Modeling of "Living" Free-Radical Polymerization Processes. II. Tubular Reactors

Min Zhang, W. Harmon Ray

Department of Chemical Engineering, University of Wisconsin–Madison, 1415 Engineering Drive, Madison, Wisconsin 53706

ABSTRACT: A tubular reactor model for "living" free-radical polymerization is developed in this study. The model may be used as a tool to design efficient processes for tailored polymers from "living" free-radical polymerization. Examples presented include preparing bimodal polymers and copolymers of *n*-butyl acrylate and styrene. Residence time distribution effects on polymer properties are investi-gated by varying the Peclet number, to show the degree of backmixing that adversely affects polymer properties. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1047–1056, 2002

Key words: modeling; "living" free-radical polymerization; tubular reactor; bimodal polymer; residence time distribution

INTRODUCTION

In Part I[1] of this series, we present a stirred tank reactor model for "living" free-radical polymerization and showed that the residence time distribution can have a significant effect on polymer properties. Even with 16 continuous stirred tank reactors (CSTRs) in series, the polymer polydispersity at the outlet of the last reactor is somewhat higher than that for polymers prepared in a batch reactor with similar operating conditions. In this study we used a tubular reactor model to explore under what con-ditions a tubular reactor can be a better candidate for operating a continuous "living" free-radical po-lymerization process.

There has been very limited work reported on the use of tubular reactors for "living" free-radical po-lymerization. Shen et al.[2] reported on the continu-ous operation of methyl methacrylate atom transfer radical polymerization in a column reactor packed with silica gel–supported CuBr–HMTETA catalyst. It was found that the molecular weight increases linearly with respect to conversion at the exit, with some broadening in the molecular weight distribu-tions. They attributed this broadening to possible backmixing and polymer trapping in the pores of silica gel. Faliks et al.[3] used a simple model for nitroxide-mediated styrene polymerization in an idealized plug flow reactor with no residence time distribution. They proposed a control strategy through which the reaction time is reduced, while low polydispersity of polymer products is simulta-neously maintained by creating a distributed nitrox-ide radical flux along the tube. By contrast, here we used the detailed kinetic model developed in the earlier study[1] together with an axial dispersion tu-bular reactor model to analyze the interactions be-tween reactor behavior and "living" free-radical po-lymerization chemistry. In this way, we are able to determine the best type of reactor operation for the polymer product desired.

In practice, a tubular reactor may have significant radial mixing and axial dispersion, resulting from non-Newtonian rheology or the secondary flows aris-ing from bends in the tube, flow through fittings, and so forth. For example, these effects are demonstrated for a helical reactor by Stevens and Ray[4] and Paquet and Ray[5,6] where even for Reynolds numbers below 1000, the residence time distribution is much narrower and radial mixing much larger than would be pre-dicted from laminar flow. Built-in static mixers may also be intentionally inserted into the tube to achieve better radial mixing. Stevens and Ray[4] showed that a physically detailed three-dimensional CFD model can be closely approximated by an axial dispersion model for the purpose of designing a practically useful tubu-lar polymerization reactor. The axial dispersion model has been used previously to describe a variety of tubular polymerization reactors [emulsion polymer-ization (Paquet and Ray[5]) and condensation poly-merization (Hipp and Ray[6])]. Hence, it seems to be a good choice for studying "living" free-radical poly-merization.

In this study we used the tubular reactor axial dis-persion model to simulate single and multistage pro-

TABLE I
"Living" Free-Radical Polymerization Mechanisms

Initiation

Initiator
$$I \xrightarrow{fk_{inid}} 2P_0$$

Reversible reaction of
primary capped species
$$P_0 + CAP \xrightleftharpoons{k_{cappri}} \text{PriCapped}(+CAT)$$

Special initiation
$$y(i)M_i \xrightarrow{k_{spinii}} x(i)P_{\delta_i,i}$$

Chain initiation
$$P_0 + M_i \xrightarrow{k_{pi}} P_{\delta_i,i}$$

Propagation
Chain transfer
$$P_{\mathbf{n},j} + M_i \xrightarrow{k_{pij}} P_{\mathbf{n}+\delta_i,i}$$

to solvent
$$P_{\mathbf{n},j} + S \xrightarrow{k_{ctsj}} D_{\mathbf{n}} + S\cdot$$

to agent
$$P_{\mathbf{n},j} + CTA \xrightarrow{k_{ctCTAj}} D_{\mathbf{n}} + CTA\cdot$$

to monomer
$$P_{\mathbf{n},j} + M_i \xrightarrow{k_{ctMij}} D_n + P_{\delta_i,i}$$

spontaneous
$$P_{\mathbf{n},j} \xrightarrow{k_{ctspj}} D_{\mathbf{n}} + H\cdot$$

Reinitiation
$$S\cdot, CTA\cdot, H\cdot + M_i \xrightarrow{k_{pi}} P_{\delta_i,i}$$

Reversible capping reaction
$$P_{\mathbf{n},j} + CAP \xrightleftharpoons{k_{capj}} Q_{\mathbf{n},j}(+ CAT)$$

Degenerative reaction
Chain termination
$$P_{\mathbf{n},j} + Q_{\mathbf{m},i} \xrightleftharpoons{k_{cdij}} P_{\mathbf{m},i} + Q_{\mathbf{n},j}$$

by inhibitor
$$P_{\mathbf{n},j} + X \xrightarrow{k_{txj}} D_{\mathbf{n}}$$
$$P_0 + X \xrightarrow{k_{tx}} \text{fragments}$$

by disproportionation
$$P_{\mathbf{n},j} + P_{\mathbf{m},i} \xrightarrow{k_{tdij}} D_{\mathbf{n}} + D_{\mathbf{m}}$$

by combination
$$P_{\mathbf{n},j} + P_{\mathbf{m},i} \xrightarrow{k_{tcij}} D_{\mathbf{m}+\mathbf{n}}$$

Decomposition of dormant species
$$Q_{\mathbf{n}} \xrightarrow{k_{decomj}} D_{\mathbf{n}} + \text{fragments}$$

cesses for homopolymers, block copolymers, and polymers with functional groups.

MODEL DEVELOPMENT

Kinetic model

The kinetic model is described in detail in Part I.[1] The kinetic scheme consists of reactions such as initiation, propagation, termination, and chain-transfer reactions [to monomer, solvent, and chain-transfer agent (CTA)] in a conventional free-radical polymerization plus the reversible reactions between growing and dormant polymer chains that result in "living" free-radical polymerization (cf. Table I). As shown in Table II, the reaction system contains three kinds of polymer species: growing polymer $P_{\mathbf{n},j}$, dormant polymer $Q_{\mathbf{n},j}$, and dead polymer $D_{\mathbf{n}}$, where the vector $\mathbf{n}$ indicates the composition of the polymer and the index j indicates the monomer type of the end group. The method of moments[7] has been used to model the polymer population as shown in Table II.

Tubular reactor model

As discussed above, an axial dispersion model[8,9] is employed to represent the tubular reactor for "living" free-radical polymerization. A basic tube reactor unit is considered, which consists of only one tube with

TABLE II
General Polymer Chain and Moment Definitions

$P_{\mathbf{n},j} \equiv$ A growing polymer chain with n_i monomer units of type i and end groups of type j

$Q_{\mathbf{n},j} \equiv$ A dormant polymer chain with n_i monomer units of type i and end groups of type j

$D_{\mathbf{n}} \equiv$ A dead polymer chain with n_i monomer units of type i

Growing polymer moments

$$\mu_{\mathbf{f},j} \equiv \Sigma_{\mathbf{n}=1}^{\infty} \mathbf{n}^{\mathbf{f}} P_{\mathbf{n},j}$$

Dormant polymer moments

$$\nu_{\mathbf{f},j} \equiv \Sigma_{\mathbf{n}=1}^{\infty} \mathbf{n}^{\mathbf{f}} Q_{\mathbf{n},j}$$

Bulk polymer moments

$$\lambda_{\mathbf{f}} \equiv \Sigma_{\mathbf{n}=1}^{\infty} \mathbf{n}^{\mathbf{f}} [\Sigma_{j=1}^{N_{mon}} (P_{\mathbf{n},j} + Q_{\mathbf{n},j}) + D_{\mathbf{n}}]$$

two inlets (one is main feed and the other side feed) and one outlet, respectively. In conjunction with other utilities (e.g., mixer, splitter, etc.) and reactor models (e.g., tank) available in the POLYRED simulation package, more complex processes can be easily simulated by constructing a flowsheet. For example, if one wants to prepare diblock copolymers, a two-stage process with intermediate feed may be represented by two tubes in series, where the second monomer is fed into the side feed of the second tube.

To have a practically useful tubular "living" free-radical polymerization model for design purposes, this basic tube unit has to satisfy the following requirements: (1) the model must be simple enough that it is computationally efficient to solve; (2) the model must have all essential features of a tubular reactor, allowing for various operating conditions by adjusting as few parameters as possible; (3) the model must be capable of describing various tube operation conditions (e.g., isothermal, jacket temperature driven, adiabatic, or wall-cooled nonisothermal operation). The model assumes that

- The reactant mixture is homogeneous.
- Only axial dispersion is considered. An empirical axial dispersion coefficient is used to describe the axial mixing in the reactor and to characterize the residence time distributions. By using a tracer experiment, the axial dispersion coefficient can be easily measured for a tubular reactor. At each specific position along the tube, perfect radial mixing and a uniform velocity profile are assumed. These assumptions are justified by the secondary flows attributed to the use of static mixers or for empty tubes, the presence of tube bends, or other fittings producing radial mixing. The tube, therefore, can be modeled as a one-dimensional tubular reactor.
- Instantaneous fluid dynamics are assumed because of the incompressibility of the liquid mixture; thus, the calculation of the velocity profile is simplified. The mass flow rate remains constant under this assumption, implying that any density changes are immediately compensated for by the velocity profile along the tube. The relationship between the bulk average axial velocity v_z and the inlet mass flow rate $\dot{m}|_{\text{inlet}}$ is given by

$$v_z = \frac{(\rho A v_z)|_{\text{inlet}}}{\rho A} = \frac{\dot{m}|_{\text{inlet}}}{\rho A} \quad (1)$$

where ρ denotes the reactant mixture density and A the cross-sectional area of the tube.

A mass balance equation for each chemical species, C_j, is given by

$$\frac{\partial C_j}{\partial t} + \frac{\partial(v_z C_j)}{\partial z} - \mathcal{D}_{\text{(eff)}} \frac{\partial^2 C_j}{\partial z^2} = R_{C_j} \quad (2)$$

where $\mathcal{D}_{\text{(eff)}}$ is the dispersion coefficient, R_{C_j} denotes the growth term of species j due to reactions and

$$C_j = C_I, C_{M_i}, C_S, C_T, C_X, C_{P_0}, \mu_{0,j}, \mu_{\delta_i,j}, \nu_0, \nu_{\delta_i}, \lambda_0, \lambda_{\delta_i}, \lambda_2$$

Considering the accumulation of enthalpy due to flow, dispersion, reaction, and wall cooling, the energy balance equation can be written as

$$\frac{\partial T}{\partial t} + \frac{\partial(v_z T)}{\partial z} = \alpha_{\text{(eff)}} \frac{\partial^2 T}{\partial z^2}$$

$$+ \frac{1}{\rho C_p} \left[\sum_{r=1}^{NR} (-\Delta H)_r R_r + \frac{4U}{D}(T_c - T) \right] \quad (3)$$

where $\alpha_{\text{(eff)}} = k_{\text{(eff)}}/\rho C_p$ is the effective thermal diffusivity.

The axial dispersion model requires one initial condition and two boundary conditions, given that the partial differential equations involved are of second order. In this study a uniform initial condition is usually imposed for all species. At the reactor entrance, Danckwerts boundary conditions are used:

$$C_j|_{z=0} = C_j|_{\text{inlet}} + \frac{\mathcal{D}_{\text{(eff)}}}{v|_{z=0}} \frac{dC_j}{dz}\bigg|_{z=0}$$

$$T|_{z=0} = T|_{\text{inlet}} + \frac{\alpha_{\text{(eff)}}}{v|_{z=0}} \frac{dT}{dz}\bigg|_{z=0} \quad (4)$$

so that zero gradients are assumed at the reactor exit

$$\frac{dC_j}{dz}\bigg|_{z=1} = 0 \quad (5)$$

$$\frac{dT}{dz}\bigg|_{z=1} = 0 \quad (6)$$

For simplicity, the dimensionless Peclet number for mass and energy dispersion has been introduced to characterize the influence of the dispersion

$$\text{Pe}_{\text{mass}} = \frac{Lv_z}{\mathcal{D}_{\text{(eff)}}} \quad (7)$$

$$\text{Pe}_{\text{thermal}} = \frac{Lv_z}{\alpha_{\text{(eff)}}} \quad (8)$$

Solution techniques

The model consists of a system of nonlinear partial differential equations. For good performance in "living" free-radical polymerization, one expects the tubular reactor to operate at large values of Peclet num-

TABLE III
Styrene Polymerization in the Presence of Alkoxyamine at the PFR Limit: Operating Conditions

$[\text{St}]_f$	$[\text{Alkoxyamine}]_f$	Temperature	Feed rate
8.0 mol/L	0.020mol/L	125°C	$0.02 \text{cm}^3/\text{s}$

ber, in the near plug flow limit, so that the effects of residence time distributions on "living" free-radical polymerization chemistry are relatively small. However, this can result in a steep front moving through the reactor during the startup and steep gradients for some species [e.g., the moments of dormant polymer chains in atomic transfer radical polymerization (ATRP)] at the tube entrance, even for steady-state operation. Thus, we expect the system is quite stiff in space. We have found that the method of orthogonal collocation on finite elements[10] is able to resolve the steep profile and works well over the entire range of Peclet numbers. The discretization of the model equations and boundary conditions is accomplished through the method of ordinates, transforming the spatial differentials into algebraic sums. The discretization yields a set of ordinary differential equations for concentrations of each species, temperature, and moments, one for each collocation point in space. The zeros of the well-known Jacobi polynomials in the interval of interest determine the collocation grid.

DDASPK, a modified version of DDASSL,[11] was used as the integrator, which implicitly solves systems of differential–algebraic equations by means of a multistep predictor–corrector method. It uses a variable step size, variable order, fixed leading coefficient implementation of backward differentiation formulae (BDF) to advance the solution from one time step to the next. A modified damped Newton method is used
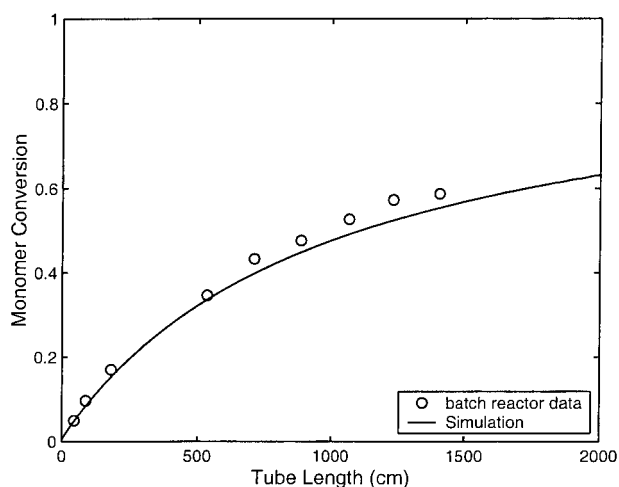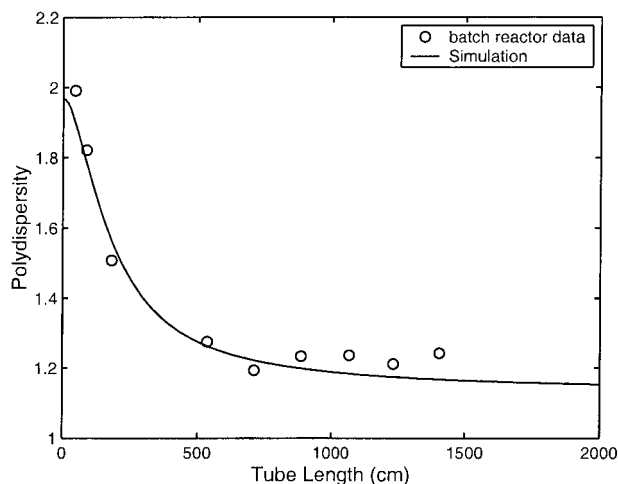

Figure 2 Polydispersity for styrene polymerization in the presence of alkoxyamine. The figure shows experimental data in a batch reactor from Tsujii et al.[12] and tube steady-state simulation results at the PFR limit.

to solve the corrector. Numerical experience shows that the rate of convergence of this iteration technique is usually quite fast. The complete set of discretized ordinary differential equations for concentrations of each species, temperature, and the moment equations finally are sent to DDASPK for integration.

RESULTS AND DISCUSSION

TEMPO-mediated styrene polymerization

The polymerization of styrene in the presence of stable nitroxide radicals [e.g. 2,2,6,6-tetramethypiperidinyl-1-oxy (TEMPO)] is one of the most studied "living" free-radical polymerization systems. For example,

Figure 1 Monomer conversion for styrene polymerization in the presence of alkoxyamine. The figure shows experimental data in a batch reactor from Tsujii et al.[12] and tube steady-state simulation results at the PFR limit.
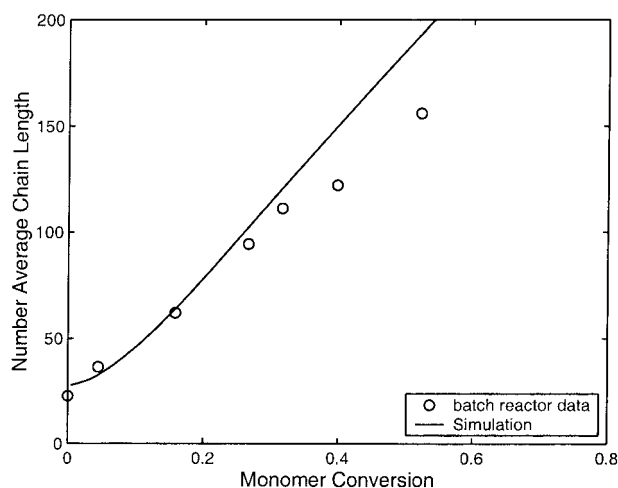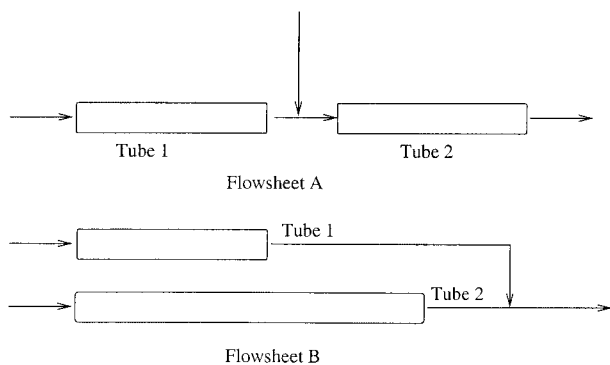

Figure 3 Dependency of number-average chain length with respect to monomer conversion for styrene polymerization in the presence of alkoxyamine. The figure shows experimental data in a batch reactor from Tsujii et al.[12] and steady-state PFR simulation results.

Figure 4 Two possible flowsheets that can be used to prepare polymers with bimodal distributions.

Figure 5 Polymers with bimodal distribution can be easily prepared through a tubular process for styrene polymerization in the presence of alkoxyamine.

Tsujii et al.[12,13] studied bulk styrene polymerization using alkoxyamine as initiator with an initial concentration of 0.02 mol/L in a batch reactor at 125°C. Alkoxyamine are preformed by either reacting peroxides and/or diazo initiators with the corresponding nitroxide radicals or reacting a large amount of nitroxide radicals with radicals from the thermal initiation of monomer. Initiation from preformed alkoxyamines permits the introduction of a specified number of polymer chains and allows for better control of polymer chain architecture compared to the case where chemical initiators are reacted with nitroxide *in situ*. Here we use this system for validation of our model.

Plug flow reactor

As is well known, the axial dispersion model must converge to the behavior of plug flow reactor (PFR) once the Peclet (Pe) number becomes large. When a tube contains a large number of built-in static mixers, bends or tight coils, and is sufficiently long, the Peclet number can be very large. For instance, Paquet et al.[5] found that the Peclet number could be as high as 600 for an experimental helical coil tubular reactor for emulsion polymerization. Under such a high Peclet number, the tube performs like a plug flow reactor. Simulations of such a case can check the validity of the model for the PFR-limiting case. The behavior of a batch reactor is the same as that for a plug flow tubular reactor at steady state; thus, the batch experimental data from Tsujii et al.[12,13] for styrene polymerization using alkoxyamine as the initiator will be compared with our model predictions. The reaction time in the batch reactor is converted to equivalent reaction
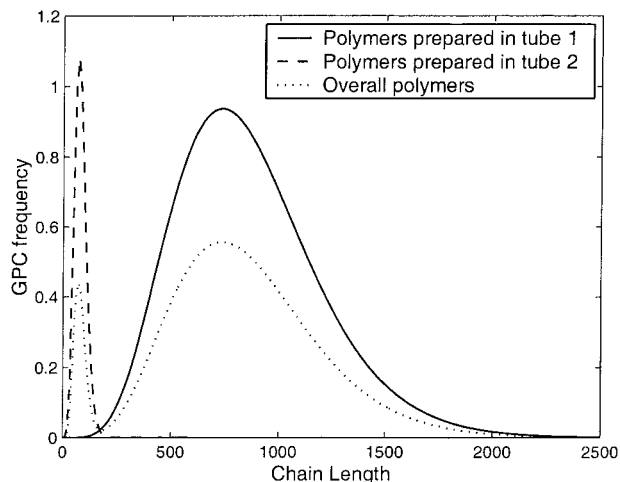
time in the tube at a specific tube length ($z = v_z t$), allowing the comparisons between the two systems. In the model simulation, a Peclet number of 500 is chosen to represent the PFR limit. The operating conditions for the tube are shown in Table III and the kinetic and physical parameters are the same as those used in the earlier companion study.[1]

Figure 1 shows excellent agreement for monomer conversion; Figure 2 shows the development of polydispersity along the tube at steady-state; whereas Figure 3 shows the dependence of number-average chain length on monomer conversion. The match with the experiment is quite good except for higher conversion measurements of chain length. These two experimental points are inconsistent with the other data and could not be modeled earlier with a batch reactor model (see companion study[1]). Thus the tubular reactor model performs very well in the limit of plug flow (Pe large).

Preparation of bimodal polymers

Because "living" free-radical polymerization is capable of preparing polymers with a narrow molecular weight distributions, it is also straightforward to use this mechanism to prepare polymers with bimodal molecular weight distributions. Figure 4 shows two possible flowsheets that can be used to prepare such bimodal polymers. In flowsheet A, two tubes in series

TABLE IV
Operating Conditions and Design Parameters of Two Tubes in Parallel for Preparation of Bimodal Polymer

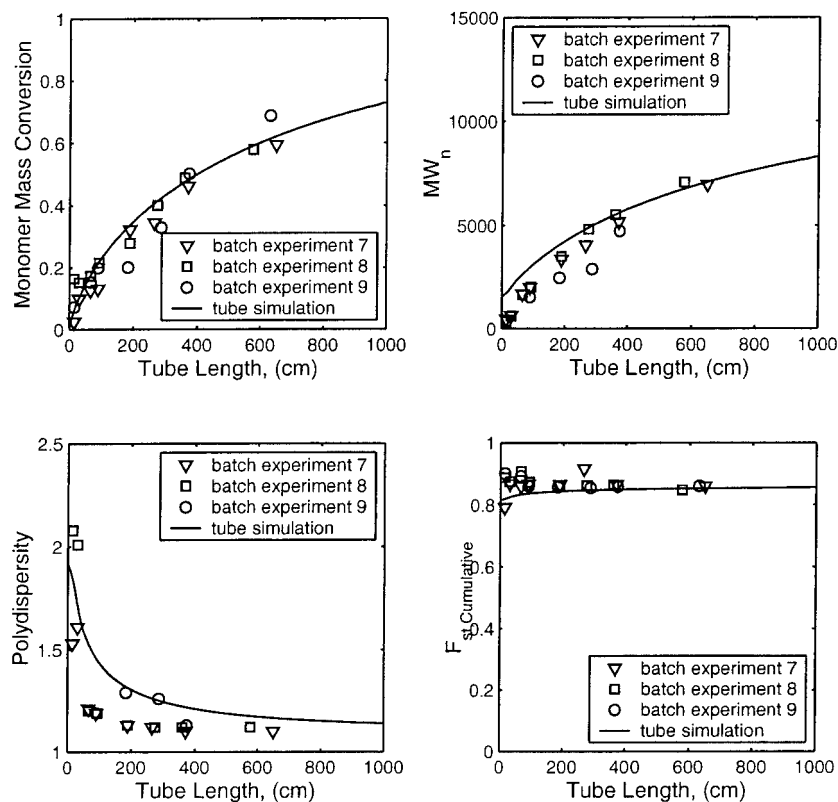| Tube	$[St]_f$	$[Alkoxamine]_f$	Temperature	Feed rate	Tube length	Tube diameter
1	8.0 mol/L	0.01 mol/L	125°C	1 cm³/s	4000 cm	5 cm
2	8.0 mol/L	0.08 mol/L	125°C	1 cm³/s	2000 cm	5 cm

Figure 6 Model predictions for ATRP of styrene and *n*-butyl acrylate. The figure shows experimental data in a batch reactor from Arehart et al.[14] and tube steady-state simulation results at the PFR limit.

are constructed. A mixture of alkoxyamine and styrene are fed into the first tube, allowing chains to build up to a certain chain length; then the product from the first tube is combined with an intermediate feed also containing alkoxyamine and fresh styrene monomer, before going to the second tube. Thus, two populations of polymer chains can be prepared, each having a specified average chain length and a low polydispersity. A second alternative is to use two tubes with different lengths in parallel as shown in flowsheet B. The products from each tube are finally blended to yield bimodal polymer.

We will simulate flowsheet B to demonstrate the product that can be made. The details of operating conditions and reactor parameters are shown in Table IV. Each tube assumes a Peclet number of 50. Simulations show that the polydispersity of polymer at the exit of tube 1 is 1.22 and the number-average chain length is 602, whereas the polydispersity of polymer at

the exit of tube 2 is 1.16 and the number-average chain length is 61. The overall polymer has a bimodal distribution with polydispersity of 3.5 and number-average chain length of 132. Figure 5 shows the molecular weight distribution curves of the polymers at the exit of each tube and the overall blend by assuming that the polymers obey a Schultz distribution with the moments noted.

Atom transfer radical copolymerization of styrene (St) and *n*-butyl acrylate (BA)

Now we will illustrate the applications of a tubular reactor model for "living" free-radical copolymerization using another important system: the ATRP of styrene and *n*-butyl acrylate. We first compare the tubular reactor simulations at the plug flow limit with the data of Arehart et al.[14] The kinetic parameters are given in Part I.[1] The Peclet number in the tube is 500.
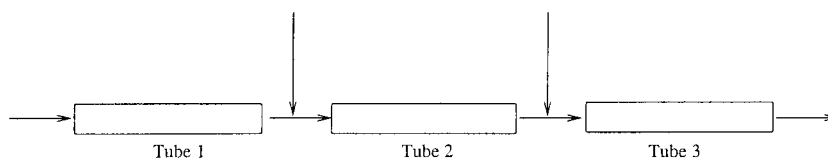

Figure 7 Flowsheet of three tubes in series. This flowsheet aims to efficiently incorporate *n*-butyl acrylate into polystyrene chains.

TABLE V
Operating Conditions of Three Tubes in Series for Preparation of Polystyrene with Precisely
Distributed *n*-Butyl Acrylate in the Middle

Condition	Tube		
	1	2	3
Feed condition	$[St]_f = 8.14$ mol/L $[BA]_f = 0$ $[MBP]_f = 0.065$ mol/L $Q_f = 1$ cm^3/s	Determined by the upstream	Determined by the upstream
Side feed condition	$[St]_{sf} = 0$ $[BA]_{sf} = 0$ $[MBP]_{sf} = 0$ $Q_{sf} = 0$	$[St]_{sf} = 0$ $[BA]_{sf} = 6.34$ mol/L $[MBP]_{sf} = 0$ $Q_{sf} = 0.04$ cm^3/s	$[St]_{sf} = 8.14$ mol/L $[BA]_{sf} = 0$ $[MBP]_{sf} = 0$ $Q_{sf} = 0.5$ cm^3/s

Figure 6 shows a comparison of the model predictions with data for monomer conversion, number-average chain length, polydispersity, and cumulative copolymer composition (fraction of styrene). The model does a good job of matching the data.

Now let us consider an example of ATRP of styrene and *n*-butyl acrylate in which the precise incorporation of *n*-butyl acrylate into polymer chains is achieved using a tubular reactor. Let us present a flowsheet that consists of three tubes in series (cf. Fig. 7). Styrene monomer combined with primary capped species is charged into the first tube, allowing polymerization to proceed. In the first tube, polymer chains are extended to a desired chain length that can be controlled by the feed rate, operating temperature, feed compositions, and so forth. Then a mixture of styrene and a small amount of *n*-butyl acrylate is charged into the second tube through a side feed. The length of the second tube allows a high conversion of *n*-butyl acrylate. In the third tube, fresh styrene is fed into the reactor through side feed to extend the chain, mainly the styrene block. The details of simulation parameters are listed in Table V. Exiting the third tube is the polymer product made up of polystyrene chains with a small fraction of *n*-butyl acrylate in the middle of the chain. Model predictions for this process where Pe = 50 in each tube are shown in Figure 8.
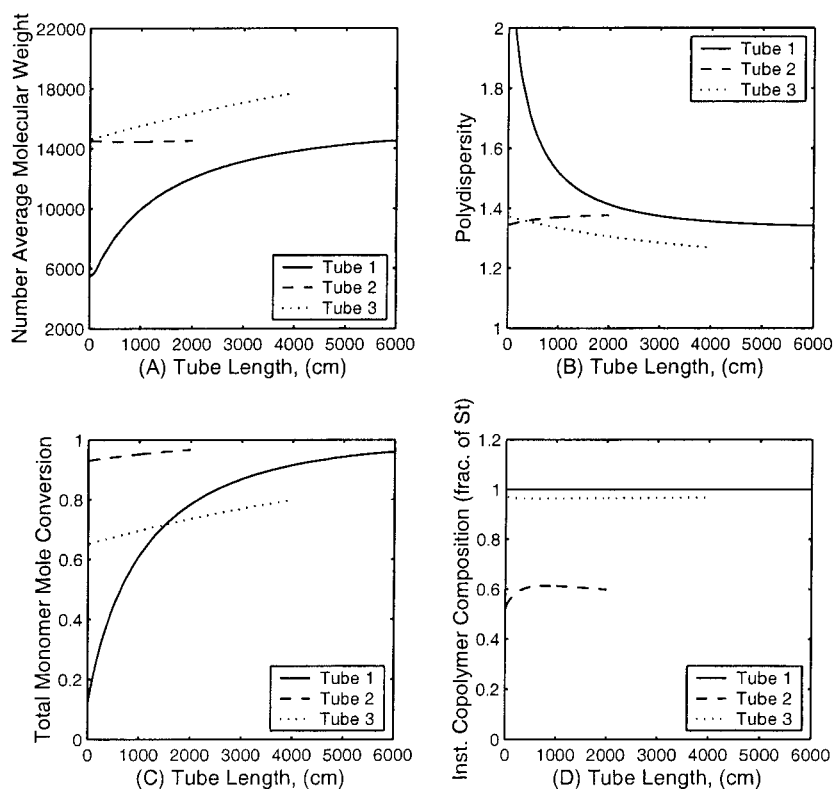

Figure 8 Development of important polymer properties in three tubes in series. Efficient incorporation of *n*-butyl acrylate into polystyrene chain is achieved in this process.

$[MBP]_f$	$[St]_f$	$[BA]_f$	Temperature	Feed rate
0.06462	3.9822 mol/L	3.2355 mol/L	110°C	1 cm³/s

The first and second tube are 6000 and 2000 cm in length, respectively, whereas the third tube is 4000 cm. All tubes have a diameter of 5 cm. Because of the "living" nature of the kinetics, persistent chain growth is maintained in all three tubes. In the first tube, the molecular weight distribution quickly becomes narrow and this trend is maintained in the second and third tubes so that the final polymer has a polydispersity of approximately 1.2. As planned, a polystyrene block is formed in the first tube, and in the second tube the incorporation of a 60% *n*-butyl acrylate block occurs. In the third tube, more styrene is introduced, allowing the polymer chain to further extend with a predominately styrene. Other chain architecture can be made in multiple tube stages in a similar way.

Effects of peclet number

The key issue in designing a tubular reactor to have a narrow residence time distribution is to achieve good radial mixing and have a sufficiently large value of Peclet number. One way this can be achieved is by using internal static mixing elements. For example, one built-in static mixer with length equal to tube diameter contributes approximately 2 to the total Peclet number and gives excellent radial mixing. Thus the total Peclet number of such a tube is about $2n$, where n is the total number of the built-in static mixers in the tube. By knowing the Peclet number, the effective axial dispersion coefficient $\mathscr{D}_{(eff)}$ can be estimated by $Pe = (v_z L/\mathscr{D}_{(eff)})$, where v_z is the velocity and L is the characteristic tube length. In the case of an empty tube, the effective diffusivities can be estimated through empirical correlations. For example, for a helical reactor, radial mixing is greatly enhanced because of the secondary flows normal to the axis; in this case, a correlation can be used to estimated the effective diffusivity[4]:

$$\frac{D_{(effective)}}{D_{(molecular)}} = 1.0 + 0.166(ScGr)^{0.22} \qquad (9)$$

where $D_{(effective)}$ is the effective diffusivity, $D_{(molecular)}$ is the molecular diffusivity, Sc is the Schmidt number, and Gr is the Grashof number. Thus one can design a tubular reactor with a narrow residence time distribution by using static mixers, helical coils, or sufficiently frequent bends in the tube.

To illustrate the effect of the Peclet number on the performance of a tubular reactor for "living" free-

radical polymerization, we chose the ATRP of styrene and *n*-butyl acrylate. The operating conditions can be found in Table VI. The kinetic parameters are as before. The simulation results are for steady-state operation.

Figure 9 shows the influence of Peclet number on the reactor performance and polymer properties. When the Peclet number is 0.01, the tube is really a perfectly mixed tank and there are uniform axial profiles. As the Peclet number is increased above 16, the monomer conversion and polymer molecular weight profiles begin to be insensitive to Pe. However, the other polymer properties are somewhat dependent on the Peclet number, even up to Pe = 500. For all values of Peclet number above 16, the average molecular weight increases linearly with conversion; however, the value of polydispersity achieved or the particular type of taper in the copolymer composition depends
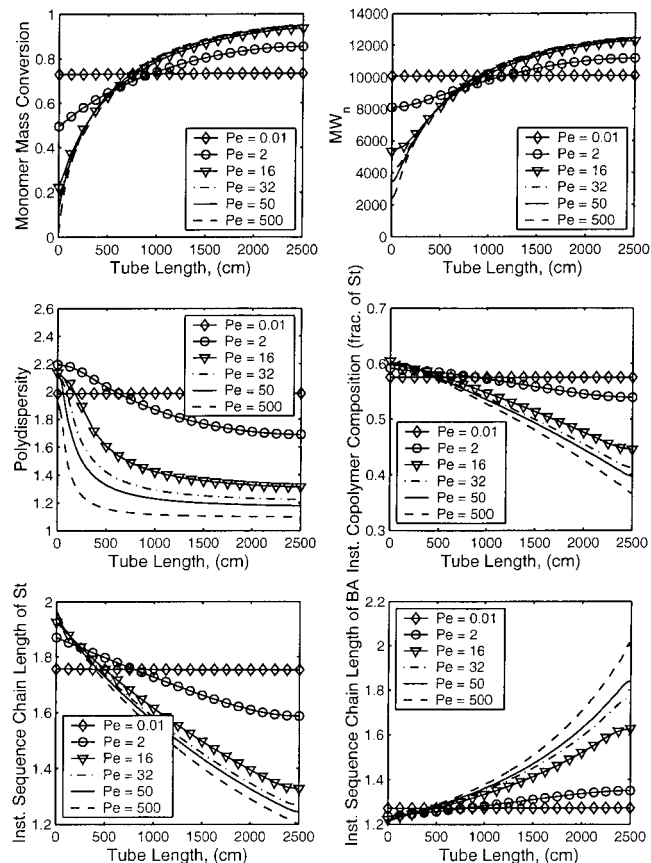

Figure 9 Effects of Peclet number on monomer mass conversion and polymer properties for ATRP of styrene and *n*-butyl acrylate.

TABLE VII
Operating Conditions of Two Tubes in Series for Preparation of Polymers with a
Uniform Copolymer Composition and a Narrow MWD

Condition	Tube	
	1	2
Feed condition	$[St]_f = 3.98$ mol/L	Determined by the upstream
	$[BA]_f = 3.24$ mol/L	
	$[MBP]_f = 0.065$ mol/L	
	$Q_f = 1$ cm^3/s	
Side feed condition	$[St]_{sf} = 0$	$[St]_{sf} = 8.14$ mol/L
	$[BA]_{sf} = 0$	$[BA]_{sf} = 0$
	$[MBP]_{sf} = 0$	$[MBP]_{sf} = 0$
	$Q_{sf} = 0$	$Q_{sf} = 0.03$ cm^3/s

on the value of the Peclet number. For Pe = 32, a polydispersity of 1.2 and a taper from 0.61 to 0.41 styrene content is possible, whereas for Pe = 500, a polydispersity of 1.1 and a taper from 0.61 to 0.37 results. The point is that a value of the Peclet number in the range of 20–30 might be adequate for many applications, and this would be easy to achieve experimentally.

Preparation of polymers with a uniform copolymer composition and a narrow MWD

In the previous section, we have shown that, for a single tube, the final polymer products will have a composition taper because monomer composition changes along the tube. However, if one uses multiple tubes in series with intermediate feed of the more reactive monomer, the monomer and polymer composition can be maintained nearly constant along the tube.

Let us illustrate through an example, again using the atom transfer radical polymerization of styrene and *n*-butyl acrylate. The flowsheet consists of two tubes in series. Each tube is 400 cm long and has a diameter of 5 cm. The operating conditions for each tube are shown in Table VII. