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Effect of Mixing on Nonuniformly Initiated Polymerization by Radiation

An analytical study was carried out on the effects of mixing on radiation-induced polymerization in which the species initiating the polymerization were not uniformly produced because of a nonuniform dose rate distribution. The analysis is based on the periodic irradiation of fluid elements circulating in a stirred-tank reactor having a high dose rate region and a very low dose rate region. It is shown that the rate of polymerization increases with agitation speed and that the bimodal molecular weight distribution of the polymer formed at low agitation speed moves to a unimodal distribution as the agitation speed increases.

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SCOPE

In this paper we present a simplified analytical method to predict the effect of mixing on radiation-induced polymerization in which the species initiating the polymerization were not uniformly produced because of a nonuniform dose rate distribution. Under the influence of the nonuniform dose rate distribution, the rate of active species formation is naturally nonuniform, and the efficiency of active species utilization in propagation reactions is low because of the high probability of their mutual deactivation in the high concentration.

The rate of radiation-induced chemical reaction usually has a dose rate exponent ranging from 0.5 to 1.0, depending on the deactivation mechanism of active species. In the case of reaction with dose rate exponent less than unity, it has been established that irradiation with a more uniform dose rate distribution gives a higher overall reaction rate for the same absorbed energy. If one can make the distribution of the active species more uniform by agitation before the deactivation, an increase in the reaction rate may be expected.

Up to this time, two different calculational methods have been reported. One is based on a diffusion model in which the radicals produced in the higher dose rate area are assumed to be dispersed throughout the reactor by diffusion (Noyes, 1959; Hill and Reiss, 1968). The other is based on a circulation flow model, in which fluid elements are assumed to be irradiated periodically by going around in the reactor (Fredrickson et al., 1961; Kawakami and Isbin, 1970).

CONCLUSIONS AND SIGNIFICANCE

The analysis is based on the periodoc irradiation of fluid elements circulating in a stirred tank reactor having a high dose rate region and very low dose rate region as shown in Figure 2. The practical consequences of the calculations are shown for the rate of polymerization and molecular weight distribution of polymer based on the polymerization of acrylamide in aqueous solution by an electron beam. It is shown that the rate of polymerization and number average molecular weight increase with agitation speed to attain values obtained under uniform irradiation by the average dose rate in the reactor. Also, the bimodal molecular weight distribution of the polymer formed at low agitation speed moves to a unimodal distribution as the agitation speed increases. If the energy absorbed in the reaction system is constant, there is a nonuniformity of dose rate distribution which gives a minimum polymerization rate.

The agitation speed required to attain perfect mixing

is given by Equation (67).

These results lead to the conclusion that the radicals produced nonuniformly in the reactor can be dispersed uniformly throughout the reaction zone. These results also show the feasibility of accelerators in liquid phase reactions carried out in tanks or tubular reactors.

The use of electron accelerators in radiation processing has been so far limited to thin layer reactions such as the crosslinking of polyethylene sheet, the modification of textiles, and the curing of coil coating because of the low penetration of electron beams. In spite of this feature, accelerators have advantages over cobalt-60, for example, in the ease of controlling beams, low cost of radiation shielding, and high efficiency of energy utilization. It is, therefore, worthwhile to explore the use of accelerators in liquid phase reactions carried out for instance in tank or tubular reactors.

Depth-dose curves of electron beams in liquids show a sharp decrease in dose with increasing depth. This leads to a nonuniform distribution of dose rate in the reaction system, particularly when the depth of the reactor is larger than the maximum range of electrons; thus only a part of reactor is irradiated.

Yemin and Hill (1969) reported that the rate of the nonuniformly initiated photopolymerization of methylmethacrylate in bulk increases with agitation speed.

Chen and Hill (1971) carried out a theoretical study on effects of nonuniform initiation on reaction rate and distribution of product in continuous stirred-tank reactors. They assumed the dose rate distribution to be exponential and showed that the nonuniformity of dose rate distribution and the radical life time relative to mixing time have large effects. The molecular weight distribution was calculated to be unimodal, and the position of the peak moves to the lower molecular weight with increase of the nonuniformity and/or the mixing time relative to the radical life time.

Muller et al. (1971) examined the molecular weight distribution of the polymer to observe a bimodal distribution. They also found that a low molecular weight species was in appreciable relative amount at low stirring speeds, and its amount became smaller with increasing stirring speeds. Kawakami and Isbin (1970) reported the effects of agitation on radiolysis of chloral hydrate aqueous solution under nonuniform dose rate distribution. They proposed a simplified analysis based mainly on the intermittent irradiation of fluid elements caused by recirculating flow in a stirred-tank reactor.

The present paper involves the development of a simplified model to provide for the effects of agitation on nonuniformly initiated polymerization. Polymerization rate, average molecular weight, and molecular weight distribution of a polymer are developed and are illustrated for the radiation polymerization of acrylamide in an aqueous solution.

SIMPLIFIED REACTION SCHEME

Most radiation polymerizations proceed via free radical chain reactions and it is accepted that the polymerization involves four elementary steps: initiation, propagation, termination, and transfer. These steps are schematically shown as follows:

	Rates
Initiation:	
$M, S \rightsquigarrow R_1\cdot$	KI
Propagation:	
$R_i\cdot + M \xrightarrow{k_p} R_{i+1}\cdot$	$k_p[M][R_i\cdot]$
Termination:	
first-order	
$R_i\cdot + Z \xrightarrow{k'_{t1}} P_i$	$k'_{t1}[R_i\cdot][Z] \equiv k_{t1}[R_i\cdot]$
recombination	
$R_i\cdot + R_j\cdot \xrightarrow{k_c} P_{i+j}$	$k_c[R_i\cdot][R_j\cdot]$
disproportionation	
$R_i\cdot + R_j\cdot \xrightarrow{k_d} P_i + P_j$	$k_d[R_i\cdot][R_j\cdot]$
Transfer:	
$R_i\cdot + M \xrightarrow{k_{trm}} P_i + R_i\cdot$ $R_i\cdot + S \xrightarrow{k_{trs}} P_i + R_i\cdot$	$k_{trm}[R_i\cdot][M] + k_{trs}[R_i\cdot][S]$

