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Photopolymerization in an Isothermal and Continuous Stirred Tank Reactor: Concentration Stability

An investigation of photopolymerization in an isothermal and continuous stirred tank reactor (CSTR) was made. The existence of multiple steady states induced by gel effects was demonstrated theoretically and experimentally. This multiple steady state problem is presented in relation to reactor stability and control. Also, the relative behavior of the batch and CSTR systems is discussed.

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SCOPE

Initiation of chemical reactions by absorption of radiation (ultraviolet or ionizing) is characterized by essentially complete lack of temperature dependence, and by physical separation of the source of the initiating agent from the reaction medium. Thus, in the case of radiation initiation, the rate of initiation may be changed very rapidly. This consequence may lead to greater reactor stability and greater ease of reactor control. This would result in less frequent instances of runaway reactions and explosive decompositions or elimination of these events altogether.

A number of studies of the design and analysis of photochemical reactors have appeared in the literature during the past ten years, with outstanding contributions in this area being made by J. M. Smith and J. S. Dranoff and their co-workers. But very little work has been done on the engineering aspect of photopolymerizations (Yemin and Hill, 1969; Jain et al., 1970; Chen and Hill, 1971; Sandru and Smith, 1973; Ibarra and Smith, 1974; Mendiratta et al., 1975; Chen and Steenrod, 1975), in part because of incomplete exploration of their characteristics and advantages.

Temperature stability of the polymerization reactor has been studied theoretically by Hoftyzer and Zwietering (1961), and Warden and Amundson (1962). Both studies were concerned with the mode of chemical initiation and concluded that, with certain modes of control, it was indeed feasible to control at certain of the metastable points. Knorr and O'Driscoll (1970) has mathematically demonstrated that there is a possibility of the existence of multiple steady states induced by viscosity effects in isothermal CSTR.

Recently, Chen and his co-workers (1980a and 1980b) have theoretically and experimentally examined the feasibility of operating a CSTR for the addition polymerization in the thermal metastable region. It has been shown that the use of ultraviolet light as a generator of free radicals offers a significant improvement in the control of polymerizations. Furthermore, the polymer formed at the metastable state has a higher number average chain length and narrower molecular weight distribution (low polydispersity) than that obtained at the low stable state. In addition, photochemical initiation has a positive temperature coefficient of the degree of polymerization, which is in contrast with the results found for the thermal chemical initiation. In this paper, the photopolymerization is an isothermal CSTR is experimentally and theoretically investigated. Emphasis is placed on steady-state multiplicity, stability, and controllability of the reaction system.

CONCLUSIONS AND SIGNIFICANCE

The photopolymerization of styrene in an isothermal and continuous stirred tank reactor was investigated. Conversion, molecular weight averages, and molecular weight distribution at the temperature of 338°K and up to 70% conversion were measured. Three steady states are found to exist if the gel effects become pronounced.

The reactor performance characteristics in terms of fractional conversion and number of average chain lengths are presented. There are three possible regions of operation: low stable (Region I), metastable (Region II) and high stable (Region III). Operation in Region III may be discounted for bulk polymerization because of very high viscosity. With regard to Regions I and II,

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the obvious advantage of operation in the metastable one is the significantly higher conversion and molecular weight attainable for the same residence time. Furthermore, it is experimentally shown that in the metastable region, conversion and polymer molecular weight are greater, and the reaction time for a given level of conversion is less than the equivalent batch reactor.

The stabilization of the metastable state in an isothermal CSTR has also been examined. The photochemical reactor exhibits accurate control of conversion and molecular weight for a simple on-off regulation of light intensity.

REACTION MECHANISM

The reaction is free radical addition polymerization of styrene in bulk. The initiation mechanism is photochemical decomposition of the sensitizer by UV light accompanied by thermal decomposition of the monomer. Not considered are other possible mechanisms, such as, thermal decomposition of the sensitizer or UV light induced initiation by the monomer. The chain reaction mechanism may be written as follows:

(a) Initiation

by absorption of UV light by sensitizer

Rate Equation

$$s \xrightarrow{I_{as}} 2s\cdot$$

$$s\cdot + M \rightarrow R_1\cdot \qquad \Omega_{is} = 2\phi_s I_{as} \qquad (1a)$$

by thermal decomposition of monomer

$$M \xrightarrow{k_{im}} R_1\cdot \qquad \Omega_{im} = 2k_{im}m^3 \qquad (1b)$$

(b) Propagation

$$R_j\cdot + M \xrightarrow{k_p} R_{j+1}\cdot \qquad \Omega_p = k_p r m \qquad (2)$$

