylor's series for the expansion of $e^{K_p M W t}$ term and by the definition of ϕ^* , becomes

$$\begin{aligned} \phi &= \frac{e^{-K_p M t'}}{K_t R^* t' + 1} \sum_{i=1}^{\infty} W^i R_i^* \times \sum_{n=0}^{\infty} \frac{(K_p M t)^n W^n}{n!} \\ &= \frac{e^{-K_p M t'}}{K_t R^* t' + 1} \sum_{i=1}^{\infty} \sum_{n=0}^{\infty} \frac{W^{n+i} (K_p M t)^n R_i^*}{n!} \end{aligned} \quad (11)$$

Comparing equation (11) with the definition of the generating function, the following relationship can be attained.

$$R_i = \frac{e^{-K_p M^* t'}}{K_t R^* t' + 1} \sum_{j=1}^{\infty} \frac{(K_p M t)^{i-j}}{(i-j)!} R_j^* \quad (12)$$

An exact equation for the final polymer concentration can not be calculated from the following equation :

$$\frac{dP_i}{dt} = \frac{1}{2} K_t \sum_{j=1}^{i-1} R_i R_{i-j}$$

But by choosing step size small enough, the polymer concentration can be calculated with required accuracy by a numerical method.

Experimental Apparatus and Procedures

The experimental apparatus is shown schematically in Fig. 4. The reactor is a stirred baffled stainless steel vessel (7cm ID and 6cm height). The reactor volume is partially illuminated with a light beam through the bottom of the reactor. The reaction vessel is maintained at a constant temperature by the use of a constant temperature bath which circulates water in the jacket. An UV spectrophotometer is used to monitor the reaction conversion. Agitation speed is measured by a tachometer. The apparatus can be also used as an isothermal CSTR except the inlet and outlet are kept open.

The optical system provides a parallel ultraviolet beam. A 1000 watt Mercury Xenon arc lamp is housed in an air lamp housing and supplied with power by a regulated DC power supply (manufactured by Driel Optical Co.). The housing contains a mirror which increases the effective intensity of the lamp. A focusing lens mounted in the housing collects the light and produces a collimated beam which passed through a water filter. The filtered beam is reflected upward by a mirror and passes through neutral density filter to improve its cross-sectional uniformity and then through a color glass filter which transmits light with a wave length

of 310-420 nm. An iris diagram located under the neutral density filter is used to provide nonuniform irradiation.

Experimental procedures

The experimental procedure for batch reactor are described as follows :

The reactor is filled with 200cc of purified styrene monomer well mixed with sensitizer. Nitrogen is then pumped to the reactor to remove oxygen and moisture. UV light initiation and circulation of constant temperature batch are started at the same time. A constant agitation speed is applied throughout the reaction. Normally, it takes about five to ten minutes for the system to reach to the desired reaction temperature. Samples are collected in the middle of the reactor and product polymer is precipitated from the mixture immediately using gravimetric method. The reaction is usually stopped at 60% conversion due to high viscosity.

Analytical Procedures

(1) Purification of Styrene Monomer

The styrene monomer used for this study is from Aldrich Chemical Co. of purity 99% inhibited with 10-15 ppm of p-tertbutylcatechol. Inhibitor is removed by passing the monomer through a column (5cm ID and 60cm length) packed with activated alumina, followed by passage through a same

size column packed with silica gel to remove moisture. The inhibited monomer is allowed at a flow rate about 1 cc/min through these two columns. The collection vessel is nitrogen blanked and nitrogen is bubbled through the monomer to remove oxygen. The sensitizer, benzoin methyl ether (manufactured by Aldrich Chemical Co.) is added to the monomer immediately before start-of run.

(2) Measurement of Polymer Conversion

Polystyrene is insoluble in methanol while the monomer, dimers, and trimers are soluble. But, as the amounts of dimers, trimers, and impurities from the styrene present in polystyrene are relatively small, the methanol-soluble portion is principally styrene and can be taken as a measure of its presence. The determination of polymer fractional conversion is by means of gravimetric technique presented by Boundy and Boyer [14]. about two or three grams of reaction mixture is collected from the reactor, the mixture is then added 100cc methyl alcohol (99.9% purity by Aldrich Chemical Co.) to precipitate the product polymer. For the mixture having more than 30% conversion, 5cc of p-dioxane is needed to add to the solution before precipitation. The polymer is then dried in a vacuum oven at 70oC for at least 12 hours to remove traces of monomer and the conversion can thus be determined.

Gravimetric method gives satisfactory results, but the time involved is lengthy. A rapid spectrophotometric procedure by Newell [15] and McGovern et al. [16] is used. The concentration of styrene monomer dissolved in tetrahydrofuran (THF) at the order of 0.001 wt %, monomer absorbance at wave length 250 μ varies linearly with its concentration. Thus, the fraction of styrene monomer in the reaction mixture can be expressed as,

$$g = \frac{\text{absorbance of unknown sample}}{\text{absorbance of pure styrene}}$$

and the conversion can be determined as,

$$x = 1 - g$$

A Bausch and Lomb spectronic 710 spectrophotometer is used for conversion measurement.

(3) Measurement of Incident Light Intensity

The light intensity of the Mercury Xenon Arc Lamp was measured by using the potassium ferrioxalate actiometer developed by Parker [17] and Hatch and Parker [18]. The experiment was carried out in an acrylic reactor (38cm ID and 5cm height). All the measurements are made in the dark room. The following procedure is used for determination of photolysis products :

1. Solution A : dissolve 0.006 molar of $K_3 Fe (C_{204}) \cdot 3H_2O$ (2.947 g) into 100 c.c. of 1 N H_2SO_4 and then diluted to 1000 c.c.
2. Solution B : Dissolve 0.1 g of 1, 10 phenanthroline into 100 c.c. of H_2O (0.1% wt).
3. Solution C : 600 c.c. of 1 N sodium acetate is added to 360 c.c. of 0.1 N H_2SO_4 and then diluted to 1000 c.c.
4. 25 c.c. of A is added into the reactor under exposure of ultraviolet light. Exposing time ranges from 3 to 20 seconds for each run.
5. 1 c.c of solution A from the reactor is transferred to a 25 c.c. calibrated flask. 2 c.c. of solution B is added followed by 0.5 c.c. of buffer solution C, and then diluted to 25 c.c.
6. After making up and mixing, the liquid is allowed to stand at least one hour for complete reaction. The measurement is then made at 5100 Å and 9 C through the use of a spectrophotometer.

The incident light intensity can be varied by either changing the number of neutral density filters or the opening of iris diaphragm. Experimental measurements of light intensity are summarized in Table 1 and Figure 1. Detailed calculations can be found elsewhere [20] .

(4) Measurement of Molecular Weight Distribution

The molecular weight distribution of product polymer is determined via gel permeation chromatography manufactured by water Associates model 6000 A. The chromatography is equipped with five styrgel columns. The columns are packed in series having permeability limits of 10^6 , 10^5 , 10^4 , 10^3 and 500 A's respectively. There are six standard polystyrene samples (supplied by Water Associates) with molecular weights of 4×10^3 , 9×10^3 , 5×10^4 , 2.4×10^5 , 4.7×10^5 and 2.7×10^6 . Calibrations were made monthly and the calibration curve can be expressed a semilogarithmic relation of molecular weight with elution volume. A typical curve is shown in Figure 6. The polymer sample is prepared at a concentration of 0.025 wt % dissolved in toluene prior to the injection. The solvent, toluene is allowed at a flow rate of 2.5 cc/min through the columns. Number average and weight average molecular weights are determined from the GPC evolution curves by numerical quadrature using Simpson's rule.

