

EXPERIMENTAL STUDY AND MODEL SIMULATION OF A TWO-STAGE CONTINUOUS POLYMERIZATION PROCESS FOR POLYSTYRENE

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Abstract—Free radical solution polymerization of styrene in two stage polymerization process has been studied using a binary mixture of symmetrical bifunctional initiators. The continuous reactor system was composed of two reactor units; a prepolymerization reactor (e.g. stirred tank reactors) and a filled tubular reactor packed with static mixers. When the stirred tank reactor was used as a prepolymerizer, a feed stream to the filled tubular reactor was more viscous than the monomer/solvent mixture. It was of interest to investigate how the performance of the filled tubular reactor has been investigated by the feed of viscous prepolymer solution. A dynamic model of the continuous two stage polymerization process was presented by experimental data and model simulation. A reasonably good agreement between the model and the experimental data was obtained without using any adjustable parameters. The experimental results of the two stage polymerization were compared with the results without prepolymerization reactor. It was found that the addition of a prepolymerization reactor has almost no effect on the performance of the filled tubular reactor.

Key words: Polystyrene, Bifunctional Initiators, Static Mixer

INTRODUCTION

Batch polymerization processes are widely used in the polymer industry for the production of various polymers in small-to-medium volume. Inherent advantages of batch polymerization processes include flexibility of reactor operation and low capital investment. However, drawbacks in batch operation are low reactor productivity and inconsistent batch-to-batch product quality variations. Moreover, batch stirred reactors are, in general, not suitable for high conversion bulk polymerization of vinyl monomers because of rapidly increasing viscosity of the polymerizing mixture.

It is well known that continuous polymerization processes offer many advantages over batch processes and that they are more suitable for the production of large volume commodity polymers. In continuous processes polymer quality control can be accomplished relatively more easily than batch processes. However, the design of reactor controls is not always easy. This is due partly to the complexity of the polymerization kinetics and nonlinear reactor behavior which are often poorly understood. A lack of on-line sensors for product quality measurements is another problem common in batch and continuous polymerization processes.

Continuous polymerization processes are used in the polymer industry for the production of a wide variety of polymers in solution, emulsion and bulk phases. Although reactor configurations may vary from process to process, the reactors employed in industrial continuous polymerization processes can be categorized broadly into the following: continuous stirred tank reactors (CSTR) including cascade of CSTRs, linear flow reactors (LFR), tubular reactors, and fluidized bed reactors (for transition metal catalyzed olefin polymerizations). The three most important criteria in selecting a specific reactor configuration are the nature of polymerization medium (e.g., homogeneous vs. heterogeneous, low viscosity vs. high viscosity, etc.), reactor productivity and operability,

and the controllability of polymer properties. In the following, a brief review of some important features of industrial continuous polymerization reactors is presented and some incentives for the filled reactor system studied in this work are discussed.

Continuous stirred tank reactors are used mostly for solution, emulsion and slurry polymerization in which the viscosity of the polymerization mixture is not very high. When stirred reactors used for bulk polymerization or for solution polymerization with a low solvent volume fraction, monomer conversion attainable is often limited to only about 20-30% due to high viscosity and poor heat transfer capability of the reaction mixture at higher conversions. There is a plethora of literature on the modeling of ideal continuous stirred tank polymerization reactors. These reactors may exhibit highly nonlinear steady state and dynamic behaviors as reported by many workers [Knorr and O'Driscoll, 1970; Jaisinghani and Ray, 1977; Hamer et al., 1981; Brooks, 1981; Schmidt and Ray, 1981; Schmidt et al., 1984; Thiele, 1984, 1986; Carratt et al., 1984; Taylor and Reichert, 1985; Choi, 1986; Mankin and Hudson, 1986; Henderson, 1987, 1989; Kim and Choi, 1988; Kim et al., 1990]. These workers show that steady state multiplicity, parametric sensitivity and oscillatory phenomena observed in many CSTRs would make the design of reactor controls difficult. In some industrial processes, stirred tank reactors are modified to such as horizontal multicompartimented reactors and tower reactors to deal with viscosity polymer solutions. Such reactors are often called linear flow reactors and they can be viewed as a cascade of CSTRs.

Because of their geometrical simplicity and relatively large surface to volume ratio for heat transfer, empty tubular reactors have been considered to be potentially good polymerization reactors. Indeed, tubular reactors have been used in the polymer industry for many years, notably for free radical ethylene polymerization to synthesize low density polyethylene (LDPE) at high pressure and high temperature. For the polymerization of vinyl monomers,

however, the use of tubular reactors on a commercial scale has not been quite successful. One of the major problems in using the empty tubular reactors for the polymerization of vinyl monomers is that the viscosity of the polymerizing liquid increases significantly as monomer conversion increases, leading to large radial and axial temperature gradients and a significant distortion of velocity profiles that leads to a buildup of slowly moving liquid layer at the reactor walls. Hamer and Ray [1986] indicate that the velocity profile at the reactor entrance is parabolic; however, a significant velocity distortion occurs as the polymer solution flows downward. This is because the fluid near the reactor wall moves slower and as a result its conversion increases faster than that of the fluid at the center. Therefore, the velocity near the wall is reduced. The distorted velocity profile results in a broadening of the polymer molecular weight distribution. The accumulation of stagnant layers at the reactor walls causes poor heat transfer and an excessive pressure buildup. When a multitubular reactor system is used for a large scale production, a significant variation in fluid viscosity may occur during the reaction, leading to the maldistribution of the polymer solution and serious flow instability over the various reactor tubes [Mallikarjun and Nauman, 1986]. A broad residence time distribution and composition heterogeneity may also cause nonuniform product properties, thermal runaway and/or flow instability problems.

In view of the fact that many of today's high performance polymers are produced in small-to-medium volume, it is desirable to develop new polymerization methods which have the advantages of both batch and continuous reactors and are suitable for the production of high quality polymers. Free radical polymerization of vinyl monomers such as styrene, methyl methacrylate and vinyl acetate in tubular reactors has been studied by many works in the past. The potential advantages of using empty tubular reactors as polymerization reactors are, for example, design simplicity, good heat transfer capability, and narrow molecular weight distribution of the product polymer. However, the problems in using the empty tubular reactors for the polymerization of vinyl monomers is that the viscosity of the polymerizing liquid increase significantly as monomer conversion increases, leading to large radial axial temperature gradients and a significant distortions of velocity profiles. As a result, a building of slowly moving liquid layer occurs at the reactor walls, causing a large variation in residence time distribution, plugging problems, poor heat transfer, and poor product quality [Lynn, 1977].

In our previous reports, we have been studied filled tubular reactor with some axial dispersion effect, such as a near plug flow pattern, due to intensive radial mixing induced by static mixers [Yoon and Choi, 1995]. In-line mixing devices or static mixers are widely used in chemical industry. A static mixer is a specially designed geometric structure placed in a pipe. It has no moving parts or external power requirements. It mixes materials flowing through it solely by redirecting fluid flow using the geometry of the channels. Mixing elements are installed within the tube to promote radial flow and to alleviate the composition and temperature difference which would otherwise arise. Each static mixer element is a specially designed rigid structure that divides the incoming flow and recombines it in a geometric sequence so that intensive radial mixing is obtained. Mixing and contacting take place as the fluids are sheared and directed radially across the pipe or duct. The major objective of all element design is to eliminate radial temperature and/or composition gradients that would arise during the flow in an empty tube. In addition, the

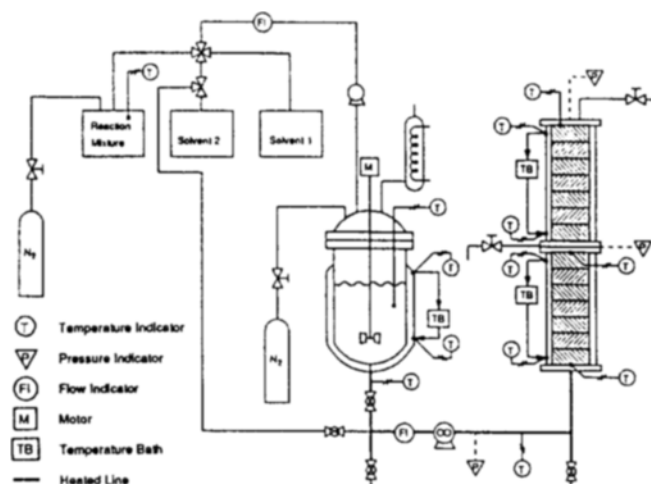


Fig. 1. Schematic diagram of continuous two stage polymerization system.

heat transfer through the tube walls is enhanced due to intensive radial mixing. A solution polymerization of styrene was investigated using a filled tubular reactor packed with static mixing elements. In order to characterize the liquid flow pattern in the filled tubular reactor, a residence time distribution (RTD) test was carried out [Yoon and Choi, 1995]. We reported $U_z/D_{ax} = 70.4 \text{ m}^{-1}$ (or Peclet number = 106), corresponding to approximately 35 ideal stirred tanks per meter. This RTD test indicated that the flow pattern in the filled tubular reactor was close to that of the plug flow but the axial mixing effect was not negligibly small.