(c) Chain Transfer to the Monomer

$$R_j\cdot + M \xrightarrow{k_f} P_j + R_1\cdot \qquad \Omega_f = k_f r m \qquad (3)$$

(d) Termination

by combination

$$R_i\cdot + R_j\cdot \xrightarrow{k_{tc}} P_{i+j} \qquad \Omega_{tc} = k_{tc} r^2 \qquad (4a)$$

by disproportionation

$$R_i\cdot + R_j\cdot \xrightarrow{k_{td}} P_i + P_j \qquad \Omega_{td} = k_{td} r^2 \qquad (4b)$$

where $r = \Sigma r_i$ = total active polymer concentration. By application of the stationary state approximation, the rates of formation and destruction of free radicals are equal:

$$\Omega_i = k_t r^2$$

where

$$k_t = k_{tc} + k_{td}, \; \Omega_i = \Omega_{is} + \Omega_{im}$$

and

$$r = (\Omega_i/k_t)^{1/2} \qquad (5)$$

then the rate of monomer consumption is given by

$$\Omega_m = k_p(\Omega_i/k_t)^{1/2} m \qquad (6)$$

The kinetic data due to "gel effect" is based on the work of Hui and Hamielec (1972). The gel effect in polymer reactions is due to a decrease in the mobility of long-chain radicals with increasing viscosity and that as a result the termination reaction, being diffusion controlled at that stage, will be reduced. The rate of the propagation reaction, which involves only one large radical, will be less affected, hence the net result will be a progressive increase in the rate of polymerization.

THEORY

Reactor Equations

The isothermal CSTR is assumed to be perfectly mixed and fully illuminated. If I_o is the flux of light incident upon the reactor, the total rate of light absorbed by the sensitizer is

$$I_{as} = I_o \left[\frac{\epsilon_S S}{\epsilon_S S + \epsilon_m m + \sum \epsilon_{P_i} P_i}\right] \times \left[\frac{1\text{-}\exp[-(\epsilon_S S + \epsilon_m m + \sum \epsilon_{p_i} p_i)L]}{L}\right] \qquad (7a)$$

Assumptions employed in the use of Eq. 7a are: axial nonuniformities due to light attenuation are negligible, the rates of reaction are uniform throughout the reactor. If the monomer conversion is small (i.e., $\epsilon_S S + \epsilon_m m \gg \Sigma \epsilon_{p_i} p_i$), Eq. 7a becomes (Mendiratta et al., 1975),

$$I_{as} = I_o \left[\frac{\epsilon_s s}{\epsilon_s s + \epsilon_m m}\right] \left[\frac{1 - \exp[-(\epsilon_s s + \epsilon_m m)L]}{L}\right] \qquad (7b)$$

For this work, it is assumed that the fraction of light absorbed by the monomer and the polymer is constant (i.e., $\epsilon_m m_o = \epsilon_m m + \Sigma \epsilon_{p_i} p_i$),

$$I_{as} = I_o \left[\frac{\epsilon_s s}{\epsilon_s s + \epsilon_m m_o}\right] \left[\frac{1 - \exp[-(\epsilon_s s + \epsilon_m m_o)L]}{L}\right] \qquad (7)$$

A considerable volume change is involved in the styrene polymerization. A linear relationship of volume versus the conversion of monomer will be used (Hui and Hamielec, 1972), i.e.

volumetric flow rate for the inlet
stream $= q$

volumetric flow rate for the outlet
stream $= q(1 + EX)$

where E is defined as the fractional change in volume of the system between zero and complete conversion, and conversion X, is defined as the fractional weight of monomer converted.

$$X = \frac{m_o q - mq(1 + EX)}{m_o q}$$

or

$$X = \frac{m_o - m}{m_o + mE} \qquad (10)$$

The material balance equations for the reactor are:

For sensitizer:

$$\frac{ds}{dt} = -\phi_s I_{as} + \frac{s_o - s\,(1 + EX)}{\theta} \qquad (11)$$