In the initiation step, the initiating radical $R_1\cdot$ is formed from solvent S and/or monomer M molecules by absorption of radiation energy. In the rate equation, K is the specific rate of free radical formation expressed in moles of radicals per liter per unit radiation dose and equals $\Psi_M[M] + \Psi_S[S]$ where Ψ_M and Ψ_S are functions of the G values of the radical formation from the monomer and solvent, respectively. When $\Psi_S[S] >> \Psi_M[M]$ or $[M]$ is taken as constant, K is a constant independent of time. Successive addition of monomer to the radicals resulting in long chain radicals is the propagation step. The growing radicals are terminated via three different processes, that is, first-order termination with respect to the radical, and second-order termination via recombination or disproportionation of radicals. Another important elementary step is the chain transfer reaction in which the growing radicals react with monomer and/or solvent molecules to transfer their activity. This step lowers the average molecular weight of the polymer but does not affect the overall polymerization rate.

DOSE RATE DISTRIBUTION AND FLOW PATTERN IN A STIRRED-TANK REACTOR

For electron beam irradiation, the depth profile of dose rate, which is referred to as depth dose curve, has been investigated for various materials (Trumps et al., 1940). It is generally known that there is an initial increase of dose rate followed by a rapid decrease to zero at the maximum range of the electrons. The curve shown with a broken line in Figure 1 is typical for electrons of 1 MeV. A maximum dose is observed at a point approximately one-third of the maximum range. A dose at the surface of material is roughly 60% of the maximum dose.

As an approximation of the dose rate distribution, a step-like distribution shown with a solid line in Figure 1 is assumed in the calculations. The low dose rate irradiation is brought about by X-ray or bremsstrahlung. κ is the volume fraction of the reactor in the high dose rate region (region I). $1 - \kappa$, is the volume fraction irradiated with a very low dose rate (region II).

Mixing processes in a stirred vessel have been studied by Rushton et al. (1946), Nagata et al. (1956), and Marr and Johnson (1963). The studies indicate that there is a flow pattern of circulation caused by the pumping action of impeller and that the volumetric pumping rate Q may be expressed as follows,

$$Q = fND^3 \tag{1}$$

where N is the agitation speed, D is the impeller diameter, and f is the coefficient of impeller discharge. The average time required for a fluid element to make one circulation in the vessel is approximately given by V/Q.

A simplified schematic diagram of the flow in the reactor is assumed, as shown in Figure 2. Perfect mixing is presumed in the both regions.

THEORETICAL ANALYSIS

In region I, mass balances on the growing radicals and monomer are expressed by the following equations:

$$\frac{dn_1}{dt} = KI_1 + k_{trm}C_1 n + k_{trs}Sn + \frac{m_1 - n_1}{\tau_1} - (k_{t1} + k_p C_1 + k_{trm}C_1 + k_{trs}S + k_{t2}n) n_1 \tag{2}$$

$$\frac{dn_i}{dt} = k_p C_1 n_{i-1} + \frac{m_i - n_i}{\tau_1} - (k_{t1} + k_p C_1 + k_{trm}C_1 + k_{trs}S + k_{t2}n) n_i \tag{3}$$

$$\frac{dC_1}{dt} = \frac{C_2 - C_1}{\tau_1} - (k_p + k_{trm}) C_1 n \tag{4}$$

and in region II

$$\frac{dm_1}{dt} = KI_2 + k_{trm}C_2 m + k_{trs}Sm + \frac{n_1 - m_1}{\tau_2} - (k_{t1} + k_p C_2 + k_{trm}C_2 + k_{trs}S + k_{t2}m) m_1 \tag{5}$$

$$\frac{dm_i}{dt} = k_p C_2 m_{i-1} + \frac{n_i - m_i}{\tau_2} - (k_{t1} + k_p C_2 + k_{trm}C_2 + k_{trs}S + k_{t2}m) m_i \tag{6}$$

$$\frac{dC_2}{dt} = \frac{C_1 - C_2}{\tau_2} - (k_p + k_{trm}) C_2 m \tag{7}$$

where

$$k_{t2} = k_c + k_d \tag{8}$$

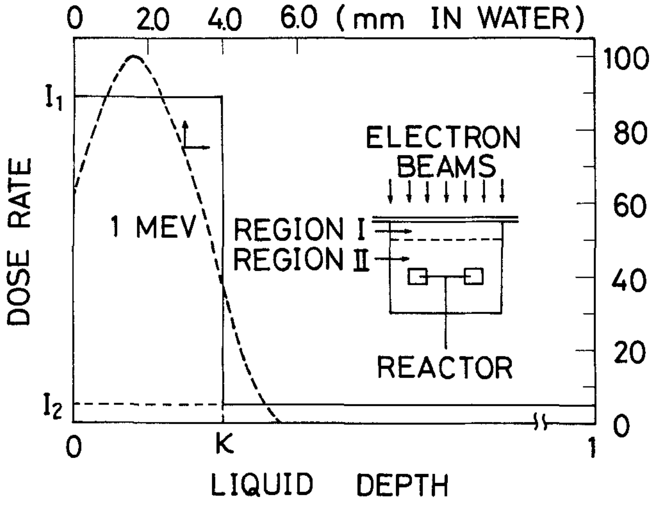

Fig. 1. Depth-dose curve in water and schematic dose rate distribution in reactor.

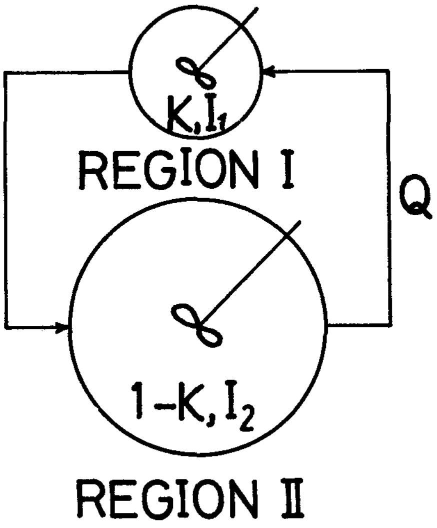

Fig. 2. Schematic flow pattern in reactor.

$$\tau_1 = \kappa T \tag{9}$$

$$\tau_2 = (1 - \kappa) T \tag{10}$$

$$n = \Sigma n_i \tag{11}$$

$$m = \Sigma m_i \tag{12}$$

To solve Equations (2), (3), (5), and (6), we assume the so-called "steady state" approximation with respect to radical concentrations for each chain length, leading to the following equations:

$$m = n + \tau_1 (k_{t1} + k_{t2} n) n - \tau_1 K I_1 \tag{13}$$

$$n = m + \tau_2 (k_{t1} + k_{t2} m) m - \tau_2 K I_2 \tag{14}$$

The monomer concentrations in region I and II at a time t are given in Equations (15) and (16) which are obtained by solving Equations (4) and (7), respectively,

$$C_1 = g_1 \exp(-\gamma t) + h_1 \exp(-\delta t) \tag{15}$$

$$C_2 = g_2 \exp(-\gamma t) + h_2 \exp(-\delta t) \tag{16}$$

where

$$\gamma = (E + \sqrt{E^2 - 4F})/2 \tag{17}$$

$$\delta = F/\gamma \tag{18}$$

$$E = 1/\tau_1 + 1/\tau_2 + (k_p + k_{trm})(n + m) \tag{19}$$

$$F = m(k_p + k_{trm})/\tau_1 + n(k_p + k_{trm})/\tau_2 + (k_p + k_{trm})^2 nm \tag{20}$$

$$g_1 = Co\{(k_p + k_{trm})n - \delta\}/(\gamma - \delta) \tag{21}$$

$$h_1 = Co\{\gamma - (k_p + k_{trm})n\}/(\gamma - \delta) \tag{22}$$

$$g_2 = \{1 + (k_p + k_{trm})\tau_1 n - \gamma \tau_1\} g_1 \tag{23}$$

$$h_2 = \{1 + (k_p + k_{trm})\tau_1 n - \delta \tau_1\} h_1 \tag{24}$$

As a first approximation, the following equations are assumed in order to derive the concentration distribution of the growing radicals (Zeeman and Amundson, 1963):

$$dn_i/di = n_i - n_{i-1} \tag{25}$$

$$dm_i/di = m_i - m_{i-1} \tag{26}$$

If we assume steady state concentrations for each chain length i as well as for all chains collectively, then we may let the index i in Equations (25) and (26) start at 1 provided we define n_0 and m_0 as follows:

$$n_0 = \frac{KI_1 + (k_{trm}C_1 + k_{trs}S)n}{k_pC_1} \tag{27}$$

$$m_0 = \frac{KI_2 + (k_{trm}C_2 + k_{trs}S)m}{k_pC_2} \tag{28}$$

Following equations are then derived from Equations (3), (6), (25), and (26),

$$dn_i/di + \left(\frac{1}{\nu_1} - 1\right) n_i = \frac{m_i}{\tau_1 k_p C_1} \tag{29}$$

$$dm_i/di + \left(\frac{1}{\nu_2} - 1\right) m_i = \frac{n_i}{\tau_1 k_p C_2} \tag{30}$$

where

$$\nu_1 = k_pC_1/(k_{t1} + k_{trm}C_1 + k_{trs}S + k_pC_1 + k_{t2}n + 1/\tau_1) \tag{31}$$

$$\nu_2 = k_pC_2/(k_{t1} + k_{trm}C_2 + k_{trs}S + k_pC_z + k_{t2}m + 1/\tau_2) \tag{32}$$

ν_1 and ν_2 correspond to the probability of propagation of the radicals in region I and II, respectively. Solving Equations (29) and (30), n_i and m_i are expressed by the following equations:

$$n_i = U_1 \exp(-iX) + V_1 \exp(-iY) \tag{33}$$

$$m_i = U_2 \exp(-iX) + V_2 \exp(-iY) \tag{34}$$

where

$$U_1 = \left(\frac{1}{\nu_1} - \frac{1}{\nu_2} + W\right)\left(\frac{n_0}{2W}\right) - \frac{m_0}{\tau_1 k_p C_1 W} \tag{35}$$

$$V_1 = \frac{m_0}{\tau_1 k_p C_1 W} - \left(\frac{1}{\nu_1} - \frac{1}{\nu_2} - W\right)\left(\frac{n_0}{2W}\right) \tag{36}$$

$$U_2 = (1/\nu_1 - 1/\nu_2 - W)(\tau_1 k_p C_1 U_1/2) \tag{37}$$

$$V_2 = (1/\nu_1 - 1/\nu_2 + W)(\tau_1 k_p C_1 V_1/2) \tag{38}$$

$$W = \sqrt{(1/\nu_1 + 1/\nu_2 - 2)^2 - 4\{(1/\nu_1 - 1)(1/\nu_2 - 1) - 1/(\tau_1\tau_2 k_p{}^2 C_1 C_2)\}} \tag{39}$$

$$X = (1/\nu_1 + 1/\nu_2 - 2 + W)/2 \tag{40}$$

$$Y = (1/\nu_1 + 1/\nu_2 - 2 - W)/2 \tag{41}$$

The production rate of dead polymer composed of i monomers at a time t is given by

$$\begin{aligned} dP_i/dt = \kappa & \left\{ k_{t1}n_i + k_{trm}C_1 n_i + k_{trs}S n_i \right. \\ & \left. + k_d n n_i + k_c \left[\sum_{j=1}^{i-1} n_{i-j} n_j \right] \Big/ 2 \right\} \\ & + (1-\kappa) \left\{ k_{t1}m_i + k_{trm}C_2 m_i + k_{trs}S m_i \right. \\ & \left. + k_d m m_i + k_c \left[\sum_{j=1}^{i-1} m_{i-j} m_j \right] \Big/ 2 \right\} \\ = & \exp(-iX) \{\kappa U_1(k_{t1} + k_{trm}C_1 + k_{trs}S + k_d n) \\ & + (1-\kappa) U_2 (k_{t1} + k_{trm}C_2 + k_{trs}S + k_d m)\} \\ & + \exp(-iY) \{\kappa V_1 (k_{t1} + k_{trm}C_1 + k_{trs}S + k_d n) \\ & + (1-\kappa) V_2 (k_{t1} + k_{trm}C_2 + k_{trs}S + k_d m)\} \\ & + (i-1)\exp(-iX) k_c \{\kappa U_1^2 + (1-\kappa) U_2^2\}/2 \\ & + (i-1)\exp(-iY) k_c \{\kappa V_1^2 + (1-\kappa) V_2^2\}/2 \\ & + k_c \{\kappa U_1 V_1 + (1-\kappa) U_2 V_2\} \\ & [\exp\{-(X + iY)\} - \exp\{-(Y + iX)\}]/ \\ & \{\exp(-Y) - \exp(-X)\} \end{aligned} \tag{42}$$

Polymerization Rate

The total rate of dead polymer formation at a time t is expressed by

$$X(t) = \sum_{i=1}^{\infty} \frac{d}{dt}(iP_i) \tag{43}$$

This is essentially equal to the rate of monomer consumption which is given by $(k_p + k_{trm})\{\kappa C_1 n + (1-\kappa) C_2 m\}$.

Average Molecular Weight of Polymer

The number and weight average molecular weight of the dead polymer instantaneously formed at a time t is given by

$$m_n(t) = \sum_{i=1}^{\infty} \frac{d}{dt}(iP_i) \Bigg/ \sum_{i=1}^{\infty} \frac{d}{dt}(P_i) \tag{44}$$

$$m_w(t) = \sum_{i=1}^{\infty} \frac{d}{dt}(i^2P_i) \Bigg/ \sum_{i=1}^{\infty} \frac{d}{dt}(iP_i) \tag{45}$$

In addition those of all the polymer formed during the reaction time t are given by the following equations:

$$M_n(t) = \frac{\int_0^t \sum_{i=1}^{\infty} \frac{d}{dt}(iP_i)dt + \sum_{i=1}^{\infty}\{i\kappa n_i + i(1-\kappa)m_i\}}{\int_0^t \sum_{i=1}^{\infty} \frac{d}{dt}(P_i)dt + \sum_{i=1}^{\infty}\{\kappa n_i + (1-\kappa)m_i\}} \tag{46}$$

$$M_w(t) = \frac{\int_0^t \sum_{i=1}^{\infty} \frac{d}{dt}(i^2P_i)dt + \sum_{i=1}^{\infty}\{i^2\kappa n_i + i^2(1-\kappa)m_i\}}{\int_0^t \sum_{i=1}^{\infty} \frac{d}{dt}(iP_i)dt + \sum_{i=1}^{\infty}\{i\kappa n_i + i(1-\kappa)m_i\}} \tag{47}$$

Molecular Weight Distribution

The weight distribution function of molecular weight of the dead polymer instantaneously formed at a reaction time t is expressed by

$$f_w(t) = \frac{d}{dt}(iP_i) \Bigg/ \sum_{i=1}^{\infty} \frac{d}{dt}(iP_i) \tag{48}$$

and the distribution function for all the polymer formed during the reaction time is given by

$$F_w(t) = \frac{\int_0^t \frac{d}{dt}(iP_i)\,dt + i\kappa n_i + i(1-\kappa)m_i}{\int_0^t \sum_{i=1}^{\infty} \frac{d}{dt}(iP_i)\,dt + \sum_{i=1}^{\infty}\{i\kappa n_i + i(1-\kappa)m_i\}} \tag{49}$$

Agitation Speed for Perfect Mixing

The agitation speed required to attain perfect mixing is calculated by the following analytical procedure. Let us introduce a parameter ϵ, defined by Equation (50), which compares the attained polymerization rate with those at no mixing and perfect mixing:

$$\epsilon = \frac{X(0) - X_{NM}(0)}{X_{PM}(0) - X_{NM}(0)} \tag{50}$$

where $X_{PM}(0)$ and $X_{NM}(0)$ are the initial rates of polymerization with perfect mixing and without mixing. They are given by

$$X_{PM}(0) = (k_p + k_{trm})C_0\bar{n} \tag{51}$$

$$X_{NM}(0) = (k_p + k_{trm})C_0\,\{\kappa n_s + (1-\kappa)m_s\} \tag{52}$$

where

$$\bar{I} = \kappa I_1 + (1-\kappa)I_2 \tag{53}$$

$$\bar{n} = \frac{1}{2k_{t2}}\left(\sqrt{k_{t1}^2 + 4k_{t2}K\bar{I}} - k_{t1}\right) \tag{54}$$

$$n_s = \frac{1}{2k_{t2}}\left(\sqrt{k_{t1}^2 + 4k_{t2}KI_1} - k_{t1}\right) \tag{55}$$

$$m_s = \frac{1}{2k_{t2}}\left(\sqrt{k_{t1}^2 + 4k_{t2}KI_2} - k_{t1}\right) \tag{56}$$