In some industrial continuous styrene polymerization process, a train of reactors consisting of stirred tank reactors and linear flow reactors is often used (e.g. high impact polystyrene process). In this study, a two stage was proposed wherein a continuous stirred tank is used as a prepolymerization reactor for styrene polymerization in filled tubular reactor.

The purpose of this study is to investigate the feasibility of the two stage polymerization process. The polymerization reactor which used to only the filled tubular reactor must have a vessel to preheat and mix the reaction mixture. When the prepolymerizer can be replaced the vessel, the economical view of the industry have a good advantage. When the stirred tank reactor is used as a prepolymerizer, a feed stream to the filled tubular reactor is more viscous than the monomer/solvent mixture in our previous experiments. Therefore the main objective of this work is to investigate how the performance of the filled tubular reactor will be affected by the feed of viscous prepolymer solution. Both start-up transient and steady state behaviors of the reactor was investigated through laboratory experimentation and model simulations.

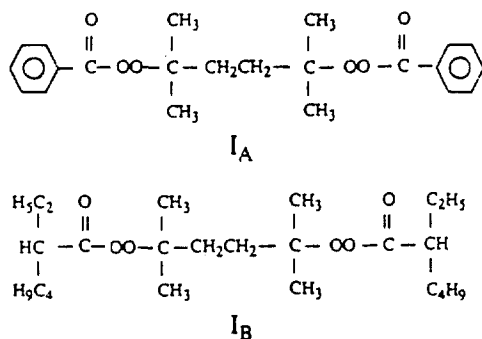
EXPERIMENT

A bench scale continuous two stage polymerization reactor facility has been built for styrene polymerization experiments. A schematic diagram of the experimental reactor system is illustrated in Fig. 1. The continuous reactor system is composed of two reactor units: a prepolymerization reactor and a filled tubular reactor. A jacketed glass reactor with a maximum working volume of 1 liters can be used either a continuous stirred tank prepolymerizer or a preheater. The prepolymerizer is pumped to inlet

of the main tubular reactor via a gear pump. The main reactor consists of two equal sized jacketed tubes made of stainless steel. The L/D ratio of each reactor segment is 28 and the tube diameter is 2.62 cm (I.D.). Each reactor segment is packed with 24 Sulzer SMX static mixers and the voidage of the packed tube is 0.91. Each static mixing element is turned around its main axis by 90 against its neighboring elements. The two reactor segments are connected by a short hollow connector unit ($L=10.2$) to which a ball valve has been attached for the sampling of small amounts of reactor fluids. There are three thermocouples (J-type) to measure the temperature at the reactor inlet, middle section and outlet. The 4 liter vented glass tanks are used as solvent and reaction mixture storage tanks. Predetermined amounts of bifunctional initiators, Luperox 118 (initiator A) and Lupersol 256 (initiator B), are added to the measured quantity of purified styrene and solvent mixture to prepare the feed monomer solution. The feed monomer solution is always purged with nitrogen during the experiment. Ethylbenzene (solvent 1) is used as a solvent. Toluene (solvent 2) is used to flush the reactors feed lines and pumps after polymerization experiments are completed. All the reactor feed lines are made of chemically inert TEFLON, high density polyethylene, and stainless steel tubings. The reactor is first filled with ethylbenzene and heated to a desired reaction temperature. Then the feed monomer solution containing a mixture of initiators is pumped to the bottom of the reactor. The polymer samples is dissolved in toluene and precipitated by the adding excess methanol. This procedure is repeated several times to ensure that unreacted monomer is completely removed. The samples are dried overnight in vacuo at 40°C. Then, the monomer conversion is determined by gravimetric method. The polymer molecular weight has been determined by gel permeation chromatography using four Ultrastaygel columns (Waters; 10^4 , 10^3 , 500 Å, and linear).

KINETIC MODEL

For the solution polymerization of styrene in two stage polymerization process, we used a binary mixture of symmetrical bifunctional initiators that have different thermal decomposition activities. The initiators used are 2,5-dimethyl-2,5-bis(benzoyl peroxy) hexane [Luperox 118, *Initiator I_A*] and 2,5-dimethyl-2,5-bis(2-ethyl hexanoyl peroxy) hexane [Lepersol 256, *Initiator I_B*] which are commercially available.

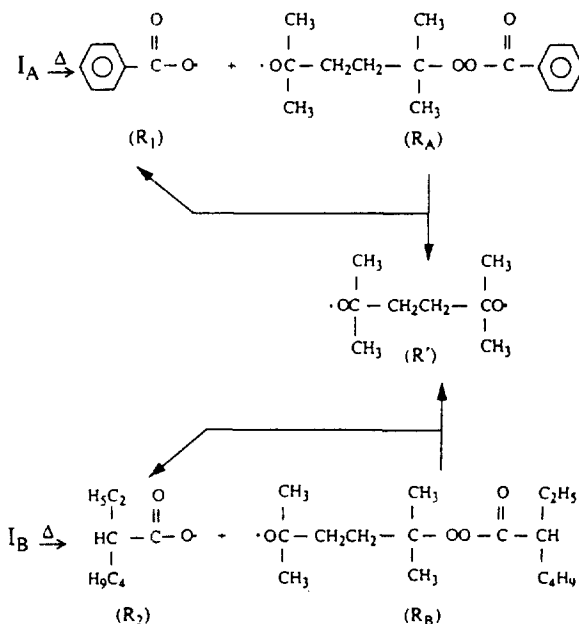


Since the peroxide groups in each initiator are separated by a fairly long hydrocarbon bridge for an inductive effect being negligible, the thermal stabilities of the peroxides are assumed not affected by whether or not the neighboring peroxide group has decomposed. Also notice that the hydrocarbon ligands between

Table 1. Polymeric species

Symbols	Note
P_n : $[\text{---}]$	live polymer without peroxides
Q_n : $A\text{---}$	live polymer with undecomposed peroxide A
S_n : $B\text{---}$	live polymer with undecomposed peroxide B
T_n : $\bullet\text{---}$	polymeric diradical
M_n' : $[\text{---}]$	dead polymer
U_n : $[\text{---}A]$	inactive polymer with undecomposed peroxide A
V_n : $[\text{---}B]$	inactive polymer with undecomposed peroxide B
W_n : $A\text{---}B$	inactive polymer with undecomposed peroxides A and B
U_n' : $A\text{---}A$	inactive polymer with two undecomposed peroxides A
V_n' : $B\text{---}B$	inactive polymer with two undecomposed peroxides B

the two peroxide groups in both initiators are identical. The peroxide group in Luperox 118 has a half-life of 9.9 hr at 100°C whereas the peroxide group in Lupersol 256 has a half-life of 21 min at 100°C. Thus, Luperox 118 is labeled as slow initiator and Lupersol 256 as fast initiator. Primary radicals are generated by homolytic scission reactions as follows:



Note that when the primary radicals R_A and R_B decompose further, diradical species R' is generated. The primary radical R_1 and R_2 may also undergo decarboxylation reactions but there will be no net change in radical concentrations.