For monomer:

$$\frac{dm}{dt} = \frac{m_o - m(1 + EX)}{\theta} - \Omega_m$$

$$= \frac{m_o - m(1 + EX)}{\theta} - \Omega_i^{1/2}\, m \left(\frac{k_p^2}{k_t}\right)^{1/2} \qquad (12)$$

where $(k_p^2/k_t)^{1/2}$ is allowed to vary with conversion as follows (Hui and Hamielec, 1972)

$$\left(\frac{k_p}{k_t^{1/2}}\right) - \left(\frac{k_p}{k_t^{1/2}}\right)_o \exp(A_1 X + A_2 X^2 + A_3 X^3) \qquad (13)$$

The subscript o means value at zero conversion, and A_1, A_2 and A_3 and $(k_p/k_t^{1/2})_o$ are independent of conversion X for any temperature and are shown in Table 1. Thus, Eq. 12 may be written as,

Table 1. Model Parameters (Hui & Hamielec, 1972; Mendiratta et al., 1975)

$\epsilon(\text{styrene}) = 1.55\ \text{m}^3/\text{kg-mol}\cdot\text{m}$

$\epsilon(\text{BME}) = 88.5 \times 10^2\ \text{m}^3/\text{kg-mol}\cdot\text{m}$

$\phi_s = 1.2 \times 10^{-5}$ kg-mol/Eins.

$E = -0.173$ at 338°K

$m_o = 8.31\ \text{kg-mol/m}^3$

$(k_p)_o = 1.051 \times 10^7 \exp(-3557/T)$, $\text{m}^3/(\text{kg-mol})\cdot\text{s}$

$(k_f)_o = 2.31 \times 10^6 \exp(-6377/T)$, $\text{m}^3/(\text{kg-mol})\cdot\text{s}$

$(k_t)_o = 1.255 \times 10^9 \exp(-844/T)$, $\text{m}^3/(\text{kg-mol})\cdot\text{s}$

$k_{tm} = 2.19 \times 10^5 \exp(-13{,}810/T)$, $\text{m}^6/(\text{kg-mol})^2\cdot\text{s}$

$A_1 = 2.57 - 5.05 \times 10^{-3}\, T$

$A_2 = 9.56 - 1.76 \times 10^{-2}\, T$

$A_3 = -3.03 + 7.85 \times 10^{-3}\, T$

$B_1 = -1.013 \times 10^{-3} \text{Log}_{10} \dfrac{473.12 - T}{202.5}$

$$\frac{dm}{dt} = \frac{m_o - m(1 + EX)}{\theta} - \Omega_i^{1/2}\, m \left(\frac{k_p^2}{k_t}\right)_0^{1/2} \times \exp[A_1X + A_2X^2 + A_3X^3] \quad (14)$$

The number and weight average chain lengths are defined as

$$\overline{X}_n = \frac{\Sigma i p_i}{\Sigma p_i} \quad (15)$$

$$\overline{X}_w = \frac{\Sigma i^2 p_i}{\Sigma i p_i} \quad (16)$$

where Σp_i, $\Sigma i p_i$ and $\Sigma i^2 \text{p}_\text{i}$ are, respectively, the zero-th, first and second moments of the dead polymer size distribution in the outlet stream, and can be expressed as (Chen and Hill, 1971):

$$\frac{d\Sigma p_i}{dt} = -\frac{\Sigma p_i(1 + EX)}{\theta} + \left(k_{td} + \frac{1}{2}k_{tc}\right)\left(\frac{\Omega_i}{k_t}\right) + \frac{k_f}{k_p}\, m\, \Omega_i^{1/2}\left[\frac{k_p}{k_t^{1/2}}\right] \quad (17)$$

$$\frac{d\,\Sigma i p_i}{dt} = -\frac{\Sigma i p_i(1 + EX)}{\theta} + \left(\frac{k_p}{k_t^{1/2}}\right) m\, \Omega_i^{1/2} \quad (18)$$

and

$$\frac{d\Sigma i^2 p_i}{dt} = -\frac{\Sigma i^2 p_i(1 + EX)}{\theta} + \left[\frac{m\, \Omega_i^{1/2}}{\frac{k_t^{1/2}}{k_p}\Omega_i^{1/2} + \frac{k_f}{k_p} m}\right]^2 \left(\frac{k_{tc}}{k_t}\right) + \frac{2m^2\Omega_i^{1/2}\,(k_p/k_t^{1/2})}{\frac{k_t^{1/2}}{k_p}\,\Omega_i^{1/2} + \frac{k_f}{k_p} m} + \left(\frac{k_p}{k_t^{1/2}}\right) m\, \Omega_i^{1/2} \quad (19)$$