From Equation (43) is $X(0)$ given by

$$X(0) = (k_p + k_{trm})C_0\,\{\kappa n + (1-\kappa)m\} \tag{57}$$

Rearranging Equations (50), (51), (52), and (57), we get

$$1 - \epsilon = \frac{1}{\phi}\left\{1 - \frac{\kappa n + (1-\kappa)m}{\bar{n}}\right\} \tag{58}$$

where

$$\phi = 1 - \frac{\kappa n_s + (1-\kappa)m_s}{\bar{n}} \tag{59}$$

From Equation (58), $m/\bar{n}$ is expressed by

$$m/\bar{n} = \frac{1-(1-\epsilon)\phi}{1-\kappa} - \frac{\kappa}{1-\kappa}\left(\frac{n}{\bar{n}}\right) \tag{60}$$

Dividing the sum of Equation (13) and (14) by $k_{t2}\bar{n}^{\,2}$, the following equation is obtained:

$$\left(\frac{n}{\bar{n}}\right)^2 + \frac{k_{t1}}{k_{t2}\bar{n}}\left(\frac{n}{\bar{n}}\right) + \frac{1-\kappa}{\kappa}\left(\frac{m}{\bar{n}}\right)^2 + \frac{1-\kappa}{\kappa}\,\frac{k_{t1}}{k_{t2}\bar{n}}\left(\frac{m}{\bar{n}}\right) - \frac{K\bar{I}}{\kappa k_{t2}n^{\,2}} = 0 \tag{61}$$

Using the relations, $k_{t2}\bar{n}^{\,2} + k_{t1}\bar{n} - G\bar{I} = 0$ and $n/\bar{n} > 1$, $(n/\bar{n})$ and $(m/\bar{n})$ are solved as follows:

$$n/\bar{n} = 1 - (1-\epsilon)\,\phi + \sqrt{\frac{1-\kappa}{\kappa}(1-\epsilon)\phi\left\{2 - (1-\epsilon)\phi + \frac{k_{t1}}{k_{t2}\bar{n}}\right\}} \tag{62}$$

$$m/\bar{n} = 1 - (1-\epsilon)\phi - \frac{\kappa}{1-\kappa}\sqrt{\frac{1-\kappa}{\kappa}(1-\epsilon)\phi\left\{2 - (1-\epsilon)\phi + \frac{k_{t1}}{k_{t2}\bar{n}}\right\}} \tag{63}$$

From Equations (9) and (13) the following equation is derived:

$$T = \left(\frac{n}{\bar{n}} - \frac{m}{\bar{n}}\right) \Big/ \kappa\left\{\frac{KI_1}{\bar{n}} - k_{t2}\bar{n}\left(\frac{n}{\bar{n}}\right)^2 - k_{t1}\left(\frac{n}{\bar{n}}\right)\right\} \tag{64}$$

The life time of the radicals l_t at the perfect mixing is given by

$$l_t = \bar{n}/K\bar{I} \tag{65}$$

The required agitation speed for an arbitrary value of ϵ is calculated from

$$T_\epsilon = l_t\sqrt{\frac{(1-\epsilon)\phi}{\kappa(1-\kappa)}\left\{2 - (1-\epsilon)\phi + \frac{k_{t1}}{K\bar{I}k_{t2}l_t}\right\}} \Big/ \kappa\left\{\frac{I_1}{\bar{I}} - \frac{k_{t2}n^2 + k_{t1}n}{K\bar{I}}\right\} \tag{66}$$

The agitation speed for the perfect mixing (that is, $\epsilon \doteqdot 1$) is approximately calculated from

$$T_p = l_t\sqrt{\frac{(1-\epsilon)\phi}{\kappa(1-\kappa)}\left(2 + \frac{k_{t1}}{K\bar{I}k_{t2}l_t}\right)} \Big/ \kappa\left(\frac{I_1}{\bar{I}} - 1\right) \tag{67}$$

If $\kappa << 1$ and $I_1 >> I_2$, ϕ is almost equal to unity and T_p is expressed by

$$T_p = l_t\sqrt{\frac{1-\epsilon}{\kappa}\left(2 + \frac{k_{t1}}{K\bar{I}k_{t2}l_t}\right)} \tag{68}$$

PRACTICAL CONSEQUENCES AND DISCUSSION

In order to inquire into the practical results of these calculations, we selected the radiation polymerization of acrylamide in aqueous solution as a model reaction system. Kinetic studies of this polymerization using cobalt-60 and X-rays have been reported by Collinson et al. (1957) and Curries et al. (1965). They concluded that there is no chain transfer and no first-order termination and that the initiating radicals are formed essentially from water under the conditions employed. The rate constants and other informations are listed in Table 1.

Influence of Agitation on Polymerization Rate

In Figure 3 ϵ is plotted against the fluid circulation period T at various dose rates of irradiation. It can be seen that the polymerization rate increases approaching the rate at perfect mixing with decreasing period and decreases to the rate at no mixing as the period increases. The figure also indicates that a higher value of ϵ is obtained at lowered dose rate at constant T and κ. In other words, when the higher dose rate is employed, the higher

TABLE 1. DATA ON THE RADIATION POLYMERIZATION OF ACRYLAMIDE IN AQUEOUS SOLUTION

Parameter	
K, mole/(liter)(rad)	7.75×10^{-9}
k_p, liter/(mole)(s)	1.72×10^4
k_c, liter/(mole)(s)	1.63×10^7
k_{t1}, 1/s	0
k_{tr}, liter/mole)(s)	0
temp., °C	25
pH	1.0

Monomer conc.; 0.1-2.0 mole/liter.