The kinetic modeling of bulk styrene polymerization with these initiators has been reported elsewhere [Yoon and Choi, 1992a, 1992b]. When the polymerization is initiated by the mixture of these symmetrical bifunctional initiators, as in situ unsymmetry of initiator functions is obtained and the resulting polymerization kinetics become quite complicated. The use of the initiator mixture has an effect of continuously supplying radicals through thermal decomposition of peroxides attached to polymer chain ends even at high reaction temperatures, allowing the production of high molecular weight polymers at high reaction rate. Thus, it will be possible to regulate radical concentrations and concomitantly the polymerization rate and polymer molecular weight by using multiple tubular reactor segments at different temperatures.

Table 1 shows ten polymeric species present in the reaction

Table 2. A kinetic model with a binary mixture of symmetrical bifunctional initiators

Decomposition of peroxides:	
$I_A \xrightarrow{2k_{dA}} R_1 + R_4$	$T_n + M \xrightarrow{2k_p} T_{n+1}$
$I_B \xrightarrow{2k_{dB}} R_2 + R_8$	Chain transfer to monomer ($n \geq 1$):
$R_1 \xrightarrow{k_{dA}} R_1 + R'$	$P_n + M \xrightarrow{k_{pm}} M_n + P_1$
$R_8 \xrightarrow{k_{dB}} R_2 + R'$	$Q_n + M \xrightarrow{k_{qm}} U_n + P_1$
$Q_n \xrightarrow{k_{dA}} R_1 + T_n$ ($n \geq 1$)	$S_n + M \xrightarrow{k_{sm}} V_n + P_1$
$S_n \xrightarrow{k_{dB}} R_2 + T_n$ ($n \geq 1$)	$T_n + M \xrightarrow{2k_{tm}} P_n + P_1$
$U_n \xrightarrow{k_{dA}} R_1 + P_n$ ($n \geq 2$)	Chain transfer to solvent ($n \geq 1$):
$V_n \xrightarrow{k_{dB}} R_2 + P_n$ ($n \geq 2$)	$P_n + S_o \xrightarrow{k_{fs}} M_n + P_1$
$W_n \xrightarrow{k_{dA}} R_1 + Q_n$ ($n \geq 2$)	$Q_n + S_o \xrightarrow{k_{fs}} U_n + P_1$
$W_n \xrightarrow{k_{dB}} R_2 + S_n$ ($n \geq 2$)	$S_n + S_o \xrightarrow{k_{fs}} V_n + P_1$
$U_n' \xrightarrow{2k_{dA}} R_1 + Q_n$ ($n \geq 2$)	$T_n + S_o \xrightarrow{2k_{ts}} P_n + P_1$
$V_n' \xrightarrow{2k_{dB}} R_2 + S_n$ ($n \geq 2$)	Termination ($n, m \geq 1$):
Initiation:	$P_n + P_m \xrightarrow{k_t} M_{n+m}$
$R_1 + M \xrightarrow{k_i} P_1$	$P_n + Q_m \xrightarrow{k_t} U_{n+m}$
$R_2 + M \xrightarrow{k_i} P_1$	$P_n + S_m \xrightarrow{k_t} V_{n+m}$
$R_4 + M \xrightarrow{k_i} Q_1$	$P_n + T_m \xrightarrow{2k_t} P_{n+m}$
$R_8 + M \xrightarrow{k_i} S_1$	$Q_n + Q_m \xrightarrow{k_t} U_{n+m}'$
$R' + M \xrightarrow{2k_i} T_1$	$Q_n + S_m \xrightarrow{k_t} W_{n+m}$
$3M \xrightarrow{k_{dm}} 2P_1$ (thermal initiation)	$Q_n + T_m \xrightarrow{2k_t} Q_{n+m}$
Propagation ($n \geq 1$):	$S_n + S_m \xrightarrow{k_t} V_{n+m}'$
$P_n + M \xrightarrow{k_p} P_{n+1}$	$S_n + T_m \xrightarrow{2k_t} S_{n+m}$
$Q_n + M \xrightarrow{k_p} Q_{n+1}$	$T_n + T_m \xrightarrow{4k_t} T_{n+m}$
$S_n + M \xrightarrow{k_p} S_{n+1}$	

mixture when styrene is polymerized by the mixture of two symmetrical bifunctional initiators. Here, the polymer molecules are identified by the type of their end units. The subscript n indicates the number of repeating units in the polymer chain. The formation of various polymeric species listed in Table 1 is due to the presence of two different peroxides which are redistributed in the polymer chains through chain transfer and termination reactions. Note that there are two polymeric radical species (Q_n and S_n) containing an undecomposed peroxide and five inactive polymer species (U_n , V_n , W_n , U_n' and V_n') containing either one or two undecomposed peroxides which are subject to further thermal scission reactions. In such applications, it will be important to estimate the concentrations of various polymers containing undecomposed peroxides that can be decomposed further in a controlled manner in the presence of comonomers. Table 2 shows various reactions occurring in bulk styrene polymerization reactor. The kinetic modeling equations for bulk styrene polymerization with these initiators have been reported by Yoon and Choi [1992a, 1992b]. At high reaction temperatures, thermal initiation also becomes important. According to the thermal initiation mechanism

proposed by Pryor and Coco [1970], the thermal initiation reaction is third order with respect to monomer. Since ethylbenzene is used as a solvent, the kinetic model reported in Yoon and Choi [1992a] is modified by including the solvent chain transfer reactions (rate constant: k_{fs}) in the kinetic model.

MODEL DEVELOPMENT

1. Modeling of a CSTR (Prepolymerizer)

For free radical polymerization of styrene with a binary mixture of symmetrical bifunctional initiators in a CSTR of constant volume V , the following mass and energy balance equations are derived:

$$V \frac{dM}{dt'} = q(M_f - M) - V k_p M (P + Q + S + 2T) \quad (1)$$

$$V \frac{dI_A}{dt'} = q(I_{Af} - I_A) - 2V k_{dA} I_A \quad (2)$$

$$V \frac{dI_B}{dt'} = q(I_{Bf} - I_B) - 2V k_{dB} I_B \quad (3)$$

$$V \frac{dS_o}{dt'} = q(S_{of} - S_o) - V k_{fs} (P + Q + S + 2T) \quad (4)$$

$$\rho C_p V \frac{dT_R}{dt'} = \rho C_p q (T_f - T_R) + V (-\Delta H) k_p M (P + Q + S + 2T) - h A_c (T_R - T_c) \quad (5)$$

Where q is the volumetric flow rate and the subscript f denotes the feed condition. Physical properties of the polymerizing mixture [e.g., ρ , C_p , $(-\Delta H)$] are assumed constant and perfect back-mixing is assumed. It is assumed that monomer consumption through initiation reactions and chain transfer to monomer is negligible.

The k -th moments of live and dead polymers are defined as follows:

$$\lambda_{\xi,k} \equiv \sum_{n=j}^{\infty} n^k \xi_n [\xi = P, Q, S, T, U, V (j=1); W, U', V' (j=2)] \quad (6)$$

$$\lambda_k^d \equiv \sum_{n=2}^{\infty} n^k M_n \quad (7)$$

where $\lambda_{\xi,k}$ and λ_k^d denote the k -th moment of polymeric species ξ and dead polymers, respectively. The number average and weight average degrees of polymerization are expressed as follows:

$$X_n = \frac{\sum_{\xi} \lambda_{\xi,1} + \lambda_1^d}{\sum_{\xi} \lambda_{\xi,0} + \lambda_0^d} \quad (\xi = P, Q, S, T, U, V, W, U', V') \quad (8)$$

$$X_w = \frac{\sum_{\xi} \lambda_{\xi,2} + \lambda_2^d}{\sum_{\xi} \lambda_{\xi,1} + \lambda_1^d} \quad (\xi = P, Q, S, T, U, V, W, U', V') \quad (9)$$

The following molecular weight moment equations are derived and solved simultaneously with the above reactor modeling equations:

$$V \frac{d\lambda_{u,0}}{dt'} = -q\lambda_{u,0} + V[-k_{dA}\lambda_{u,0} + k_{pm}MQ + k_{fs}SQ + k_iPQ] \quad (10)$$

$$V \frac{d\lambda_{u,1}}{dt'} = -q\lambda_{u,1} + V[-k_{dA}\lambda_{u,1} + k_{pm}M\lambda_{q,1} + k_{fs}S\lambda_{q,1} + k_i(\lambda_{p,1}Q + \lambda_{q,1}P)] \quad (11)$$

$$V \frac{d\lambda_{u,2}}{dt'} = -q\lambda_{u,2} + V[-k_{dA}\lambda_{u,2} + k_{pm}M\lambda_{u,2} + k_{fs}S_0\lambda_{u,2} + k_i(\lambda_{p,2}Q + 2\lambda_{p,1}\lambda_{q,1} + \lambda_{q,2}P)] \quad (12)$$

$$V \frac{d\lambda_{u,0}}{dt'} = -q\lambda_{u,0} + V[-k_{dB}\lambda_{u,0} + k_{pm}MS + k_{fs}S_0S + k_iPS] \quad (13)$$

$$V \frac{d\lambda_{u,1}}{dt'} = -q\lambda_{u,1} + V[-k_{dB}\lambda_{u,1} + k_{pm}M\lambda_{u,1} + k_{fs}S_0\lambda_{u,1} + k_i(\lambda_{p,1}S + \lambda_{s,1}P)] \quad (14)$$

$$V \frac{d\lambda_{s,2}}{dt'} = -q\lambda_{s,2} + V[-k_{dB}\lambda_{s,2} + k_{pm}M\lambda_{s,2} + k_{fs}S_0\lambda_{s,2} + k_i(\lambda_{p,2}S + 2\lambda_{p,1}\lambda_{s,1} + \lambda_{s,2}P)] \quad (15)$$

$$V \frac{d\lambda_{u,0}}{dt'} = -q\lambda_{u,0} + V[-(k_{dA} + k_{dB})\lambda_{u,0} + k_iQS] \quad (16)$$

$$V \frac{d\lambda_{u,1}}{dt'} = -q\lambda_{u,1} + V[-(k_{dA} + k_{dB})\lambda_{u,1} + k_i(\lambda_{q,1}S + \lambda_{s,1}Q)] \quad (17)$$

$$V \frac{d\lambda_{u,2}}{dt'} = -q\lambda_{u,2} + V[-(k_{dA} + k_{dB})\lambda_{u,2} + k_i(\lambda_{q,2}S + 2\lambda_{q,1}\lambda_{s,1} + \lambda_{s,2}Q)] \quad (18)$$

$$V \frac{d\lambda_{u,0}}{dt'} = -q\lambda_{u,0} + V[-2k_{dA}\lambda_{u,0} + \frac{1}{2}k_iQ^2] \quad (19)$$

$$V \frac{d\lambda_{u,1}}{dt'} = -q\lambda_{u,1} + V[-2k_{dA}\lambda_{u,1} + k_i\lambda_{q,1}Q] \quad (20)$$

$$V \frac{d\lambda_{u,2}}{dt'} = -q\lambda_{u,2} + V[-2k_{dA}\lambda_{u,2} + k_i(\lambda_{q,2}Q + \lambda_{q,1}^2)] \quad (21)$$

$$V \frac{d\lambda_{s,0}}{dt'} = -q\lambda_{s,0} + V[-2k_{dB}\lambda_{s,0} + \frac{1}{2}k_iS^2] \quad (22)$$

$$V \frac{d\lambda_{s,1}}{dt'} = -q\lambda_{s,1} + V[-2k_{dB}\lambda_{s,1} + k_i\lambda_{s,1}S] \quad (23)$$

$$V \frac{d\lambda_{s,2}}{dt'} = -q\lambda_{s,2} + V[-2k_{dB}\lambda_{s,2} + k_i(\lambda_{s,2}S + \lambda_{s,1}^2)] \quad (24)$$

$$V \frac{d\lambda_{M,0}}{dt'} = -q\lambda_{M,0} + V[(k_{pm}M + k_{fs}S_0)(P - P_1) + \frac{1}{2}k_iP^2] \quad (25)$$

$$V \frac{d\lambda_{M,1}}{dt'} = -q\lambda_{M,1} + V[(k_{pm}M + k_{fs}S_0)(\lambda_{p,1} - P_1) + k_i\lambda_{p,1}P] \quad (26)$$

$$V \frac{d\lambda_{M,2}}{dt'} = -q\lambda_{M,2} + V[(k_{pm}M + k_{fs}S_0)(\lambda_{p,2} - P_1) + k_i(\lambda_{p,2}P + \lambda_{p,1}^2)] \quad (27)$$

In actual model simulations, the original modeling equations were reduced to the following dimensionless form for computational convenience.

$$\begin{aligned} X_T &= \frac{T - T_f}{T_f}, \quad X_M = \frac{M_f - M}{M_f}, \quad y_{Af} = \frac{I_{Af}}{I_f}, \\ X_{LA} &= \frac{y_{Af}I_f - I_A}{y_{Af}I_f}, \quad X_{LB} = \frac{(1 - y_{Af})I_f - I_B}{(1 - y_{Af})I_f}, \\ \delta &= \frac{T_f - T_f}{T_f}, \quad \theta = \frac{V}{q}, \quad X_S = \frac{S_0}{S_f}, \\ t &= \frac{t'}{\theta}, \quad \beta = \frac{(-\Delta H)M_f}{\rho C_p T_f}, \quad \alpha = \frac{hA_c}{\rho C_p V} \end{aligned} \quad (28)$$

The numerical values of kinetic and physical constants and CSTR operating conditions used in the numerical simulations are listed in Table 3.

Table 3. Kinetic and physical constants and the reactor operating conditions for styrene polymerization

	[ref.]
$k_{dA} = 4.267 \times 10^{18} \exp(-36,800/RT), \text{ min}^{-1}$	[Luperox 118] [a]
$k_{dB} = 1.251 \times 10^{17} \exp(-31,700/RT), \text{ min}^{-1}$	[Lupersol 256] [a]
$k_{dm} = 1.314 \times 10^7 \exp(-27,440/RT), (\text{L/mol})^2 \cdot \text{min}^{-1}$	[b]
$k_p = 6.306 \times 10^8 \exp(-7,060/RT), \text{ L/mol} \cdot \text{min}$	[c]
$k_{t0} = 7.530 \times 10^{10} \exp(-1,680/RT), \text{ L/mol} \cdot \text{min}$	[c]
$k_i \approx k_p$	
$k_{pm,0} = 2.319 \times 10^8 \exp(-10,790/RT), \text{ L/mol} \cdot \text{min}$	[d]
$k_{fs} = 1.247 \times 10^9 \exp(-13,769/RT), \text{ L/mol} \cdot \text{min}$	[c]
$(-\Delta H) = 16.24 \text{ Kcal/mol}, \rho C_p = 0.43 \text{ Kcal/L}^\circ\text{K}$	[c]
$k^* = 0.018 \text{ cal/cm}^2 \cdot \text{min}^\circ\text{K}$	[c]
$h = 0.0747 \text{ cal/cm}^2 \cdot \text{min}^\circ\text{K}$	[e]
$L = 152.4 \text{ cm}, D = 2.621 \text{ cm}, P_e = 106$	
$\alpha = 0.324 \text{ min}^{-1}$	
$V = 753 \text{ cm}^3, q = 4.7 \text{ cm}^3/\text{min}$	
$\rho_m = 0.909 \text{ g/cm}^3, \rho_s = 0.867 \text{ g/cm}^3$	
$S_0 = 2.368 \text{ mol/L}, S_f = 8.167 \text{ mol/L}$	
$M_f = 6.197 \text{ mol/L}, T_f = 298^\circ\text{K}$	
[a] Product Bulletin Peroxyesters [1983]	
[b] Hui and Hamielec [1972]	
[c] Brandup and Immergut [1989]	
[d] Yoon and Choi [1992]	
[e] Nguyen et al. [1985]	

2. Modeling of a Filled Tubular Reactor (Main Reactor)

From the RTD analysis of the filled tubular reactor, it appears that axial dispersion effect is small but not negligible. In the following, a dynamic axial dispersion model is developed for solution polymerization of styrene with a binary mixture of symmetrical bifunctional initiators. The mass and energy balance equations are represented as:

$$\frac{\partial M}{\partial t'} + u_z \frac{\partial M}{\partial Z} = D_{uM} \frac{\partial^2 M}{\partial Z^2} - k_p M(P + Q + S + 2T) \quad (29)$$

$$\frac{\partial I_A}{\partial t'} + u_z \frac{\partial I_A}{\partial Z} = D_{uA} \frac{\partial^2 I_A}{\partial Z^2} - 2k_{dA}I_A \quad (30)$$

$$\frac{\partial I_B}{\partial t'} + u_z \frac{\partial I_B}{\partial Z} = D_{uB} \frac{\partial^2 I_B}{\partial Z^2} - 2k_{dB}I_B \quad (31)$$

$$\frac{\partial S_0}{\partial t'} + u_z \frac{\partial S_0}{\partial Z} = D_{uS} \frac{\partial^2 S_0}{\partial Z^2} \quad (32)$$

$$\begin{aligned} \frac{\partial T_R}{\partial t'} + u_z \frac{\partial T_R}{\partial Z} &= \frac{k^*}{\rho C_p} \frac{\partial^2 T_R}{\partial Z^2} + \frac{(-\Delta H)}{\rho C_p} k_p M(P + Q + S + 2T) \\ &\quad - \frac{4h}{\rho C_p D} (T_R - T_f) \end{aligned} \quad (33)$$

In the above, it has been assumed that the monomer consumption by initiation and chain transfer reactions is negligible and that the solvent consumption by chain transfer reaction is also negligible. The jacket temperature (T_f) is also assumed to be constant. The following molecular weight moment equations are derived and solved simultaneously with the above reactor modeling equations:

$$\begin{aligned} \frac{\partial \lambda_{u,0}}{\partial t'} + u_z \frac{\partial \lambda_{u,0}}{\partial Z} &= D_{uP} \frac{\partial^2 \lambda_{u,0}}{\partial Z^2} - k_{dA}\lambda_{u,0} + k_{pm}MQ + k_{fs}S_0Q \\ &\quad + k_iPQ \end{aligned} \quad (34)$$

$$\frac{\partial \lambda_{u,1}}{\partial t'} + u_z \frac{\partial \lambda_{u,1}}{\partial Z} = D_{aP} \frac{\partial^2 \lambda_{u,1}}{\partial Z^2} - k_{dA} \lambda_{u,1} + k_{fm} M \lambda_{q,1} + k_{fs} S_0 \lambda_{q,1} + k_i (\lambda_{p,1} Q + \lambda_{q,1} P) \quad (35)$$

$$\frac{\partial \lambda_{u,2}}{\partial t'} + u_z \frac{\partial \lambda_{u,2}}{\partial Z} = D_{aP} \frac{\partial^2 \lambda_{u,2}}{\partial Z^2} - k_{dA} \lambda_{u,2} + k_{fm} M \lambda_{q,2} + k_{fs} S_0 \lambda_{q,2} + k_i (\lambda_{p,2} Q + 2 \lambda_{p,1} \lambda_{q,1} + \lambda_{q,2} P) \quad (36)$$

$$\frac{\partial \lambda_{u,0}}{\partial t'} + u_z \frac{\partial \lambda_{u,0}}{\partial Z} = D_{aP} \frac{\partial^2 \lambda_{u,0}}{\partial Z^2} - k_{dA} \lambda_{u,0} + k_{fm} M S + k_{fs} S_0 S + k_i P S \quad (37)$$

$$\frac{\partial \lambda_{u,1}}{\partial t'} + u_z \frac{\partial \lambda_{u,1}}{\partial Z} = D_{aP} \frac{\partial^2 \lambda_{u,1}}{\partial Z^2} - k_{dA} \lambda_{u,1} + k_{fm} M \lambda_{s,1} + k_{fs} S_0 \lambda_{s,1} + k_i (\lambda_{p,1} S + \lambda_{s,1} P) \quad (38)$$

$$\frac{\partial \lambda_{u,2}}{\partial t'} + u_z \frac{\partial \lambda_{u,2}}{\partial Z} = D_{aP} \frac{\partial^2 \lambda_{u,2}}{\partial Z^2} - k_{dA} \lambda_{u,2} + k_{fm} M \lambda_{s,2} + k_{fs} S_0 \lambda_{s,2} + k_i (\lambda_{p,2} S + 2 \lambda_{p,1} \lambda_{s,1} + \lambda_{s,2} P) \quad (39)$$

$$\frac{\partial \lambda_{u,0}}{\partial t'} + u_z \frac{\partial \lambda_{u,0}}{\partial Z} = D_{aP} \frac{\partial^2 \lambda_{u,0}}{\partial Z^2} - (k_{dA} + k_{dB}) \lambda_{u,0} + k_i Q S \quad (40)$$

$$\frac{\partial \lambda_{u,1}}{\partial t'} + u_z \frac{\partial \lambda_{u,1}}{\partial Z} = D_{aP} \frac{\partial^2 \lambda_{u,1}}{\partial Z^2} - (k_{dA} + k_{dB}) \lambda_{u,1} + k_i (\lambda_{q,1} S + \lambda_{s,1} Q) \quad (41)$$

$$\frac{\partial \lambda_{u,2}}{\partial t'} + u_z \frac{\partial \lambda_{u,2}}{\partial Z} = D_{aP} \frac{\partial^2 \lambda_{u,2}}{\partial Z^2} - (k_{dA} + k_{dB}) \lambda_{u,2} + k_i (\lambda_{q,2} S + 2 \lambda_{q,1} \lambda_{s,1} + \lambda_{s,2} Q) \quad (42)$$

$$\frac{\partial \lambda_{u,0}}{\partial t'} + u_z \frac{\partial \lambda_{u,0}}{\partial Z} = D_{aP} \frac{\partial^2 \lambda_{u,0}}{\partial Z^2} - 2 k_{dA} \lambda_{u,0} + \frac{1}{2} k_i Q^2 \quad (43)$$

$$\frac{\partial \lambda_{u,1}}{\partial t'} + u_z \frac{\partial \lambda_{u,1}}{\partial Z} = D_{aP} \frac{\partial^2 \lambda_{u,1}}{\partial Z^2} - 2 k_{dA} \lambda_{u,1} + k_i \lambda_{q,1} Q \quad (44)$$

$$\frac{\partial \lambda_{u,2}}{\partial t'} + u_z \frac{\partial \lambda_{u,2}}{\partial Z} = D_{aP} \frac{\partial^2 \lambda_{u,2}}{\partial Z^2} - 2 k_{dA} \lambda_{u,2} + k_i (\lambda_{q,2} Q + \lambda_{q,1}^2) \quad (45)$$

$$\frac{\partial \lambda_{u,0}}{\partial t'} + u_z \frac{\partial \lambda_{u,0}}{\partial Z} = D_{aP} \frac{\partial^2 \lambda_{u,0}}{\partial Z^2} - 2 k_{dA} \lambda_{u,0} + \frac{1}{2} k_i S^2 \quad (46)$$

$$\frac{\partial \lambda_{u,1}}{\partial t'} + u_z \frac{\partial \lambda_{u,1}}{\partial Z} = D_{aP} \frac{\partial^2 \lambda_{u,1}}{\partial Z^2} - 2 k_{dB} \lambda_{u,1} + k_i \lambda_{s,1} S \quad (47)$$

$$\frac{\partial \lambda_{u,2}}{\partial t'} + u_z \frac{\partial \lambda_{u,2}}{\partial Z} = D_{aP} \frac{\partial^2 \lambda_{u,2}}{\partial Z^2} - 2 k_{dB} \lambda_{u,2} + k_i (\lambda_{s,2} S + \lambda_{s,1}^2) \quad (48)$$