where (Hui and Hamielec, 1972; also Table 1):

$$\frac{k_f}{k_p} = \left(\frac{k_f}{k_p}\right)_o + B_1 X \quad (20)$$

Multiple Steady State

By setting the left hand side of Eq. 14 equal to zero, one can determine the possible steady state points for the operation of the reactor. The general method of solution is to separate Eq. 14 into two terms, Mass Supply Rate (MSR) and Mass Consumption Rate (MCR):

$$\text{MSR} = \frac{m_o - m(1 + EX)}{\theta} = \frac{m_o X}{\theta} \quad (21)$$

$$\text{MCR} = \Omega_i^{1/2} \frac{m_o(1 - X)}{1 + EX}\left(\frac{k_p^2}{k_t}\right)_o^{1/2} \exp(A_1X + A_2X^2 + A_3X^3] \quad (22)$$

where the initiation rate, Ω_i can be calculated by Eqs. 1a, 1b, 5 and 7 along with Eq. 11 (by setting $ds/dt = 0$).

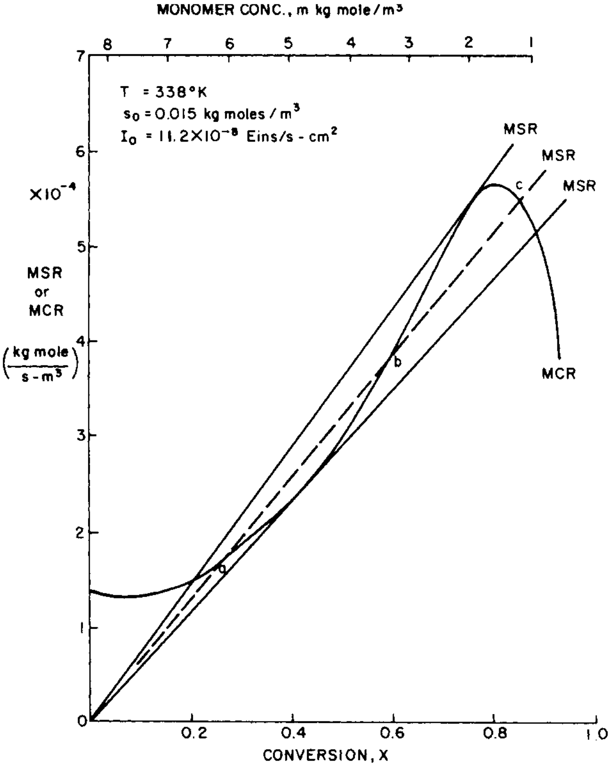

Figure 1. MSR and MCR vs. *X* or *m*.

Figure 1 shows typical solutions obtained for styrene polymerization. At steady state MSR should be equal to MCR. The MSR is a linear function of X with a slope of m_o/θ. The existence of the two steady states shown in the figure requires the supply and consumption curves be tangent at one point, a physically unlikely situation. More likely is the occurrence of one or three steady states. When three steady states (a, b, c) are found, the central one (b) is metastable. At this state, a decrease in X results in less mass consumption, and the monomer concentration m increases (or X decreases) until it reaches the lower steady state (a). On the other hand, if the X is increased (or m is decreased) from the metastable steady state value, MCR > MSR, and the mass continues to fall (or X continues to increase) until the upper steady state (c) is reached. A detailed discussion on multiplicity and uniqueness criteria can be found elsewhere (Chen et al., 1981).

It should be pointed out that a plot similar to Figure 1 was also obtained by Knorr and O'Driscoll (1970). However, they were concerned with thermal chemical initiation, and the results presented here are based on photochemical initiation.

Reactor Performance Characteristics

Figure 2 shows the calculated results representing the reactor performance characteristics in terms of fraction conversion X, and number average chain length, $\overline{X}_n$. Note that there are three regions in Figure 2: the curve a-b (Region I, low stable), curve b-c (Region II, metastable) and curve c-d (Region III, high stable). Operation in Region III may be discounted for the bulk polymerization because of high viscosity. With regard to Region I and II, the obvious advantage of operation in the metastable region is the significantly higher conversion and molecular weight attainable for the same residence time. While the reactor is operated in Region I, an increase in θ (residence time) at a fixed I_o results in an increase in $\overline{X}_n$ (chain length) and X. The converse is true for Region II. Also, an increase in I_o would shift the Characteristic curves to lower residence time, however, the sensitizer concentration, s_o has no appreciable effect on the curves. Note that all the region II steady-states are inherently unstable, and that the reactor will only operate there by forcing it to with appropriate control.