Run	No. of N.D. Filters	Reactant Volume (c.c.)	Time (sec)	Absorbance	$I_0 \times 10^{-8}$ Eins (-----) sec-cm ²
1	0	25	3	0.135	15.75
2	0	24	6	0.278	15.57
3	0	23	9	0.415	14.85
4	0	22	12	0.563	14.45
5	0	21	15	0.712	13.96
6	1	25	3	0.100	11.67
7	1	24	6	0.212	11.87
8	1	23	9	0.339	12.13
9	1	22	12	0.441	11.32
10	1	20	18	0.738	11.48
11	2	25	5	0.103	7.24
12	2	24	10	0.207	6.99
13	2	23	15	0.284	6.12
14	2	22	20	0.403	6.23
15	3	25	5	0.074	5.20
16	3	24	10	0.143	4.83
17	3	23	15	0.234	4.83
18	3	22	20	0.331	4.89

Table 1. Summary of Incident Light
Intensity Measurements (19)

Results and Discussions

1. Light Intensity Effect :

The variation of polymer concentration distributions by changing the light intensity were calculated according to the equations discussed previously and the result is shown in Fig 7. As may be seen, for low light intensity the distribution is broad and has higher degree of polymerization. For higher light intensity the distribution is narrow and has lower degree of polymerization. Since the radical initiation rate is proportional to the light intensity, more radicals will be generated at higher light intensity. Also the termination is the combination of two radicals while the propagation is the reaction between radicals and the monomers. As a result, when more radicals are produced, the termination rate increases more rapidly than the propagation rate. Therefore narrow polydispersity and low molecular weight can be expected. The result shown in Fig. 7 is in good agreement with the theoretical prediction.

2. Temperature Effect :

Fig. 8 show the distribution of the polymer concentration under different temperatures but with the same proceeding time and light intensity. At higher temperature,

the molecular weight is higher and the molecular weight distribution is broader. As can be seen in the Arrhenius equations of propagation and termination rate constants, the activation energy of propagation is larger than that of the termination, temperature effect on the propagation rate constant, K_p , is therefore greater than that of the termination rate constant, K_t . Since light initiation is the dominant mode of initiation and the light intensity doesn't vary during reaction, the initiation rate can be assumed to be constant. If the propagation rate increases more rapidly than the termination rate with increasing temperature under the circumstance that the initiation rate is constant, a broader molecular weight distribution and higher molecular weight should be expected at higher temperature. The graphical results in Fig. 8 agree with the predication [7].

3 Time Effect :

Figures. 9 and 10 are molecular weight distribution at 305°K and 313°K with 1.0, and 2.0 seconds of light-on period. It can be found that the concentration of each degree of polymerization is proportional to the illuminating time. It implies that there is a linear relationship between the concentration of polymer and the illuminating time. Because the monomer consumption is so small within this time frame that the total monomer concentration will not change. Therefore, the amount of the polymers is proportional to the

illuminating time.

Figs. 11 and 12 are the molecular weight distributions at the same temperature, but longer illuminating time, i.e. 2 and 4 hours. The concentration of each degree of polymerization is not linear to the illuminating time, but has a nonlinear relationship. Because of longer reaction time, the concentration of monomer in bulk has decreased significantly which, in turn, affects the production of the polymer. Fig. 13 shows the decrease of monomer with time.

4. Comparison with Experimental Results

The comparison of the calculated and experimental results are tabulated in Table 1. More experimental data were done by Kuang [19]. It can be shown that the number average degrees of polymerization, X_n , are close to the experimental data but the weight average degrees of polymerization, X_w , are lower than the experimental values. As a result, the molecular weight distributions are lower than the experimental ones. The reasons to explain to results are as follows :

(1) In a reactor as in Figure 1, the light intensity attenuates as in Fig. 14 [21]. In this model, an average of light intensity over the length of the reactor is used instead. It is shown in Fig. 7 that the molecular weight

changed as the light intensity varies, therefore, in a reactor there are dark regions that produce high molecular

Temp. (°K)	Time (min)	Theoretical			Experimental		
		Xn	Xw	PD	Xn	Xw	PD
305	600	50.5	94.6	1.87	60	169	2.80
	690	51.3	96.2	1.88	60	181	3.00
323	180	85.3	163.1	1.91	68	299	4.38
	390	86.9	165.6	1.91	64	246	3.84
338	60	126.7	243.0	1.92	92	354	3.84
	180	128.4	247.2	1.93	115	380	3.32

Table 2. Comparison of the Calculated and Experimental Results

weight polymers and light regions that produce low molecular weight polymers. The total contributions of the high and low regions should have a broader molecular weight distribution than an average light intensity does.

(2) Only the chemical reaction rates are considered in this model, but if the molecules do not have the chances to collide, the reaction can not be happened. Therefore, the transport phenomena of the polymer molecules should also be considered, especially when the solution becomes more and more viscous as the reaction goes on. Failing to pay

attention to the transport phenomena of the polymer molecules may cause errors and limit the application of this model to higher conversion of monomers.

(3) Despite all considered in the development of this model, the agitator speed and sensitizer concentration can also affect the measured data in the experiments. A lot of experiments under different conditions were made by Kuang [19]. Perfect mixing and enough sensitizer were assumed in this model that cause errors with the experimental results.

5. Results of On-Off Illumination:

From Fig. 15, it can be found that the molecular weight distribution indeed was broader but very little when comparing with the distribution while light was on. The radicals disappeared very rapidly at the first few seconds.

Most of the polymers after light is off were generated in the first few seconds. Fig. 15 reveals that the molecular weight distributions after light was turned off for 0.3 second and 1 seconds are the same. It implies that most of the radicals were consumed at the first second and, since the termination rate constant is very large, therefore, very few polymers were produced after one second.

6. Discussion of Thermal Initiation Effect:

In the development of this model, the thermal initiation rate is neglected because it is very small when compared with the photo initiation rate. This assumption is right when the temperature is low and the light intensity is large enough. The thermal initiation rate will become important when there's no light or the temperature is high. Therefor, it can be supposed that the radicals will not disappear in the instant the light is turned off. And the molecular weight distribution will not be like that in Fig. 15.

CONCLUSION

From the results and discussions above, it can be found that this model can qualitatively and semiquantatively describes the photo-initiated addition polymerization and has the advantage to calculate the concentration of any particular n-mer without calculating all of its precursors. Researches in the transport phenomena of the polymer molecules and the light attenuation in a batch reactor may cause further relaxations of some of the assumptions made in the derivation of this model and improve the model to fit the experimental data better.

