from $t=0$. However, for k_2 the standard deviation at $t_0=0$ is as high as at $t_0=34 \times 10^{-4}$ and passes through a minimum at $t_0 = 11.32 \times 10^{-4}$. The selection of the initial state in this case should come as a trade off between gains in the reliability of k_2 and losses for k_1. It appears that a good compromise is obtained when the starting point $t = 11.32 \times 10^{-4}$ is used.

SUMMARY

Quasilinearization algorithm was applied to a typical chemical engineering parameter estimation problem. Using only portions of the data length during the early iterations, as proposed by Wang and Luus (1978), the size of the region of convergence was significantly enlarged. Without the problem of having to have a good initial guess, quasilinearization becomes a very powerful tool for estimating parameters, since it possesses the property of very fast convergence rate and is easy to program.

Furthermore, the effect of using different sections of the data during the early iterations was demonstrated. Although a method to obtain the optimum section of the data is not proposed, the effect of using different starting points on the reliability of the estimated parameter values, during the early iterations, was illustrated.

NOTATION

e_i = random experimental error associated with state i
i = index relating to state variable
j = index relating to point in time
J = sum of squares of deviations performance index given by Equation (6)
k_1 = rate constant relating to first reaction (parameter to be determined)
k_2 = rate constant relating to second reaction (parameter to be determined)
n = number of state variables
p = number of parameters to be determined
r_1 = rate of first reaction given by Equation (3)
r_2 = rate of second reaction given by Equation (4)
R_{ij} = random numbers uniformly distributed between -1 and 1
t = residence time
x_1 = moles of benzene per mole of benzene feed
x_2 = moles of diphenyl per mole of benzene feed
y_i = recorded measurement of x_i
σ = maximum noise level
τ = data length used for parameter estimation

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Photopolymerization in a Continuous Stirred-Tank Reactor: Experiment

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Addition polymerizations are usually initiated through the use of catalysts. 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 ease 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 is usually strongly temperature dependent, and because the chemical initiator is in solution in the reaction medium, the initiation rate cannot be changed very quickly. 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 loss of production.

Polymerization processes 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, 1969; Jain et al., 1970; Chen and Hill, 1971; Hill and Chen, 1972; 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. Notice that a number of studies of the design and

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analysis of photochemical reactors have appeared in the literature during the past 10 yr, with outstanding contributions in this area being made by J. M. Smith and J. S. Dranoff and their co-workers.

For the type of reaction being investigated, that is, exothermic reaction, it is well known that several steady states may be obtained for the same feed conditions and that not all are naturally stable; that is, some states are metastable. The existence of this multiplicity of steady states has been demonstrated experimentally (Vejtasa and Schmitz, 1970; Ausikaitis and Engel, 1974; Guha et al., 1975; Chang and Schmitz, 1975) for the oxidation of aqueous sodium thiosulfate by hydrogen peroxide.

In polymerizations, certain of these metastable states offer increased conversion for the same residence time. Moreover, theoretical investigations have indicated that through the addition of controller action, stable operation may be obtainable in a continuous reactor. Among these investigations were those by Hoftyzer and Zwietering (1961) and by Warden and Amundson (1962) on thermal-catalytic initiation in a continuous reactor. Comparable work on the other modes of initiation has not been done, although the recent studies by Hashimoto et al. (1976*a*, *b*) indicate that a marked improvement in reactor response may be achieved through radiation dose rate regulation over that obtainable through the more conventional means of coolant flow rate regulation (as is done for thermal catalytic systems). No consideration was given to the enhancement of stability of the metastable state. To the best of our knowledge, no experimental analysis has ever been done on the stability and control of photopolymerizations.

The overall objectives of this paper are to demonstrate that in a continuous stirred-tank reactor, the use of ultraviolet light as a generator of free radicals offers a significant improvement in the control of polymerization reactions and to determine the effect on the molecular weight distribution of the polymer formed. Experimental measurements were undertaken to investigate steady state multiplicity, stability and controllability of reaction systems.

EXPERIMENTAL

Experimental investigation of the polymerizations of styrene with initiation by photodissociation of sensitizer (benzoin methyl ether) was made in a continuous stirred-tank reactor. The experimental apparatus is shown schematically in Figure 1. The reactor is a stirred baffled stainless steel vessel (7 cm ID and 6 cm height). The reactor volume is illuminated with a light beam through the bottom of the reactor. The reaction temperature is used to activate the controller which opens or closes the shutter. The controller has upper and lower set points, thereby providing a temperature dead band which may be varied. The reactor is also provided with a preheat coil and insulated with 40 mm fiberglass insulation covered by a polished aluminum jacket. The outside of the jacket is covered by an electrical heating tape which permits the jacket temperature to be maintained at approximately the same temperature as the reactor, thereby assuring adiabatic operation.