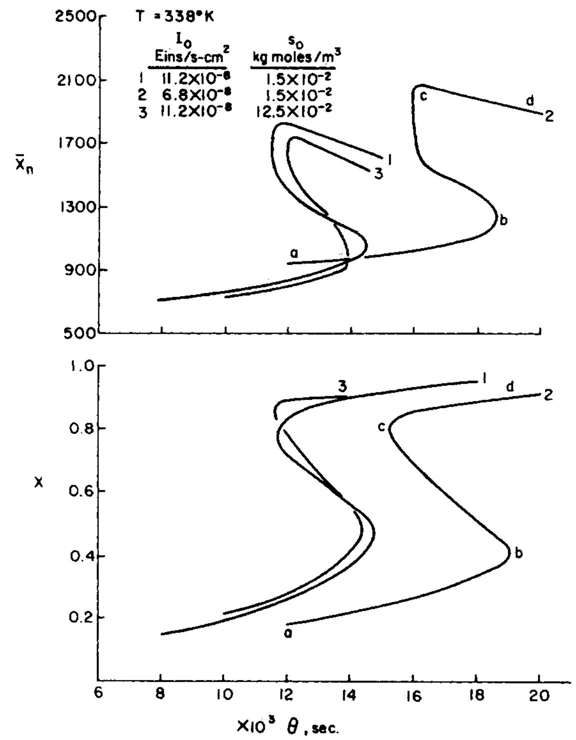

Figure 2. Reactor performance characteristics—calculated results.

The striped bands shown in Figure 3 are metastable regions. As I_0 decreases, the band becomes larger. For a given I_0, when the couple of θ and T falls into the band, the reaction conditions have three steady states, two of which are stable and another unstable one. A decrease in T results in a greater possibility of existence of multiple steady states induced by gel effects.

EXPERIMENTAL

Photopolymerization of styrene with initiation by photodissociation of sensitizer (BME) accompanied by thermal decomposition of the monomer was carried out isothermally at 338°K in a stirred baffled stainless steel vessel (0.07 m ID × 0.06 m height). The feed was prepared by passing styrene through a column packed with activated alumina to remove the inhibitor, followed by passage through a column packed with silica gel to remove moisture. Conversions were determined by UV spectrophotometry and also by the gravimetric technique (Boundy and Boyer, 1952). The molecular weight distribution was measured via a gel permeation chromatography manufactured by Water Associates. Measurement of incident light intensity was made by means of the potassium ferrioxalate actinometer (Hatchard and Parker, 1956).

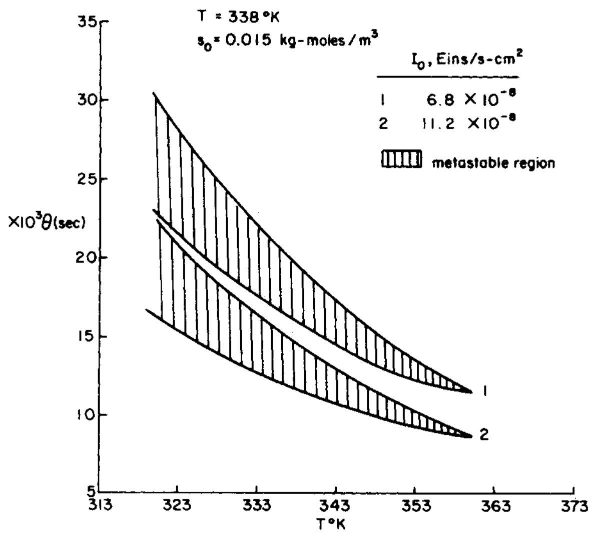

Figure 3. Metastable regions.

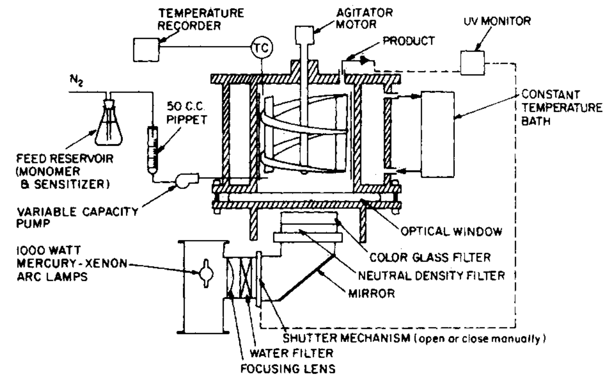

Figure 4. Arrangement of experimental apparatus.

Apparatus

The experimental apparatus similar to that used previously (Chen et al., 1980b) is shown in Figure 4. The reaction vessel was maintained at a constant temperature of 338°K by the use of a constant temperature bath which circulated water in the jacket.

The optical system provides a parallel ultraviolet beam. A 1000 W Mercury Xenon arc lamp is housed in an air-cooled lamp housing and supplied with power by a regulated D.C. power supply. A focusing lens mounted in the housing collects the light and produces a collimated beam which passes through a water filter. The filter beam is reflected upward by a mirror, and passes through neutral density filters to improve its cross-sectional uniformity and then through a color glass filter which transmits light with a wave length of 310 to 420 nm.

Low and Meta-Stable Steady States

Conversions of metastable states have been obtained by observing the effect of perturbation from stable conversions. Figure 5 shows a typical approach. The conversion is raised to the pre-

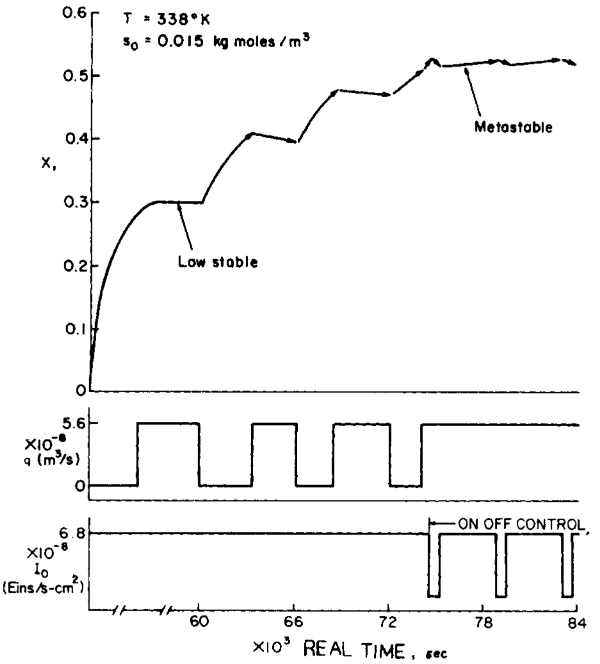

Figure 5. Transient responses to perturbation from stable conversion.

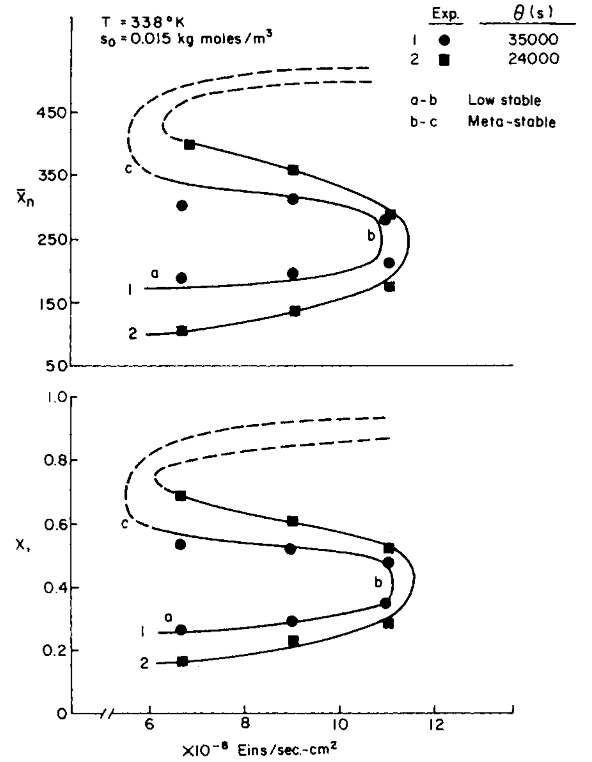

Figure 6. Reactor performance characteristics—experimental results.