NOTATION

Symbol	Definition
I_0	Incident light intensity, Eins/sec-cm ²
I_{as}	Absorbed light intensity, Eins/sec-cm ³
i, j	Number of monomer units
K_d	Rate constant for reaction of secsitizer radical with monomer, cc/g-mole-sec
K_i	Rate constant for initiation 3rd order in monomer, cc ² /g-mole ² -sec
K_f	Rate constant for chain transfer to monomer, cc/g-mole-sec
K_p	Propagation rate constant, cc/g-mole-sec
K_{tc}	Rate constant for termination by combination, cc/g-mole-sec
K_{td}	Rate constant for termination by disproportionation, cc/g-mole-sec
K_t	$K_{tc} + K_{td}$
L	Reactor length, cm
M_0	Monomer concentration in feed, g-moles/cc
M	Monomer concentration in reactor, g-moles/cc
P_i	Concentration of dead polymer of chain length i monomer units, g-mole/cc
R_i	Concentration of free radical of chain length i monomer units, g-moles/cc

Symbol	Definition
ΣR_i	Total active polymer or zeroth moment of active polymer, g-moles/cc
S	Sensitizer concentration in reactor, g-moles/cc
t	Time, sec
T	Temperature in reactor, °K
V	Reactor volume, cc
W_i	Weight fraction of polymer of chain length i monomer units, dimensionless
X_n	Number average chain length, dimensionless
X_w	Weight average chain length, dimensionless
Ω_i	Total initiation rate, g-moles/cc-sec Fractional change in volume between zero and complete conversion, dimensionless
ξ_m	Molar absorptivity of monomer, cm ² /g-moles
ξ_{p_i}	Molar absorptivity of dead polymer of chain length of i monomer units, cm ² /g-moles
ξ_s	Molar absorptivity of sensitizer, cm ² /g-moles
ψ_s	Quantum yield from sensitizer, g-moles/Eins
	Generating function

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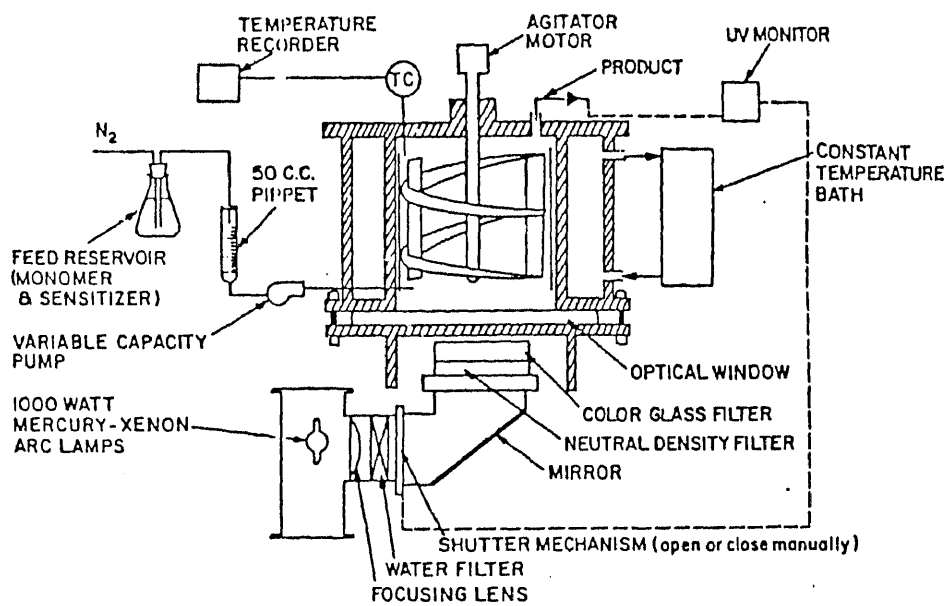