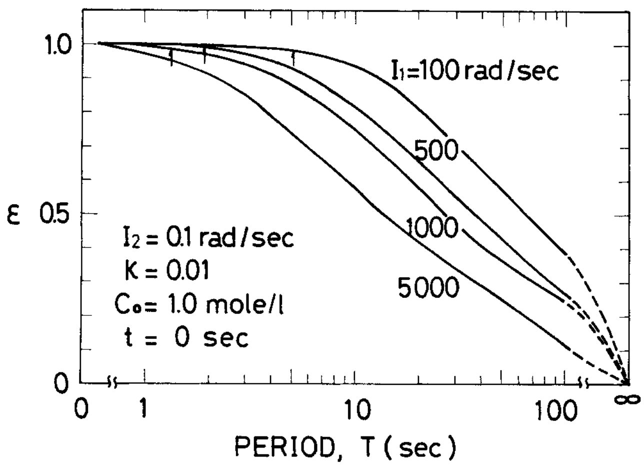

Fig. 3. Effect of T on ϵ at various dose rates of region I.

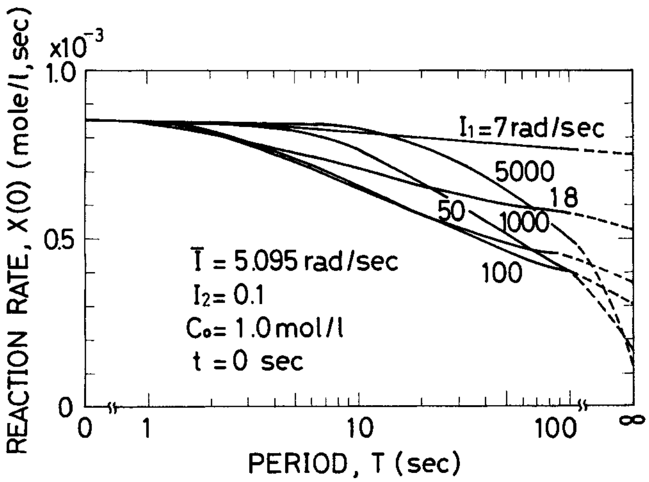

Fig. 4. Effect of agitation on polymerization rate for constant absorbed energy at different dose rate.

speed of agitation is required to get the same value of ϵ. The explanation for this behavior is that the radical concentration in region I is increased at higher dose rate irradiation and accordingly the radical life time becomes shorter. A higher speed of agitation is then required for the shorter life radicals to propagate before termination.

The period for the almost perfect mixing ($\epsilon = 0.99$) calculated by Equation (68) are shown with arrows in Figure 3.

Polymerization rates with constant absorbed energy per unit time were calculated for various values of dose rate and κ as a function of period T. κ and I_1 were adjusted to maintain constant absorbed energy. The results are shown in Figure 4 which indicates that the polymerization rate increases with dose rate in the range of high agitation speed (that is, low range of T), and that the relation is reversed at low agitation speed. Similarly in Figure 5, the same results are shown in the plot of $X(0)/X_{PM}(0)$ versus the values of I_1 and κ. As I_1 increases and hence κ decreases, the nonuniformity of dose rate distribution increases. It can be seen that there is a nonuniformity of dose rate distribution which gives a minimum reaction rate for a constant agitation speed. The practical significance of this conclusion is that the polymerization is more advantageously carried out at high dose rate when the nonuniformity of dose rate distributions is high, and at low dose rate when the uniformity is high.

The radical and monomer concentrations in region I and II at a constant reaction time ($t = 600$ s) are plotted in Figure 6 as a function of the fluid circulation period. The nonuniformity of the radical concentration illustrated by the difference in radical concentration between two regions increases to a great extent with the period. Since the radical life time is very short, a high speed of agitation is needed to produce a uniform concentration equal to that formed by uniform irradiation at the average dose rate. In contrast, in the monomer concentration, only a slight difference between the two regions is observed at the extremely slow rate of agitation.

Influence of Agitation on Molecular Weight of Polymer

The number average molecular weight of polymer instantaneously formed at a time t $[m_n(t)]$ and that of all the polymer produced during the reaction $[M_n(t)]$ are plotted versus t in Figure 7 for two different agitation speeds. The average molecular weights of the both polymers were shown to decrease with the time. This is simply due to the decrease of monomer concentration as the reaction proceeds.

The number average and weight average molecular weight of polymer and their ratio are plotted in Figure 8 as a function of the period. The number average molecular weight decreases with the period while the weight average increases. Accordingly the ratio $\overline{M}_w/\overline{M}_n$, which is an index of broadness of molecular weight distribution, increases with the period.

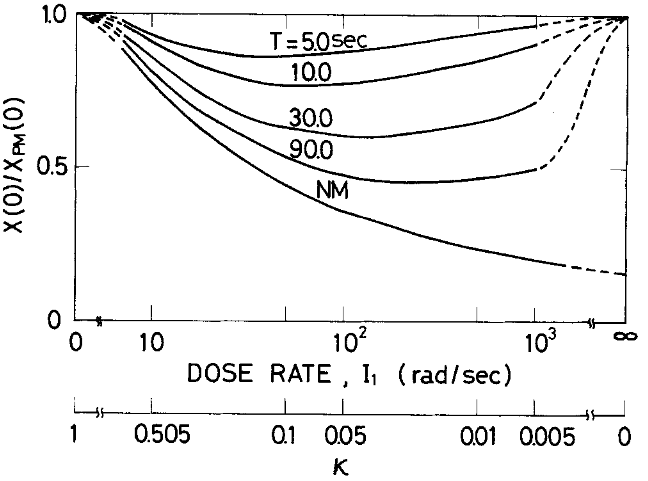

Fig. 5. Effect of dose rate and κ on reaction rate at constant absorbed energy.