The optical system provides a parallel ultraviolet beam. A 1 000 W Mercury Xenon arc lamp is housed in an air cooled lamp housing and supplied with power by a regulated DC power supply. 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 passes through a water filter. The filtered 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 wavelength of 310 to 420 nm. An iris diaphragm located under the neutral density filters is used to provide nonuniform irradiation.

The feed is prepared by passing the monomer through a column packed with activated alumina to remove the inhibitor, followed by passage through a column packed with silica gel to remove moisture. The collection vessel is nitrogen blanketed, and nitrogen is bubbled through the monomer to remove oxygen. The sensitizer is added immediately before the start of run.

Measurement of incident light intensity is made by means of the potassium ferrioxalate actinometer as described by Hatchard and Parker (1956). Note that the incident light intensity can be varied by changing the number of neutral density filters or the opening of the iris diaphragm. Conversions are determined by the gravimetric technique presented by Boundy and Boyer (1952) which involves precipitating the polymer in an excess of methanol. The polymer is then dried in a vacuum oven to remove traces of the monomer. The molecular weight distribution is measured via gel permeation chromatography.

RESULTS AND DISCUSSION

Temperatures of metastable steady states have been obtained by observing the effect of perturbation from stable temperatures. Figure 2 shows a typical approach. The reaction temperature is raised to the predicted low stable steady state temperature by means of the preheat coil. Flow through the preheat coil is then stopped, 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 reaction temperature is then raised to the predicted metastable state by means of the preheat coil. A decrease in temperature following the cessation of preheat indicates undershoot below the metastable point, and the temperature is raised via

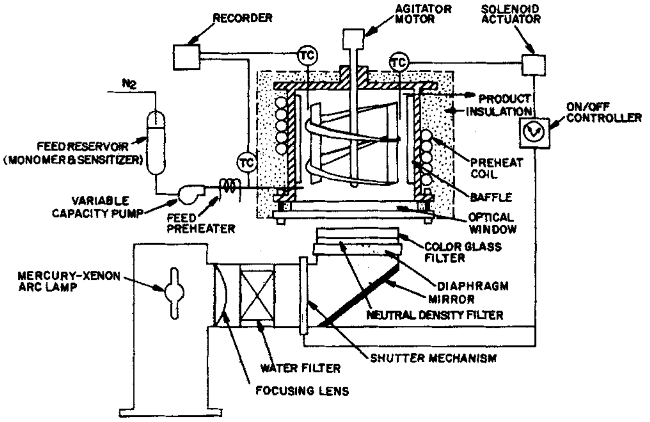

Figure 1. Arrangement of experimental apparatus.

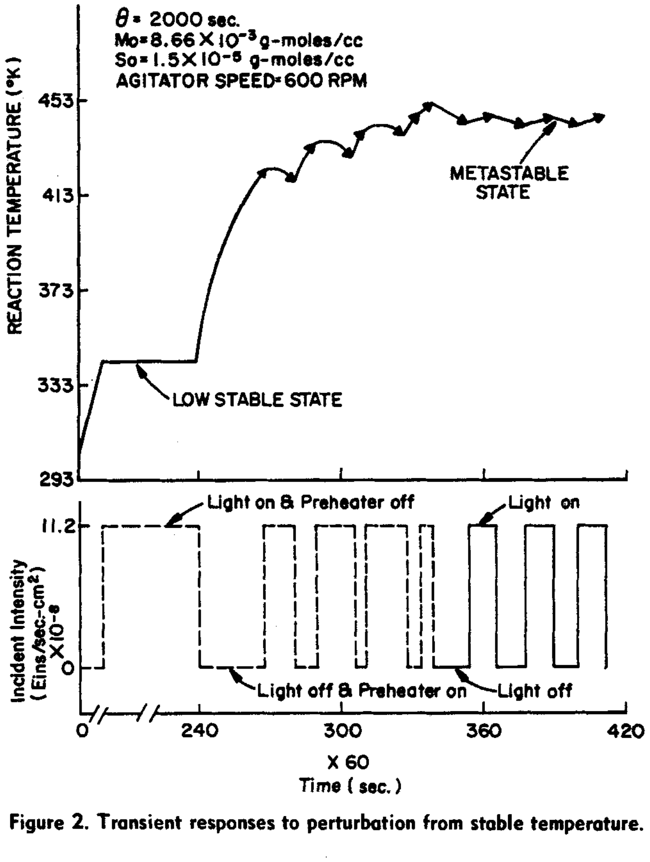

Figure 2. Transient responses to perturbation from stable temperature.

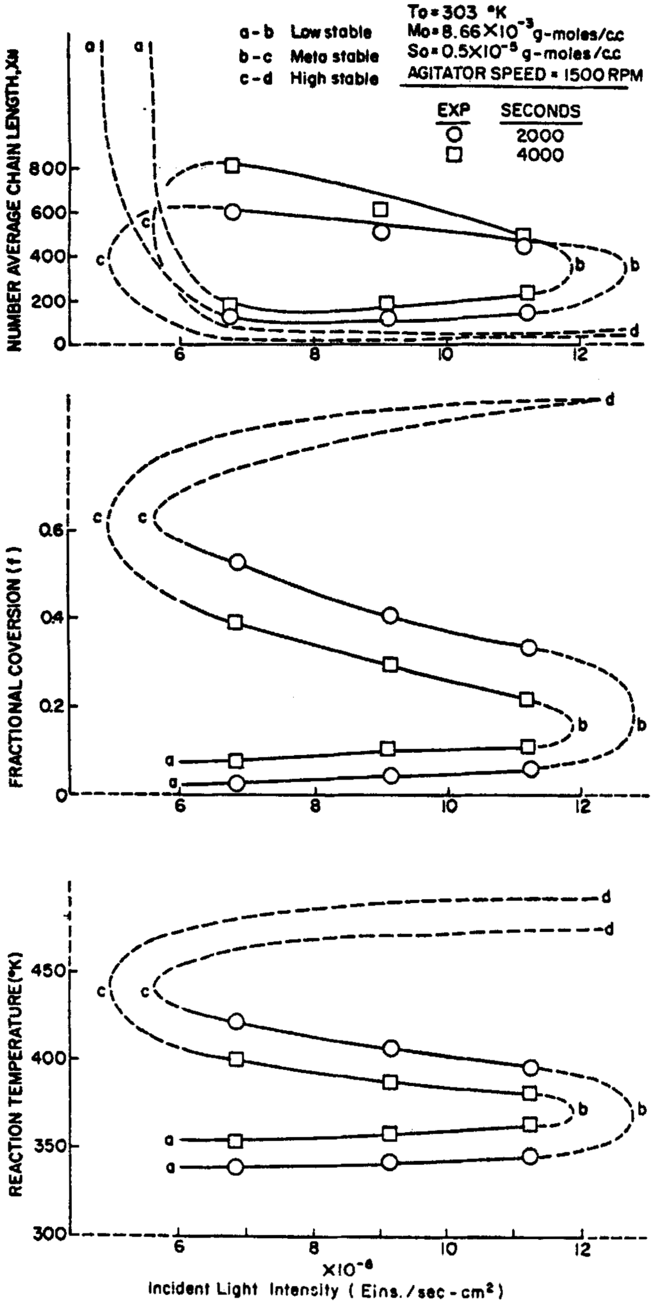

Figure 3. Steady states for photochemical initiation.

the preheat coil. Similarly, an increase in reaction temperature indicates overshoot beyond the metastable, and the shutter is closed to lower the reaction temperature. By means of this stepwise procedure, the metastable point is reached.

Figure 3 shows the experimental results representing the reactor performance characteristics in terms of fraction conversion, reaction temperature and number average chain length. The dotted lines are based on the hypothesis discussed in a paper by Chen et al. (1978). A more detailed discussion on this will be presented in subsequent papers. Note that there are three regions, the curves a-b (region I, low stable), curves b-c (region II, metastable) and curves c-d (region III, high stable).

Operation in region III may be discounted for the bulk polymerization because of very high temperature and low molecular weight. With regard to regions I and II, the obvious advantage of operation in the metastable region is the significant higher conversion attainable for the same residence time.

As shown in Figure 3, the influence of increasing the residence time (θ) from 2 000 to 4 000 s is to shift the temperature (or fraction conversion) curve towards the lower light intensity

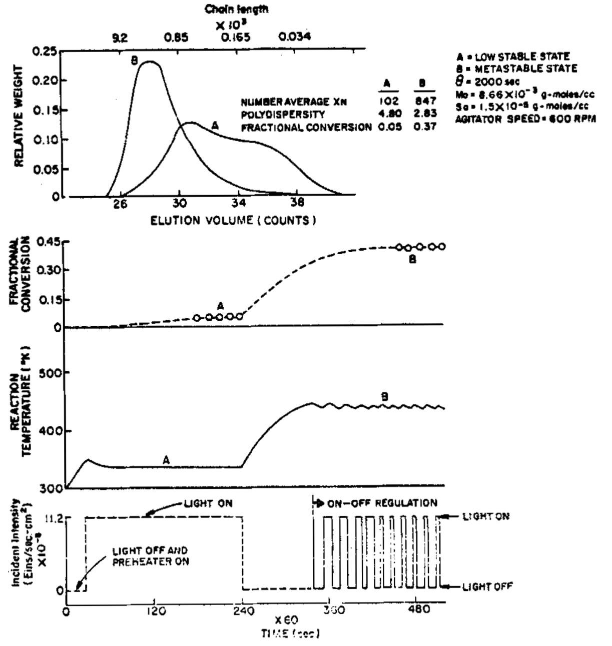

Figure 4. Experimental results for photosensitized polymerization in the controlled reactor.

to obtain the same temperature (or conversion). Also, for higher residence time the possibility of multiple steady states is lower.

The loop exhibited by the shape of the curve for number average chain length for the photochemical system is a consequence of the relative magnitudes of the rates for initiation, propagation and termination. The implication of this is that the photochemical reactor operated at the metastable region offers the advantage of high conversion without sacrifice of the product molecular weight. This is unique to the radiation initiated system. In addition, at the metastable region, an increase in θ at a fixed light intensity would result in increasing chain length.

The importance of setting the correct start-up condition for the reactor operation can be deduced from Figure 3. An incident light intensity (I_0) approximately above 13×10^{-8} Einstein/s cm^2 for $\theta = 2\ 000$ s would automatically bring the reactor to its higher steady state. The result is a substantial drop in the chain length. The opposite effects would follow for $I_0 < 5 \times 10^{-8}$, with almost zero conversions.

Experimental study has also been carried out on the reactor control by on-off regulation of the light intensity. The on-off operation with a dead band is obtained through a shutter mechanism (Figure 1). This is deemed the most suitable for a UV lamp which for proper operation must be maintained at a constant output. As shown in Figure 4, temperature is readily controlled with 2.5°K below or above the set point and responds quickly to the change in the light intensity. Furthermore, the polymer formed at the metastable state has a higher average chain length and narrower molecular weight distribution (low polydispersity) than that obtained at the low stable state. Thus, 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 (Chen et al., 1978).

ACKNOWLEDGMENT

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NOTATION

f = fraction conversion
I_0 = incident light intensity, Einstein/(cm^2)(s)
M_0 = monomer concentration in feed, g mole/cm^3
S_0 = sensitizer concentration in feed, g mole/cm^3

T_0 = temperature of feed, °K
T = reactor temperature, °K
X_N = number average chain length
θ = residence time, s

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Miscibility Limits for Salt Containing Systems

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Nonvolatile salts have been shown to influence phase equilibrium behavior (Long and McDevit, 1952; Johnson and Furter, 1957, 1960; Meranda and Furter, 1974), and considerable effort has been expended on developing models that are useful in correlating and predicting salt effects on phase equilibrium. Most of this effort, however, has been focused on vapor-liquid equilibria, with little work done on partially miscible systems. In this paper, a method for estimating miscibility limits of binary solvents will be presented. The procedure is an extension of the model proposed by Boone, Rousseau and Schoenborn (1976) and refined by Rousseau and Boone (1978) for correlating and predicting vapor-liquid equilibria in salt containing systems.

IMMISCIBILITY

A liquid solution will separate into two phases if the resultant free energy is less than that of the original mixture. For a binary system, the specific Gibbs free energy can be written in terms of the excess free energy as

$$g = g^E + g^{\text{ideal}} \tag{1}$$

where

$$g^{\text{ideal}} = x_1 g_1^{\text{pure}} + x_2 g_2^{\text{pure}} + RT(x_1 \ln x_1 + x_2 \ln x_2) \tag{2}$$

so that

$$g = g^E + x_1 g_1^{\text{pure}} + x_2 g_2^{\text{pure}} + RT(x_1 \ln x_1 + x_2 \ln x_2) \tag{3}$$

Recognizing that phase separation requires downward concavity of the function g, Prausnitz (1969) gives as a criterion for solution instability

$$\left(\frac{\partial^2 g}{\partial x_1^2}\right)_{T,\,P} < 0 \tag{4}$$

Recalling the definition of the excess Gibbs free energy

$$g^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \tag{5}$$

and activity

$$a_i = x_i \gamma_i \tag{6}$$

we can show that

$$g = RT(x_1 \ln a_1 + x_2 \ln a_2) + x_1 g_1^{\text{pure}} + x_2 g_2^{\text{pure}} \tag{7}$$

It then follows that the onset of solution instability occurs at the conditions

$$\left(\frac{\partial \ln a_1}{\partial x_1}\right)_{T,\,P} = 0 \tag{8}$$

and

$$\left(\frac{\partial^2 \ln a_1}{\partial x_1^2}\right)_{T,\,P} = 0 \tag{9}$$

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