Figure 4. Arrangement of Experimental Apparatus of Isothermal Batch Reactor

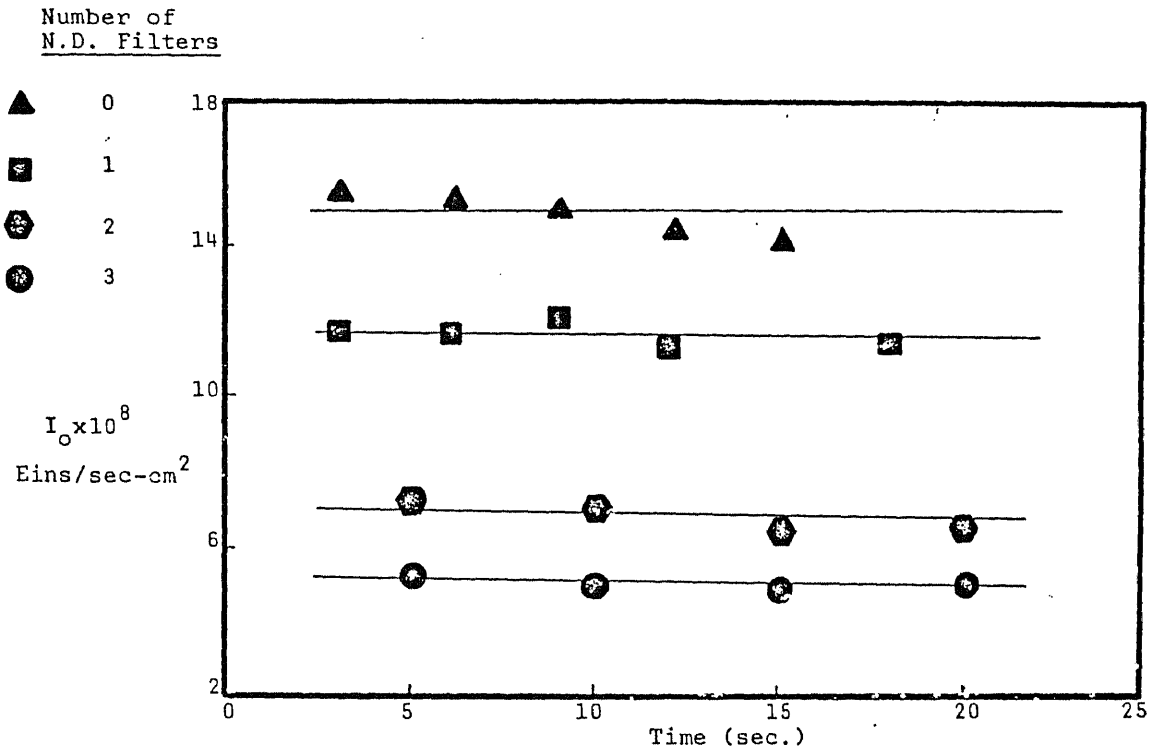


Figure 5. Experimental Measurement of Light Intensity

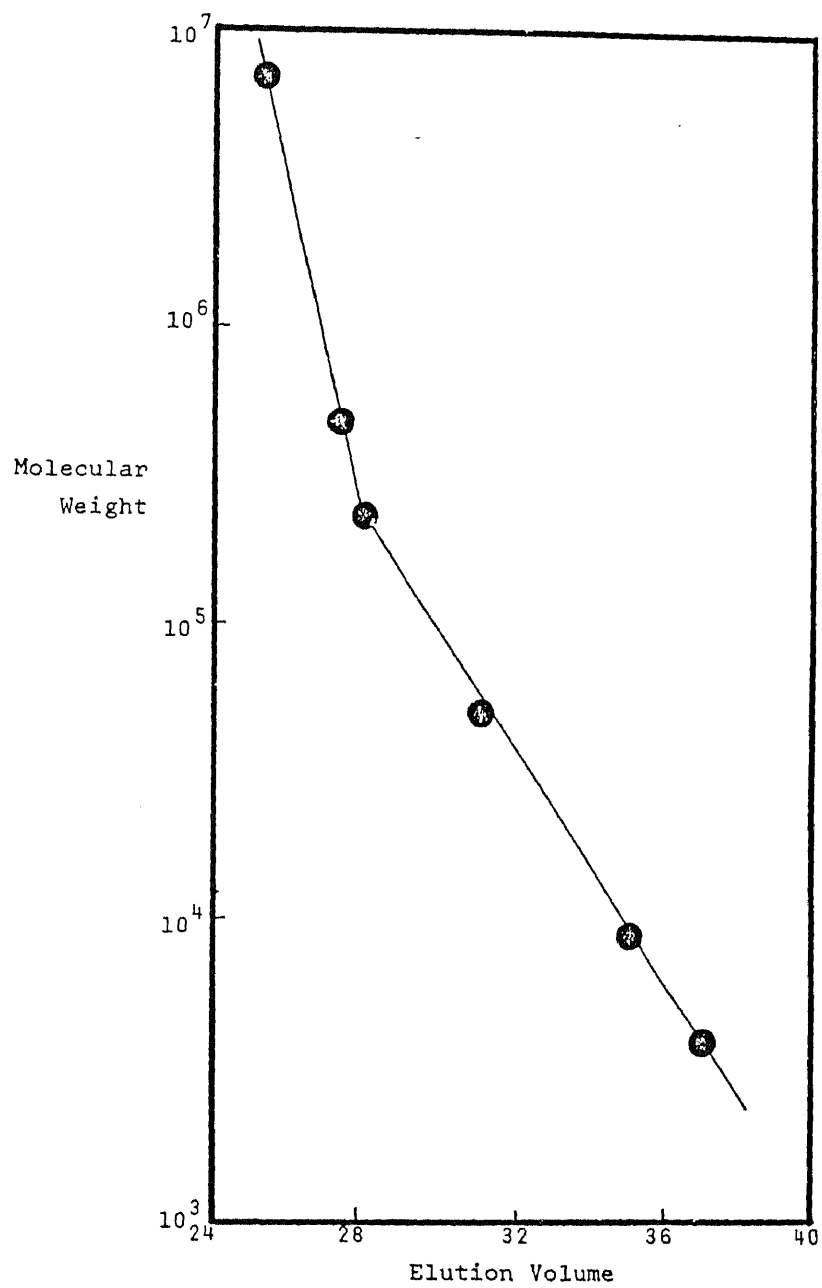


Figure 6. Molecular Weight v.s. Elution Volume for GPC Calibration

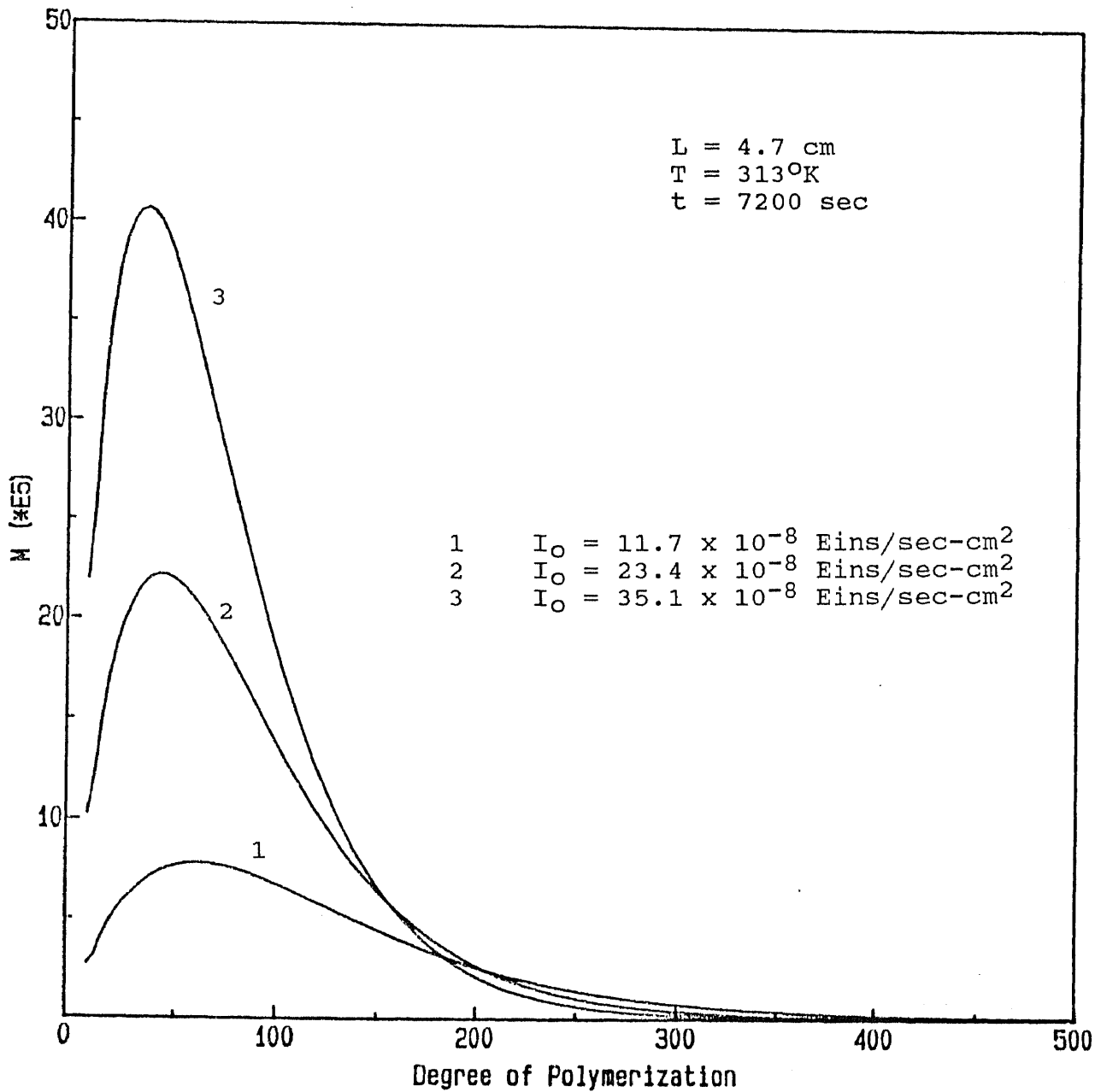


Figure 7. Effect of Light Intensity on the Molecular Weight Distribution

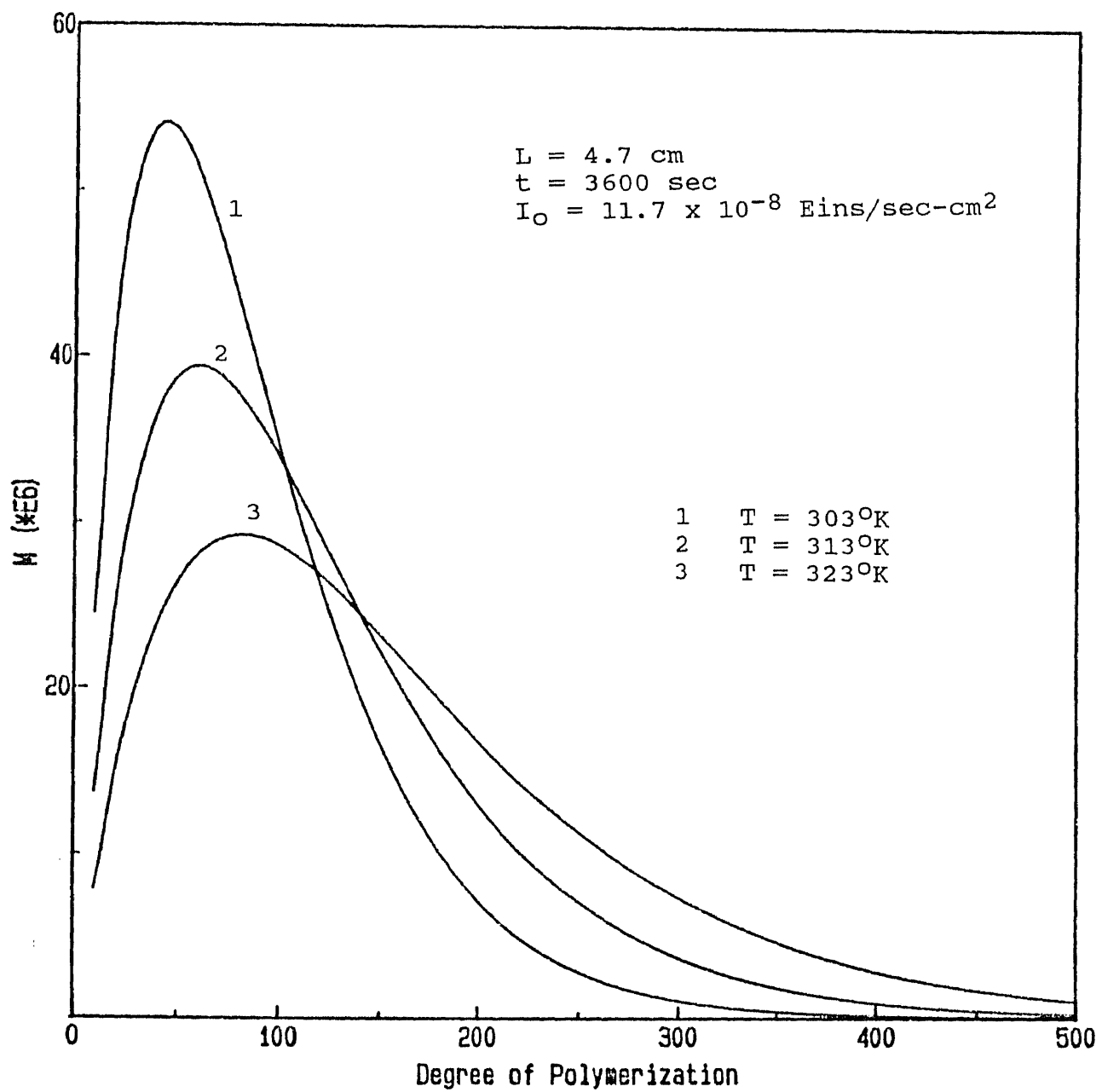


Figure 8. Effect of Temperature on the Molecular Weight Distribution

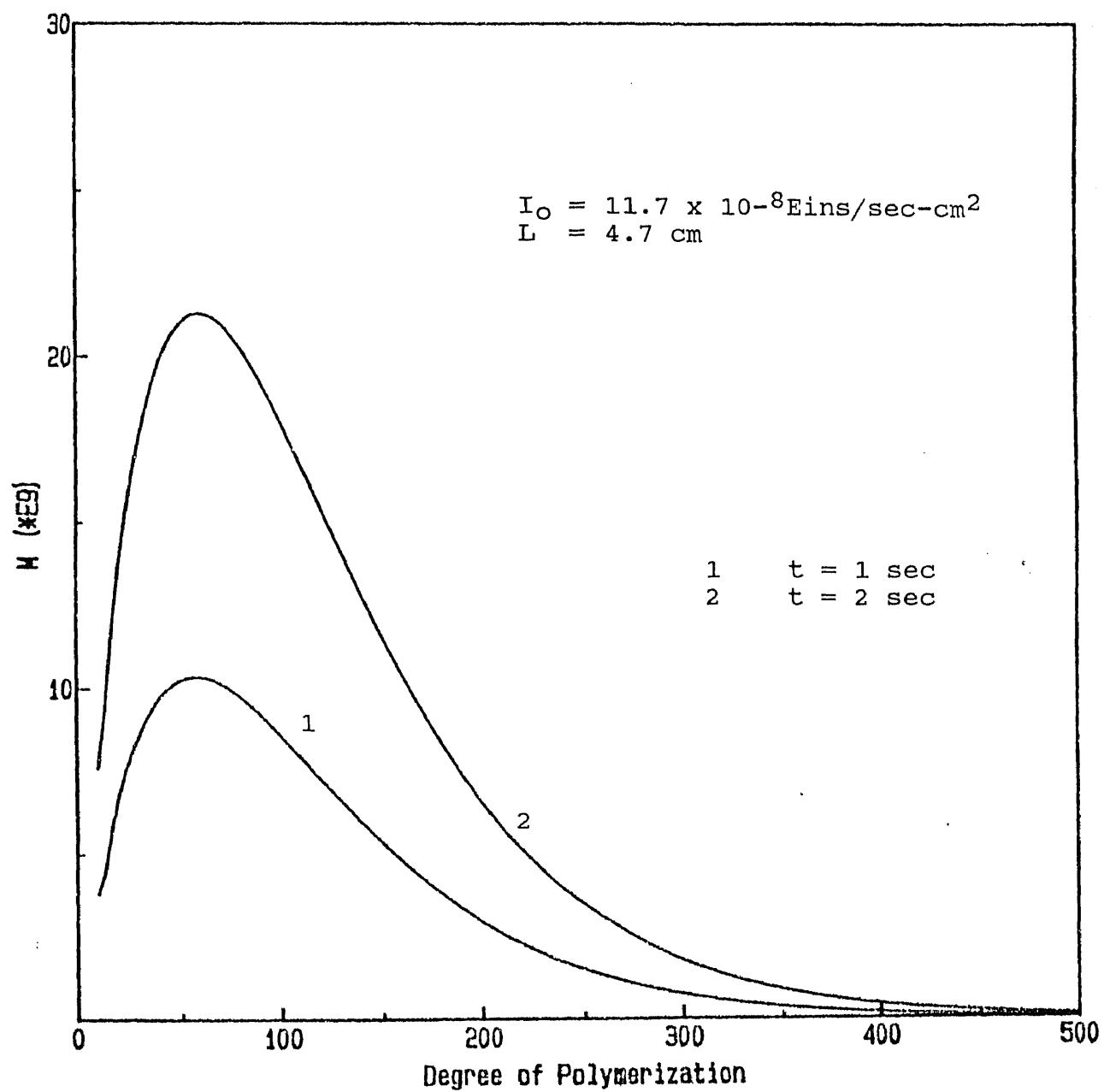


Figure 9. Molecular Weight Distribution of Polymer with a Short Illuminating Time at $T=305^\circ\text{k}$