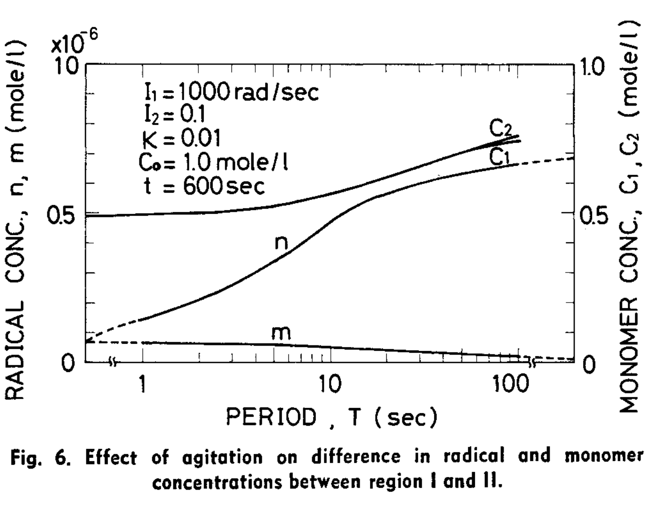

Fig. 6. Effect of agitation on difference in radical and monomer concentrations between region I and II.

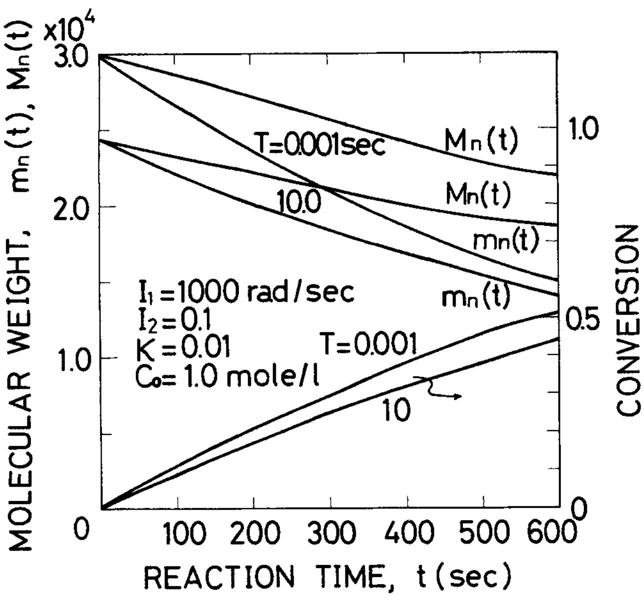

Fig. 7. Change of number average molecular weight with reaction time at two agitation speeds.

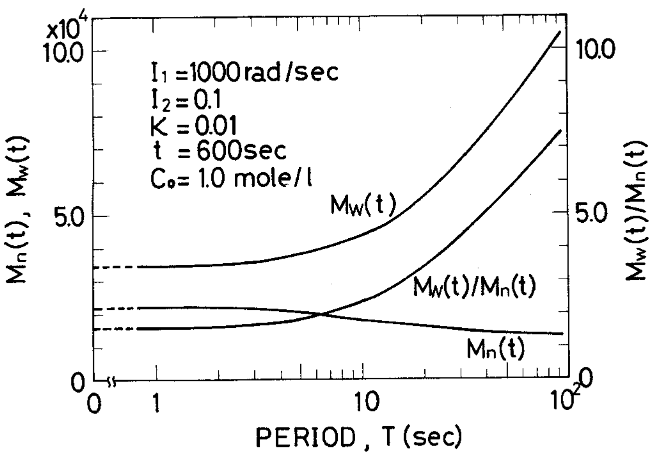

Fig. 8. $\overline{Mn}$, $\overline{Mw}$ and $\overline{Mw}/\overline{Mn}$ vs. T.

Influence of Agitation on Molecular Weight Distribution of Polymer

The molecular weight distribution curves are calculated according to Equations (48) and (49) and are shown in Figures 9 to 11.

An outstanding effect of the agitation is shown in Figure 9. At high speeds of agitation a unimodal distribution curve is obtained which coincides with the curve for the polymer produced by the uniform irradiation at the average dose rate $\bar{I}$. As the period of fluid circulation increases, another peak with lower molecular weight appears and increases in height. This is accompanied by the shift of the original peak to higher molecular weights with a corresponding decrease in its relative height. In the extreme case of the static system, the position of the two peaks coincides with those of polymer independently formed under the uniform irradiation of two dose rates I_1 and I_2. The unimodal distribution indicates that the radicals are completely dispersed within their life time uniformly throughout the two reaction zones as in the uniform irradiation case. As the agitation speed decreases, the nonuniformity of the radical concentration increases and the reactions in regions I and II take place more independently. Each peak of the bimodal distribution reflects the polymerizations in the two regions.

In Figure 10 the molecular weight distribution curves for the polymers formed instantaneously at different reaction times are shown together with the distribution curve found in the total amount of polymer formed in 600 seconds. It can be seen that the peak of the low molecular

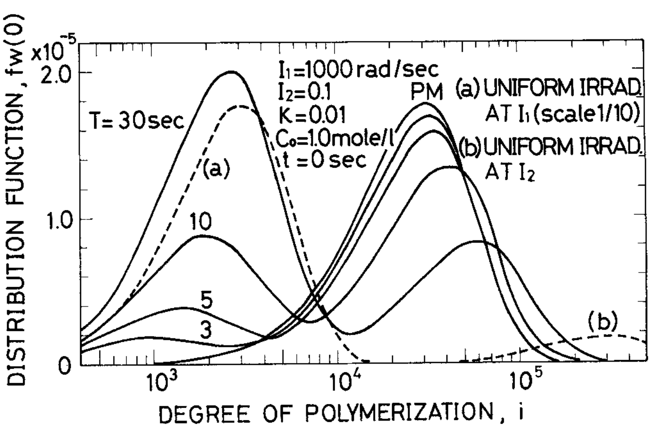

Fig. 9. Effect of agitation on molecular weight distribution.

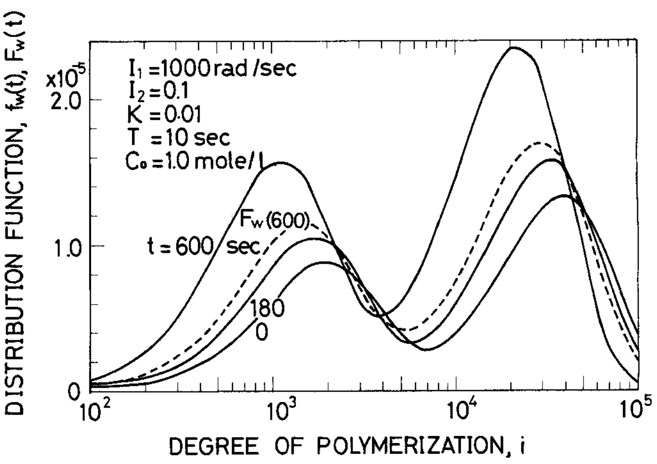

Fig. 10. Change of molecular weight distribution with reaction time.

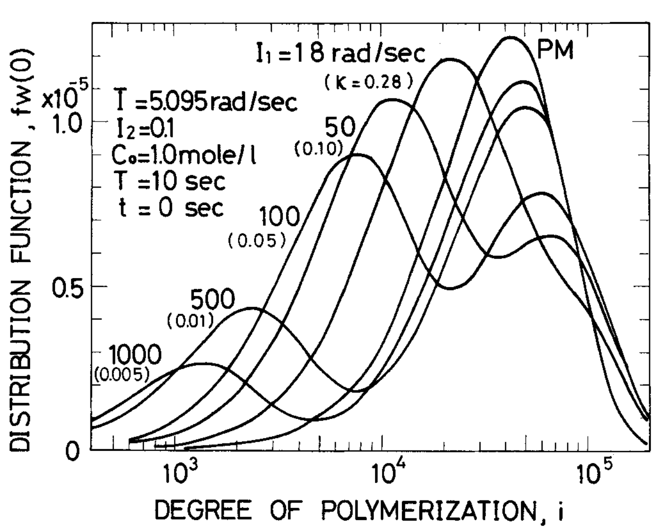

Fig. 11. Effect of dose rate distribution on molecular weight distribution at constant absorbed energy.

weight fraction increases and the bimodal distribution becomes more pronounced as the reaction proceeds. Both peaks shift in the lower molecular weight direction with increasing reaction time because of the decrease in monomer concentration.

At a constant period of the circulation and at constant absorbed energy the molecular weight distribution curve is affected by dose rate and κ. As shown in Figure 11, the distribution curve becomes unimodal when the dose rate in region I becomes very large or very small.

As described above, a bimodal molecular weight distribution was obtained at lower agitation speed under a steplike distribution of dose rate, whereas a unimodal distribution was obtained with exponential attenuation even in nonmixing state (Chen and Hill, 1971). These results show the nonuniformity of dose rate distribution in reactor as well as mixing conditions has an important effect on product distributions.

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NOTATION

C_0 = initial concentration of monomer, mole/l
C_1, C_2 = concentration of monomer in regions I and II, mole/l
D = diameter of impeller, cm
E = defined by Equation (19), 1/s
F = defined by Equation (20), $1/s^2$
$F_w(t)$ = weight distribution function as defined by Equation (49)
f = coefficient of impeller discharge
$f_w(t)$ = weight distribution function as defined by Equation (48)
g_1, g_2 = defined by Equations (21) and (23), mole/l
h_1, h_2 = defined by Equations (22) and (24), mole/l
$\bar{I}$ = average dose rate in reactor, rad/s
I_1, I_2 = dose rate in regions I and II, rad/s
K = $\Psi_M[M] + \Psi_S[S]$, mole/(l)(rad)
k_c, k_d, k_p, k'_{t1} = rate constants of recombination, disproportionation, propagation, and first-order termination reaction, l/(mole)(s)
k_{t1} = apparent rate constant of first-order termination, 1/s
k_{t2} = $k_c + k_d$, l/(mole)(s)
l_t = life time of radical at perfect mixing, s
M = monomer
$M_n(t)$, $M_w(t)$ = number average and weight average molecular weight as defined by Equations (46) and (47)
m = concentration of all radicals in region II, mole/l
m_0 = defined by Equation (28), mole/l
m_i = concentration of active i-mer in region II, mole/l
m_s = defined by Equation (56), mole/l
$m_n(t)$, $m_w(t)$ = number average and weight average molecular weight as defined by Equations (44) and (45)
N = stirring speed, rev./s
n = concentration of all radicals in region I, mole/l
n_0 = defined by Equation (27), mole/l
n_i = concentration of active i-mer in region I, mole/l
n_s = defined by Equation (55), mole/l
$\bar{n}$ = defined by Equation (54), mole/l
P_i = dead i-mer or its concentration, mole/l
Q = circulation flow rate in reactor, ml/s
$R_i\cdot$ = active i-mer
S = solvent or its concentration, mole/l
T = period of circulation, s
T_p, T_ϵ = period required for perfect mixing and or to achieve index ϵ, s
U_1, U_2 = defined by Equations (35) and (37), mole/l
V = reactor volume, ml
V_1, V_2 = defined by Equations (36) and (38), mole/l
W = defined by Equation (39)
$X(t)$ = rate of polymerization, mole of monomer/(l)(s)
X, Y = defined by Equations (40) and (41)
Z = substance to which radicals transfer their activities

Greek Letters

γ, δ = defined by Equations (17) and (18), 1/s
ϵ = index measuring average rate of polymerization relative to rates at mixing extremes. See Equation (50). At no mixing ($T \rightarrow \infty$), $\epsilon = 0$. At perfect mixing ($T \rightarrow 0$), $\epsilon = 1$
ϕ = defined by Equation (59)
Ψ_M, Ψ_S = coefficient including G-values of radical formation from monomer and solvent, 1/rad
κ = volume fraction of region I
τ_1, τ_2 = residence times in regions I and II

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