dicted low stable steady state by means of the batch operation (i.e., $q = 0$). The reactor is then operated continuously with $q = 5.6 \times 10^{-8}$ m³/s, and reaction is permitted to find its real steady state. Once at the steady state, reaction conditions are maintained for a time period of approximately one residence time. The conversion is then raised to the predicted metastable state by means of the batch operation. A decrease in conversion following the continuous operation indicates undershoot below the metastable point and the conversion is raised by the batch operation. Similarly, an increase in conversion indicates overshoot beyond the metastable point and the shutter is closed to lower the conversion. By means of this step-wise procedure, the metastable point is reached. Figure 6 shows the experimental results (low and meta-stable regions), representing the reactor characteristics in terms of fraction conversion and number average chain length.

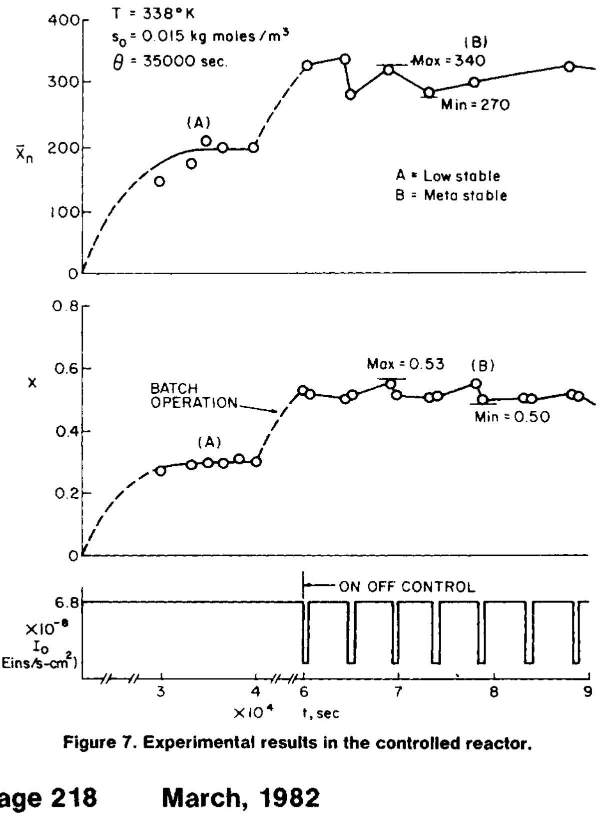

Figure 7. Experimental results in the controlled reactor.

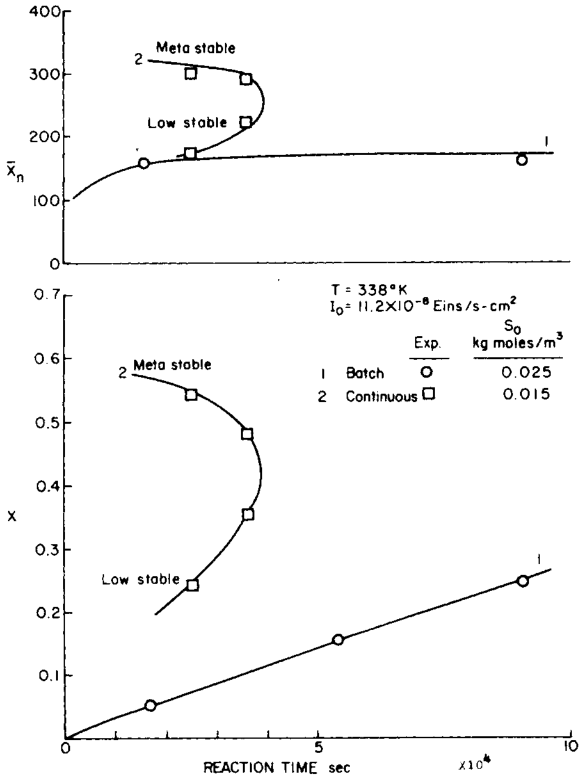

Figure 8. Comparison of experimental data between continuous and batch systems.