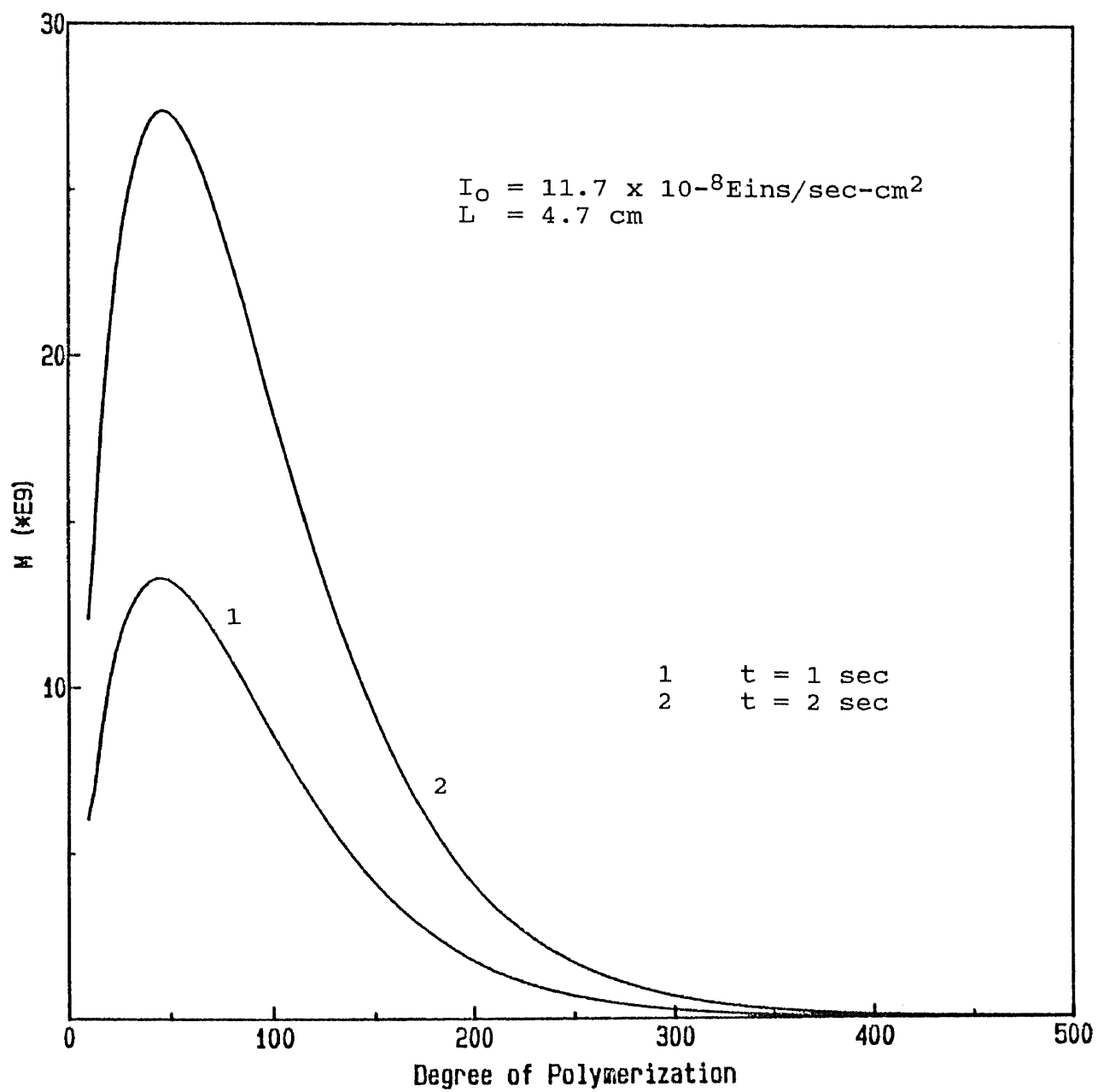


Figure 10. Molecular Weight Distribution of Polymer
with a Short Illuminating Time at $T=313^\circ\text{K}$

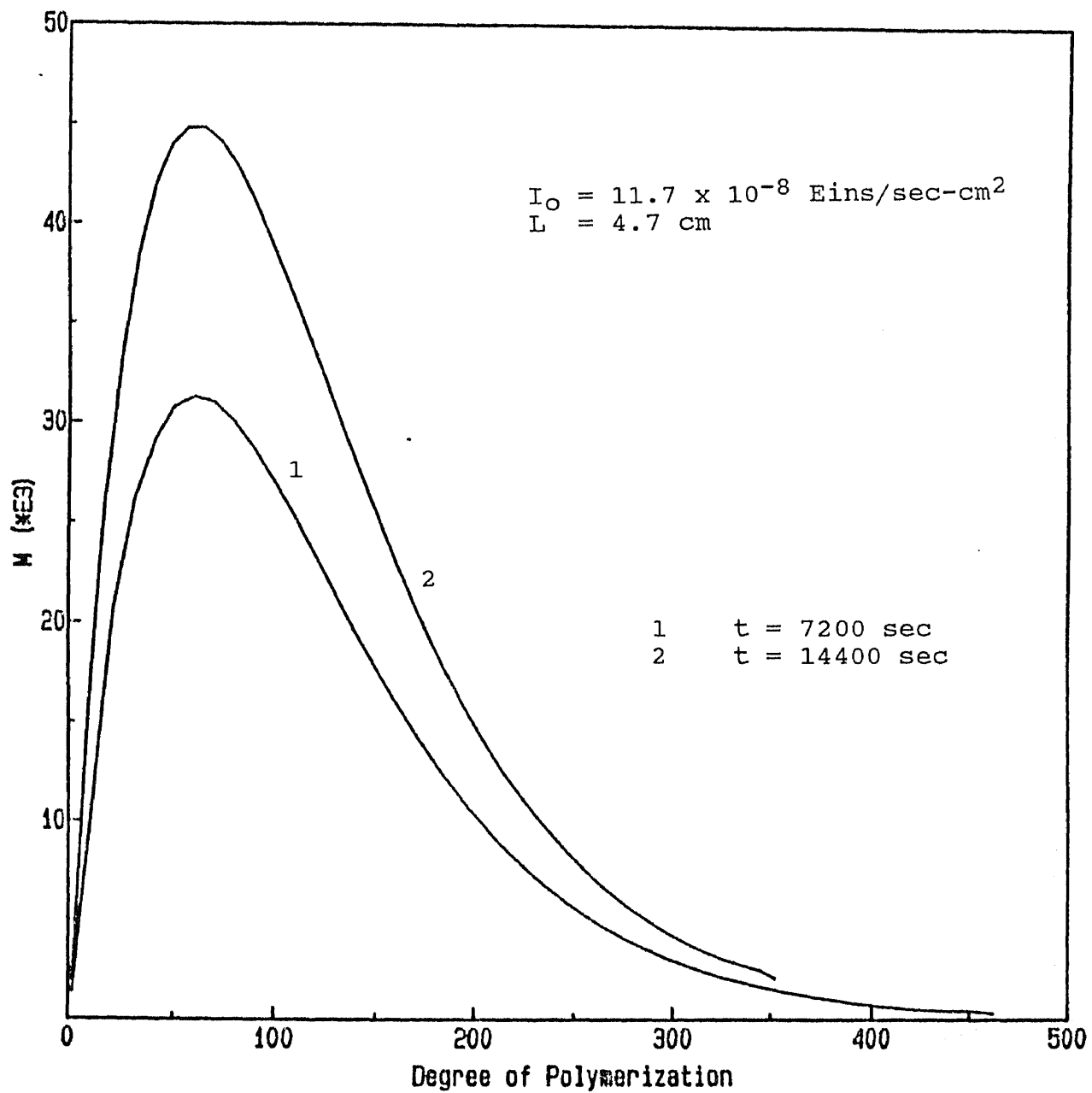


Figure 11. Molecular Weight Distribution of Polymer
with a Long Illuminating Time at $T=305^{\circ}\text{k}$

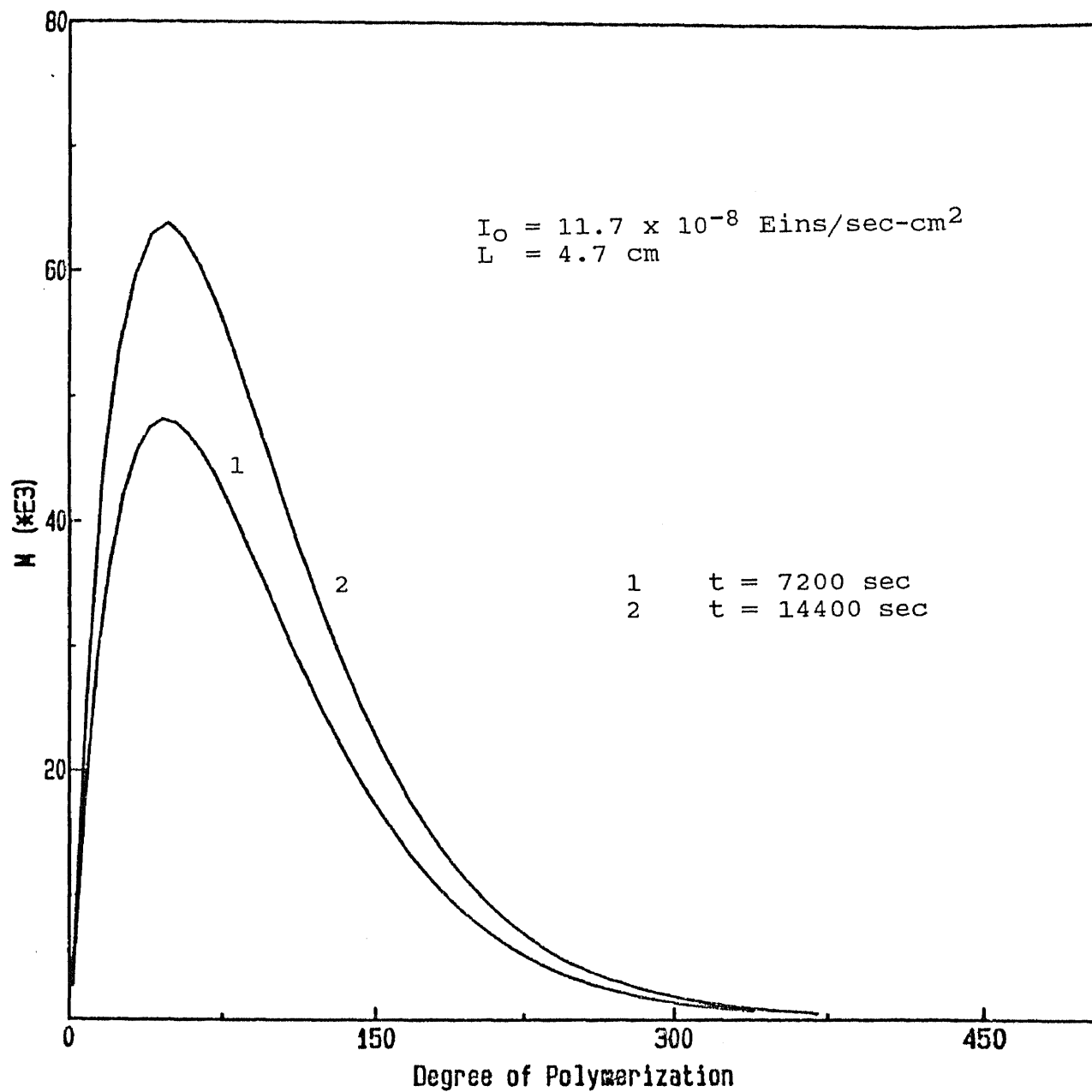


Figure 12. Molecular Weight Distribution of Polymer with a Long Illuminating Time at $T=313^{\circ}\text{K}$

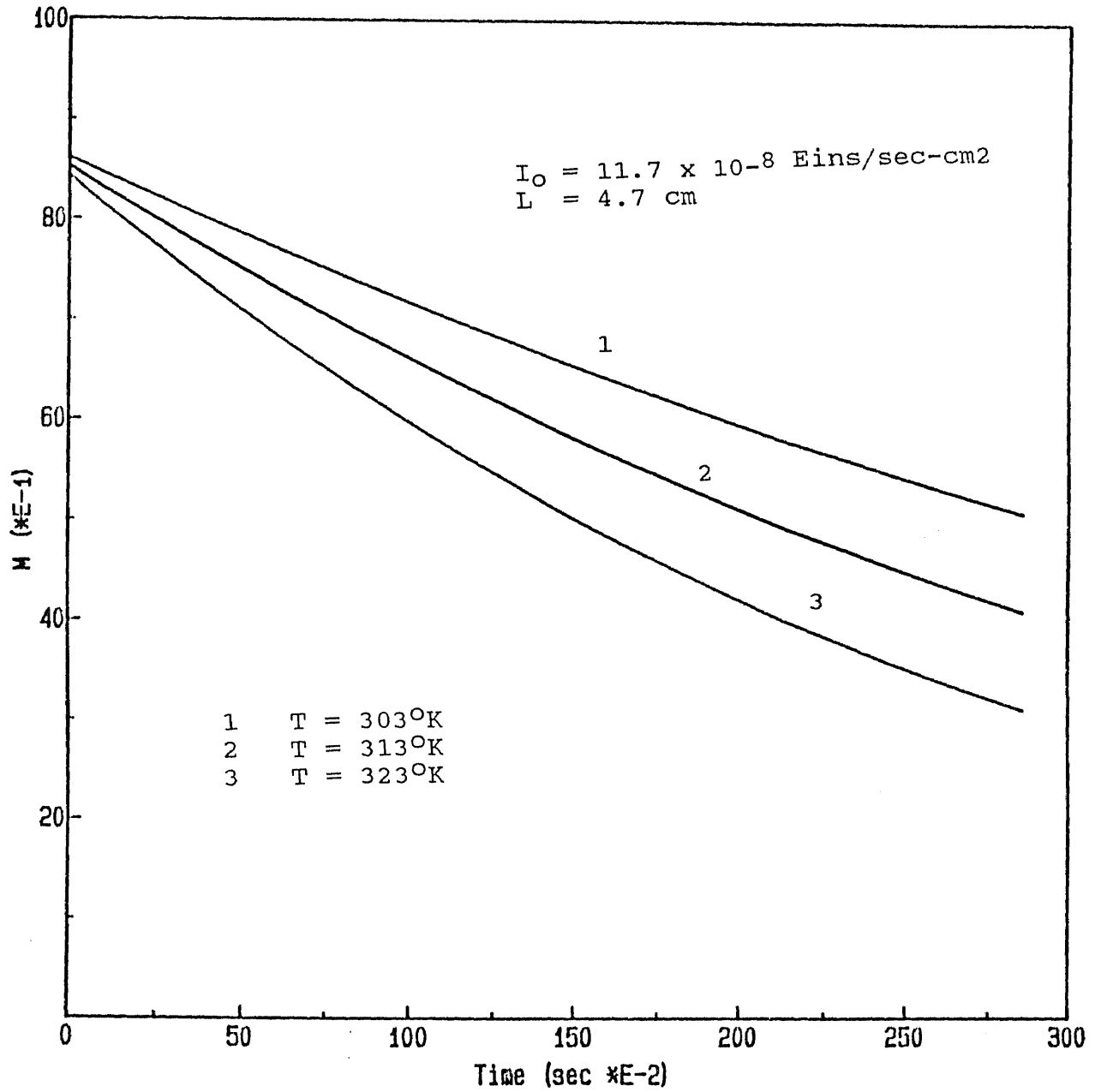


Figure 13. Monomer Concentration v.s. Time at Different Temperature

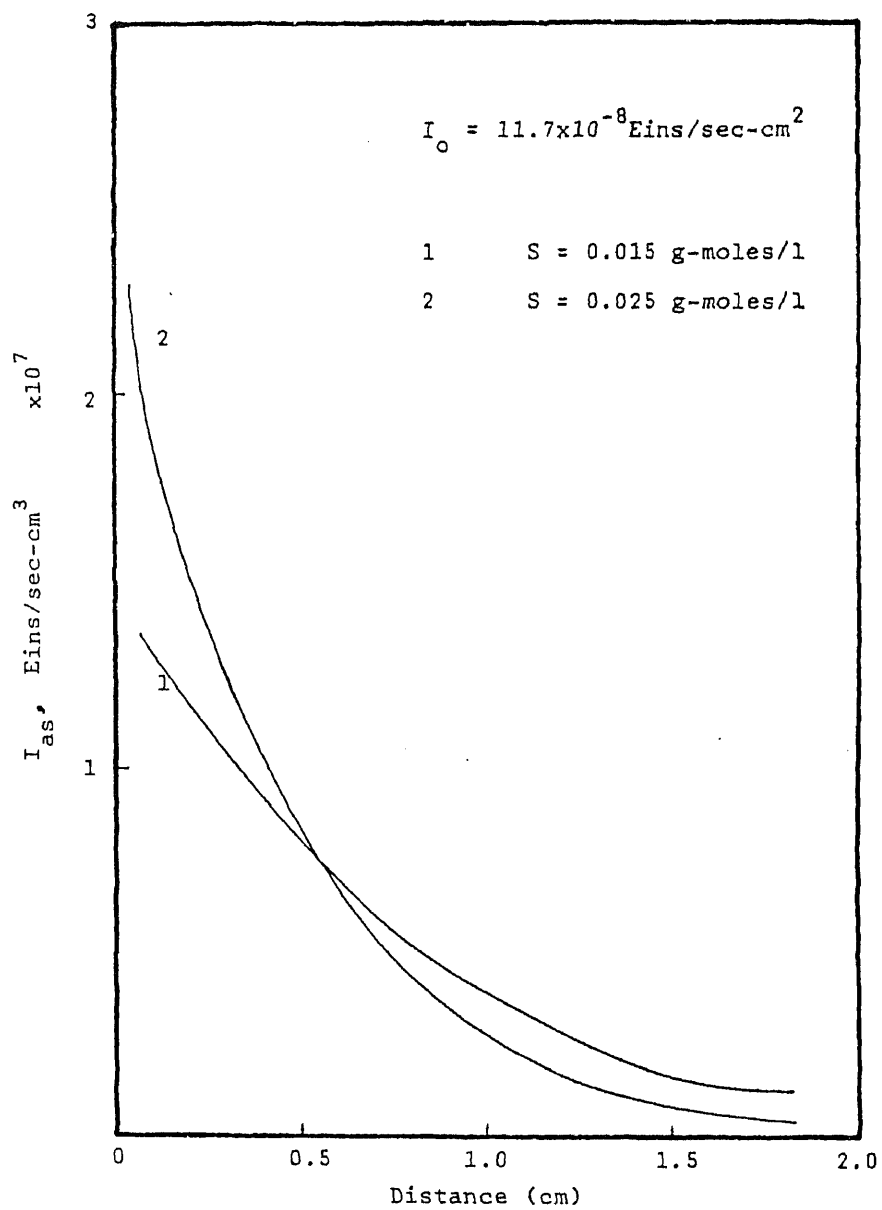


Figure 14. Rate of absorbed Light Intensity
Distribution in the reactor

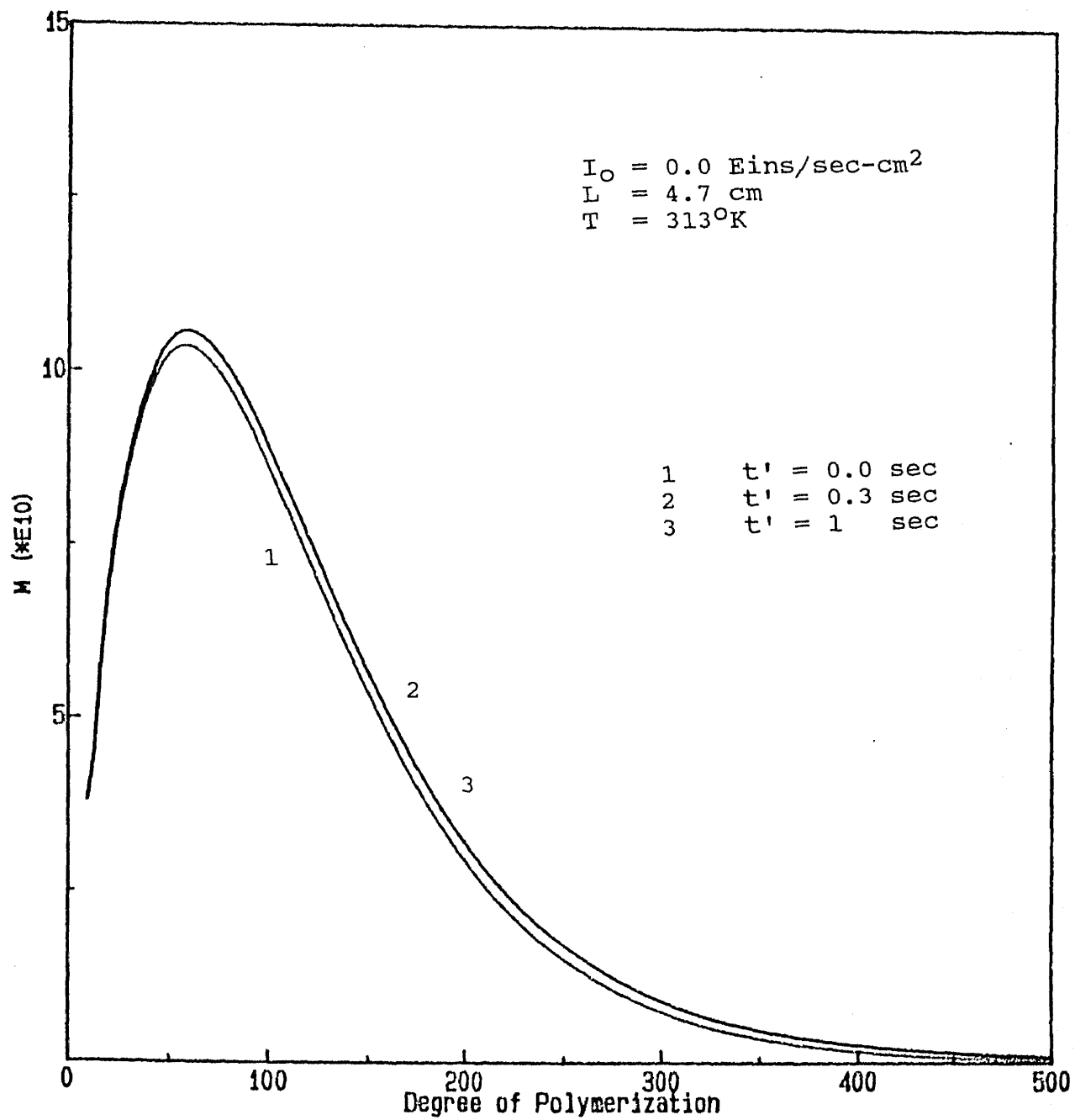


Figure 15. Molecular Weight Distribution of Polymer
After Light is Off