$$\frac{\partial \lambda_{M,0}}{\partial t'} + u_z \frac{\partial \lambda_{M,0}}{\partial Z} = D_{aP} \frac{\partial^2 \lambda_{M,0}}{\partial Z^2} + (k_{fm} M + k_{fs} S_0) (P - P_1) + \frac{1}{2} k_i P^2 \quad (49)$$

$$\frac{\partial \lambda_{M,1}}{\partial t'} + u_z \frac{\partial \lambda_{M,1}}{\partial Z} = D_{aP} \frac{\partial^2 \lambda_{M,1}}{\partial Z^2} + (k_{fm} M + k_{fs} S_0) (\lambda_{p,1} - P_1) + k_i \lambda_{p,1} P \quad (50)$$

$$\frac{\partial \lambda_{M,2}}{\partial t'} + u_z \frac{\partial \lambda_{M,2}}{\partial Z} = D_{aP} \frac{\partial^2 \lambda_{M,2}}{\partial Z^2} + (k_{fm} M + k_{fs} S_0) (\lambda_{p,2} - P_1) + k_i (\lambda_{p,2} P + \lambda_{p,1}^2) \quad (51)$$

where D_{aP} is the axial dispersion coefficient for polymeric species. In deriving the above modeling equations, a quasi-steady state approximation (QSSA) has been applied to primary radicals and live polymeric species (i.e., P_n , Q_n , S_n , T_n). It is also assumed that physical properties such as density and heat capacity are constant. We ignored the volume contraction effect because the monomer conversion is not very high and a solvent is used to dilute the

polymer solution. The concentrations for the total live polymers (P , Q , S , T) are calculated by solving the resulting non-linear algebraic equations [Yoon and Choi, 1992a]. It is also assumed that the physical properties such as fluid density and heat capacity are constant.

The initial and boundary conditions for the above modeling equations are as follows:

(i) initial conditions ($t'=0$):

$$M(0; 0 \leq Z \leq L) = 0, I_A(0; 0 \leq Z \leq L) = 0, I_B(0; 0 \leq Z \leq L) = 0, T_R(0; 0 \leq Z \leq L) = T_0, S_0(0; 0 \leq Z \leq L) = S', \lambda_{u,k}(0; 0 \leq Z \leq L) = 0 \quad (52)$$

where $\lambda_{u,k}$ is the k -th moment of species i .

(ii) boundary conditions at the tube entrance ($Z=0$, $t' \geq 0$):

$$(u_z M)_m = \left(u_z M - D_{aM} \frac{\partial M}{\partial Z} \right)_{Z=0} \quad (53a)$$

$$(u_z I_A)_m = \left(u_z I_A - D_{aIA} \frac{\partial I_A}{\partial Z} \right)_{Z=0} \quad (53b)$$

$$(u_z I_B)_m = \left(u_z I_B - D_{aIB} \frac{\partial I_B}{\partial Z} \right)_{Z=0} \quad (53c)$$

$$(\rho C_p u_z T_R)_m = \left(\rho C_p u_z T_R - k^* \frac{\partial T_R}{\partial Z} \right)_{Z=0} \quad (53d)$$

$$(u_z S_0)_m = \left(u_z S_0 - D_{aS} \frac{\partial S_0}{\partial Z} \right)_{Z=0} \quad (53e)$$

$$(u_z \lambda_{u,k})_m = \left(u_z \lambda_{u,k} - D_{aP} \frac{\partial \lambda_{u,k}}{\partial Z} \right)_{Z=0} \quad (53f)$$

(iii) boundary conditions at the tube exit ($Z=L$, $t' \geq 0$):

$$\left(\frac{\partial M}{\partial Z} \right)_{Z=L} = 0, \left(\frac{\partial I_A}{\partial Z} \right)_{Z=L} = 0, \left(\frac{\partial I_B}{\partial Z} \right)_{Z=L} = 0, \left(\frac{\partial T_R}{\partial Z} \right)_{Z=L} = 0, \left(\frac{\partial S_0}{\partial Z} \right)_{Z=L} = 0, \left(\frac{\partial \lambda_{u,k}}{\partial Z} \right)_{Z=L} = 0 \quad (54)$$

In solving the above modeling equations, axial dispersion coefficients must be known. We will assume that the degree of axial dispersion is same for all species, i.e., $D_{aj} = D_{ax}$ ($j = M, I_A, I_B, S, P$). For computational convenience. For computational convenience, reactor state variables and some parameters are transformed to dimensionless forms as follows:

$$\begin{aligned} X_T &= \frac{T_R - T_f}{T_f}, X_M = \frac{M_f - M}{M_f}, y_{Af} = \frac{I_{Af}}{(I_{Af} + I_{Bf})}, \\ X_{LA} &= \frac{y_{Af} I_f - I_A}{y_{Af} I_f}, X_{LB} = \frac{(1 - y_{Af}) I_f - I_B}{(1 - y_{Af}) I_f}, \\ \delta &= \frac{T_c - T_f}{T_f}, \xi = \frac{Z}{L}, X_S = \frac{S_0}{S'}, \\ \theta &= \frac{L}{u_z}, t = \frac{t'}{\theta}, \beta = \frac{(-\Delta H) M_f}{\rho C_p T_f}, \\ \gamma &= \frac{4h\theta}{\rho C_p D}, P_r = \frac{u_z L}{D_{ax}}, P_r^* = \frac{u_z \rho C_p}{k^*} \end{aligned} \quad (55)$$

The numerical values of various kinetic parameters and physical constants used in the model simulations are listed in Table 3. The explicit finite difference method was used to solve the above equations.

RESULTS AND DISCUSSION

The validity of the proposed reactor model is evaluated by com-

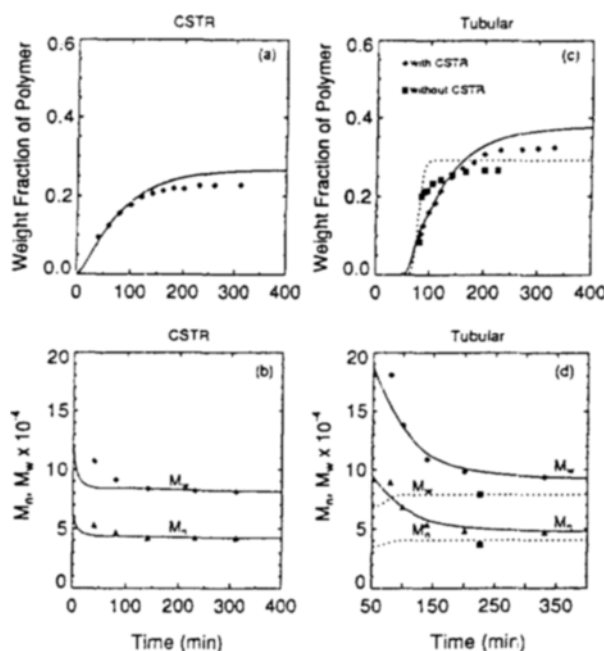


Fig. 2. Polymer weight fraction and molecular weight at reactor outlet. CSTR; $\theta = 80$ min, $T_{c0} = 373^\circ\text{K}$, tubular reactor $T_{c1} = 373^\circ\text{K}$, $T_{c2} = 373^\circ\text{K}$, (—) model simulation with CSTR, (---) model simulation without CSTR, \blacktriangle : M_n , \blacklozenge : M_w .

paring the simulation results with laboratory experimental data. In conducting the reaction experiments, the feed temperature was maintained at 24°C at which the polymerization of styrene was negligible. In these experiments, the solvent (ethylbenzene) volume fraction (f_s) was held constant at 0.3. Two experimental runs have been carried out using a CSTR-Filled Tubular Reactor train. The experimental data show the polymer weight fraction (W_p) and molecular weight averages (M_n and M_w) of the samples taken from the exit of the reactor at transient and steady state.

The first experiment was carried out at different reactor jacket temperature where the CSTR temperature is 100°C , and the temperature of the first and second tubular reactor segments are both of 100°C with $y_{A1} = 0.5$ and $\theta = 80$ min. Fig. 2 shows the polymer weight fractions and molecular weight profiles in both the CSTR and the filled tubular reactor. Also shown in Fig. 2 (c), (d) are the experimental data in which the prepolymerizer was not used. Here, \blacklozenge and \blacktriangle represent the data for the samples with CSTR and \blacksquare represents the data for the samples without CSTR. The solid lines are model simulation results. It is first observed that although the feed polymer solution to the tubular reactor contains 20% polymer, the final polymer weight fraction from the tubular reactor is only about 38% higher than the feed value (NOTE: The polymer weight fraction of 0.38 corresponds to 54.2% conversion of monomer.). Fig. 2 (b), (d) shows the polymer molecular weight averages for the first experiment. It is also seen that the polydispersity is about 2.0. The polymer weight fraction and molecular weight profiles of the first experiment is also very similar to those of without CSTR in Fig. 2 (b), (d). This indicates that the addition of a prepolymer has essentially no effect on the performance of the filled tubular reactor.

Fig. 3 shows the experimental results of the second experiment where the CSTR temperature is 90°C , and the temperature of the first and second tubular reactor segments are 100°C and 110°C ,

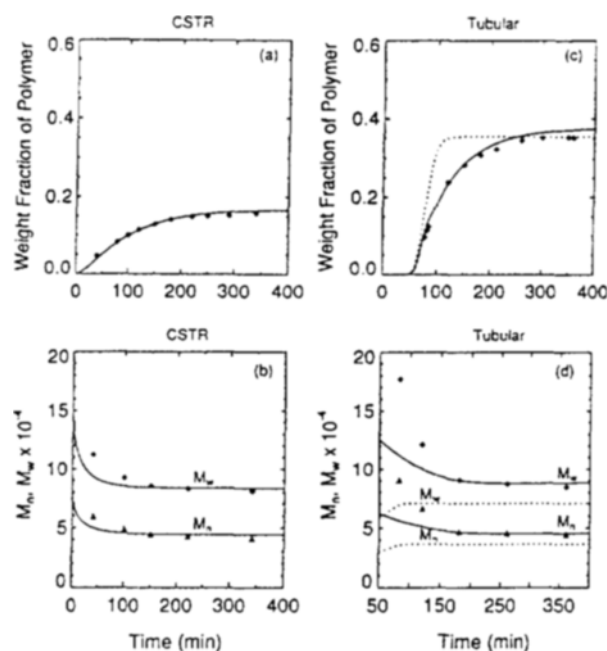


Fig. 3. Polymer weight fraction and molecular weight at reactor outlet. CSTR; $\theta = 80$ min, $T_{c0} = 363^\circ\text{K}$, tubular reactor $T_{c1} = 373^\circ\text{K}$, $T_{c2} = 383^\circ\text{K}$, (—) model simulation with CSTR, (---) model simulation without CSTR, \blacktriangle : M_n , \blacklozenge : M_w .

respectively. The quantitative behavior of the reactor is similar to that of the first run. Both Fig. 2 and Fig. 3 indicate that proposed axial dispersion model prediction of monomer conversion and polymer molecular weight averages without any model parameters adjusted to fit the data. As a result, a filled tubular reactor as a polymerization reactor has no effect on the viscosity as a reaction goes on and for the two stage polymerization process, good agreements between the model predictions and experimental data is obtained. When the vessel to mix or preheat for tubular reactor system is replaced by the prepolymerizer, it can bring some advantages in the economical point of the industry. For example, the industrial product per hour can be increased by the same amount of investments. Another potential application of bifunctional initiators is to prepare block copolymer. Currently, ionic polymerization techniques are used to synthesize block copolymers [e.g., styrene-butadiene-styrene (SBS) block copolymers and styrene isoprene-styrene (SIS) (polystyrene-*b*-polyisoprene) block copolymers]. However, it has been known that there are no easy industrial manufacturing processes to obtain block and graft copolymers of vinyl monomers by free radical polymerization [Piirma and Chou, 1979]. In such applications, it will be important to feed the sequential comonomer when two stage polymerization process was employed, it is easy to feed the second monomer right after the polymerizer.

When empty tubular reactors are used for polymerization, bimodal molecular weight distributions are often observed. For example, in a recent work by Cunningham et al. [1991] who conducted bulk polymerization of methyl methacrylate (MMA) at 70°C in a tubular reactor, the polymers recovered from the reactor exhibited a bimodality was attributed to the fouling at the reactor walls where high molecular weight distribution even at low monomer conversion (9%). The observed bimodality was attributed to the fouling at the reactor walls where high molecular polymers

move much more slowly than the polymers at the center of the tube. For all the polymer samples we analyzed, no bimodality in the molecular weight distribution curves was observed, suggesting that fouling did not occur in the reactor. It is believed that some deviations of the model predictions from the experimental data at $Z=L/2$ (or $\xi=1/2$) have been caused by the presence of an intermediate empty tube zone between the two sections of the filled tubular reactor. It is likely that poor radical mixing must have occurred in the connecting intermediate section of the reactor.

In particular, the proposed two stage polymerization systems are suitable for the continuous production of small-to-medium volume speciality polymers which are difficult or economically infeasible to make by other polymerization processes using conventional stirred reactors or empty tubular reactors. The possibility to tailor-make any desirable intermediate by prepolymerizer is a very important advantage of the free radical polymerization process compared with other one stage polymerization process. In a broad sense, the filled tubular reactors (FTR) may be viewed as another type of reactive processing systems that including single screw and twin screw plasticating extruders modified as polymerization reactors. The screw reactors are used to polymerize highly viscous materials that do not require long residence times and when the polymers are not shear sensitives.

CONCLUSIONS

A mathematical model of a two stage polymerization process has been developed and validated through laboratory experimentation. The kinetic parameters and transport parameters used in the model simulations were taken from the literature and no adjustment parameters were used to fit the model with experimental data. The overall quality of the model predictions were quite reasonable, indicating that the proposed model is adequate in describing the reactor behavior. It was found that the addition of a prepolymerization reactor has almost no effect on the performance of the filled tubular reactor. The experimental results suggest that the filled tubular reactor can be potentially a good continuous reactor for the polymerization of vinyl monomers. Therefore, the two stage polymerization using filled tubular reactor is potentially a very important new industrial polymerization technology.

NOMENCLATURE

A_c : heat transfer area [cm^2]
 C_p : heat capacity of reaction mixture [$\text{cal/g}^\circ\text{K}$]
 C_i : concentration of component i [mol/L]
 D : inside tube diameter [cm]
 D_{ax} : axial dispersion coefficient [cm^2/min]
 h : heat transfer coefficient [$\text{cal/cm}^2\text{min}^\circ\text{K}$]
 ΔH : heat of reaction [cal/mol]
 I_i : initiator concentration [$i=A, B$], [mol/L]
 I_f : total initiator concentration of feed mixture [mol/L]
 I_{fi} : initiator concentration of feed mixture [$i=A, B$], [mol/L]
 k^* : thermal conductivity of polymer solution [$\text{cal/cm}^\circ\text{min}^\circ\text{K}$]
 k_{di} : peroxide decomposition rate constant [$i=A, B$], [min^{-1}]
 k_{tm} : chain transfer to monomer rate constant [$\text{L/mol}^\circ\text{min}$]
 $k_{tm,0}$: chain transfer to monomer rate constant at zero monomer conversion [$\text{L/mol}^\circ\text{min}$]
 k_{ts} : chain transfer to solvent rate constant [$\text{L/mol}^\circ\text{min}$]

k_i : initiation rate constant [$\text{L/mol}^\circ\text{min}$]
 k_p : propagation rate constant [$\text{L/mol}^\circ\text{min}$]
 k_t : termination rate constant [$\text{L/mol}^\circ\text{min}$]
 k_{t0} : termination rate constant at zero monomer conversion [$\text{L/mol}^\circ\text{min}$]
 L : total tubular reactor length [cm]
 M : monomer concentration [mol/L]
 M_f : feed monomer concentration [mol/L]
 M_n : number average molecular weight
 M_w : weight average molecular weight
 q : volumetric feed flow rate [mol/L]
 Re : Reynolds number
 T_c : coolant temperature [$^\circ\text{K}$]
 T_{c0} : coolant temperature of CSTR [$^\circ\text{K}$]
 T_{c1} : coolant temperature of tubular reactor in the first segment [$^\circ\text{K}$]
 T_{c2} : coolant temperature of tubular reactor in the second segment [$^\circ\text{K}$]
 T_f : feed temperature [$^\circ\text{K}$]
 T_R : reactor temperature [$^\circ\text{K}$]
 S' : initial solvent concentration in the reactor [mol/L]
 S_s : solvent concentration [mol/L]
 t : dimensionless time
 t' : time [min]
 u_z : axial velocity [cm/min]
 PD : polydispersity of polymer [M_w/M_n]
 Pe : Peclet number
 V : reactor volume [L]
 W_p : weight fraction of polymer
 $X_{I,i}$: dimensionless initiator concentration [$i=A, B$]
 X_M : dimensionless monomer concentration
 X_T : dimensionless temperature
 X_S : dimensionless solvent concentration
 $y_{A,i}$: mole fraction of initiator A in the initiator feed mixture
 Z : axial distance

Greek Letters

α : dimensionless heat transfer coefficient of CSTR
 β : dimensionless heat of reaction
 γ : dimensionless heat transfer coefficient of tubular reactor
 δ : dimensionless coolant temperature
 θ : mean residence time [min]
 ρ : density of reaction mixture [g/cm^3]
 ρ_m : density of styrene monomer [g/cm^3]
 ρ_3 : density of ethylbenzene [g/cm^3]
 $\lambda_{\xi,k}$: k -th moment of live polymeric species [$(\xi=u, v, w, u', v')$, [$k=0, 1, 2$)]
 $\lambda_{M',k}$: k -th moment of dead polymers [$k=0, 1, 2$]
 ξ : dimensionless distance

REFERENCES

- ATOCHEM, Technical Bulletin, Buffalo, NY (1986).
- Brandrup, J. and Immergut, E. H., *Polymer Handbook*, 3rd Edn, Wiley, New York (1989).
- Brooks, B. W., "Dynamic Behavior of a Continuous-Flow Polymerization Reactor", *Chem. Eng. Sci.*, **36**, 589 (1981).
- Carratt, G. M., Shervin, C. R. and Soong, D. S., "Experimental Study and Computer Simulation of a Two-Stage Continuous Polymerization Process for the Production of Methyl Methacrylate", *Polym. Eng. Sci.*, **24**(6), 442 (1984).

- Choi, K. Y., "Analysis of Steady State of Free Radical Solution Polymerization in a Continuous Stirred Tank Reactor", *Polym. Eng. Sci.*, **26**(4), 975 (1986).
- Cunningham, M. F., O'Driscoll, K. F. and Mahabadi, H. K., "Bulk Polymerization in Tubular Reactors I. Experimental Observations on Fouling", *Can. J. Chem. Eng.*, **69**, 630 (1991).
- Hamer, J. W., Akramov, T. A. and Ray, W. H., "The Dynamic Behavior of Continuous Polymerization Reactors-II. Nonisothermal Solution Homopolymerization and Copolymerization in a CSTR", *Chem. Eng. Sci.*, **36**, 1897 (1981).
- Hamer, J. W. and Ray, W. H., "Continuous Tubular Polymerization Reactors-I. A Detailed Model", *Chem. Eng. Sci.*, **41**(12), 3083 (1986).
- Henderson, L. S., "Stability Analysis of Polymerization in Continuous, Stirred Tank Reactors", *Chem. Eng. Prog.*, **83**(3), 42 (1987).
- Henderson, L. S., "Temperature Control of Continuous, Bulk Styrene Polymerization Reactors and the Influence of Viscosity: an Analytical Study", *Ind. Eng. Chem. Res.*, **28**, 1644 (1989).
- Hui, A. W. and Hamiele, A. E., "Thermal Polymerization of Styrene at High Conversion and Temperature. An Experimental Study", *J. Appl. Polym. Sci.*, **16**, 749 (1972).
- Jaisinghani, R. and Ray, W. H., "On the Dynamic Behavior of a Class of Homogeneous Stirred Tank Polymerization Reactors", *Chem. Eng. Sci.*, **32**, 811 (1977).
- Kim, K. Y. and Choi, K. Y., "Steady State Behavior of a Continuous Stirred Tank Reactor of Styrene Polymerization with Bifunctional Free Radical Initiators", *Chem. Eng. Sci.*, **43**(4), 965 (1988b).
- Kim, K. Y., Alexander, J. C. and Choi, K. Y., "Dynamics of a CSTR for Styrene Polymerization Initiated by a Binary Initiator System", *Polym. Eng. Sci.*, **30**(5), 279 (1990).
- Knorr, R. S. and O'Driscoll, K. F., "Multiple Steady State, Viscosity and High Conversion in Continuous Free Radical Polymerization", *J. Appl. Polym. Sci.*, **14**, 2683 (1970).
- Lynn, S., "Comments on Polymerization of Styrene in a Tubular Reactor", *AIChE J.*, **23**(3), 387 (1977).
- Mankin, J. C. and Hudson, J. L., "The Dynamics of Coupled Non-isothermal Continuous Stirred Tank Reactors", *Chem. Eng. Sci.*, **41**, 2651 (1986).
- Mallikarjun, R. and Nauman, E. B., "A Staged Multitubular Process for Crystal Polystyrene", *Polym. Proc. Eng.*, **4**(1), 31 (1986).
- Pryor, W. A. and Coco, J. H., "Computer Simulation of the Polymerization of Styrene. The Mechanism of Thermal Initiation and the Importance of Primary Radical Termination", *Macromolecules*, **3**(5), 500 (1970).
- Piirma, I. and Chou, L. P. H., "Block Copolymers Obtained by Free Radical Mechanism-I. Methyl Methacrylate and Styrene", *J. Appl. Polym. Sci.*, **24**, 2051 (1979).
- Schmidt, A. D. and Ray, W. H., "The Dynamic Behavior of Continuous Polymerization Reactors-I. Isothermal Solution Polymerization", *Chem. Eng. Sci.*, **36**, 1401 (1981).
- Schmidt, A. D., Clinch, T. A. and Ray, W. H., "The Dynamic Behavior of Continuous Polymerization Reactors-III. An Experimental Study of Multiple Steady States in Solution Polymerization", *Chem. Eng. Sci.*, **39**(3), 419 (1984).
- Taylor, T. W. and Reichert, K. H., "The Influence of Reactor Type and Operating Conditions on the Molecular Weight Distribution in Vinyl Acetate Polymerization", *J. Appl. Polym. Sci.*, **30**, 227 (1985).
- Thiele, R., "Dynamic Behavior and Stability of Continuous Reactor for Bulk Polymerization", *Ins. Chem. Eng. Symp. Ser.*, **87**, 125 (1984).
- Thiele, R., "Dynamic Behavior, Stability and Optimism Startup Regime for a Bulk Copolymerization Reactor", *Chem. Eng. Sci.*, **41**(4), 1123 (1986).
- Yoon, W. J. and Choi, K. Y., "Polymerization of Styrene in a Continuous Filled Tubular Reactor", *Chem. Eng. Sci.*, in press.
- Yoon, W. J. and Choi, K. Y., "Free Radical Polymerization of Styrene with a Binary Mixture of Symmetrical Bifunctional Initiators", *J. Appl. Polym. Sci.*, **46**, 1353 (1992).
- Yoon, W. J. and Choi, K. Y., "Kinetics of Free Radical Styrene Polymerization with the Symmetrical Bifunctional Initiator 2,5-Dimethyl-2,5-bis (2-Ethyl Hexanoyl Peroxy) Hexane", *Polymer*, **33**(21), 4582 (1992).