The Control System

Experimental study has been carried on the reactor control by on-off regulation of the light intensity. The on-off operation is obtained through a shutter mechanism. This is deemed most suitable for a UV lamp which for proper operation must be maintained at constant output. At a given time interval (approximately 600 s) samples were taken from the product streams and analyzed by UV spectrophotometry (with $\lambda = 258\ \mu$m) to determine the styrene concentration, m. If $m > m_{sp} + db$ (m_{sp} = desired concentration, db = dead band), the shutter was closed manually, and vice versa. Conversion was readily controlled with 0.015 below or above the set point. The instantaneous number average chain length varied with the range from 262 to 340. Also, the polymer formed at the metastable state has a higher average chain length than that obtained at the low stable state (Figure 7).

Continuous and Batch Systems

Figure 8 illustrates the relative behavior of the continuous and batch systems. The reaction time or holding time (to reach a given level of conversion) for a-continuous reactor is much less than that for the equivalent batch reactor. In addition, for a given holding time conversion in the metastable region is much greater than that in the lower stable region. With respect to $\bar{X}_n$ in the metastable region, the continuous reactor is clearly superior to the equivalent batch reactor. In the low stable region, the continuous and batch systems give nearly identical results.

We have made an experimental study of photopolymerization of styrene at high conversions in an isothermal CSTR, and have developed models based on the assumption that the reactor is perfectly mixed. By comparing Figures 2 and 6, one may see that the calculated values of X and $\bar{X}_n$ are higher than those obtained experimentally. A detailed discussion on this, and the effects of mixing on the concentration stability will be presented in later publications.

SUMMARY

1. We have mathematically and experimentally demonstrated that in an isothermal and continuous stirred tank reactor, when used to conduct radiation-induced polymerization, there is a clear possibility of the existence of multiple steady states due to gel effects.
2. An experimental technique has been developed to determine meta-stable state conversions. Molecular weight averages and molecular weight distributions up to conversion 70% were measured. To our best knowledge, all of the work on photopolymerizations thus far are limited to low conversions.
3. We have shown experimentally that in the meta-stable region, conversion and polymer molecular weight are greater, and the reaction time for a given level of conversion is less than the equivalent batch reactor. Also, the photochemical reactor exhibits accurate control of conversion and molecular weight for a simple on-off regulation of light intensity.
4. The concentration stability presented in this paper offers fundamental knowledge for the design, simulation and optimization of photopolymerization reactors.

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NOTATION

E = fractional change in volume between zero and complete conversion, dimensionless
k_p, k_f, k_{tc}, k_{td} = reaction rate constant for initiation, propagation, chain transfer to monomer, termination by combination and termination by disproportionation, respectively, $m^3/kg \cdot mol \cdot s$
k_{tm} = reaction rate constant for thermal initiation, $m^6/(kg \cdot mol)^2 \cdot s$
L = depth of reaction vessel, m
I_o = incident light itensity, $Einstein/cm^2 \cdot s$
I_{as} = absorbed light intensity, $Einstein/cm^3 \cdot s$
m_0, m = monomer concentration in feed and in reaction mixture, respectively, $kg \cdot mol/m^3$
p_j = concentration of dead polymer of chain length j monomer units, $kg \cdot mol/m^3$
r_j = concentration of free radicals of chain length j monomer units, $kg \cdot mol/m^3$
r = total concentration of free radicals, $kg \cdot mol/m^3$
s_o, s = concentration of sensitizer in feed and in feed mixture, respectively, $kg \cdot mol/m^3$
T = temperature, °K
t = time, s
V = reaction volume, m^3
X = fractional conversion defined by Eq. 10, dimensionless
$\overline{X}_n$ = number average chain length, dimensionless
$\overline{X}_w$ = weight average chain length, dimensionless

Greek Letters

θ = V/q, s
$\epsilon_s, \epsilon_m, \epsilon_{pi}$ = molar absorptivity of sensitizer, monomer and polymer with i monomer units, respectively, $m^3/kg \cdot mol \cdot m$
ϕ_s = quantum yield of sensitizer, kg·mol/Einstein
$\Omega_i, \Omega_p, \Omega_f, \Omega_{tc}, \Omega_{td}, \Omega_m$ = rate of reaction for initiation, propagation, chain transfer to monomer, termination by combination, termination by disproportionation and monomer consumption, respectively, $kg \cdot mol/m^3 \cdot s$
Ω_{is} = rate of reaction for photoinitiation, $kg \cdot mol/cm^3 \cdot s$

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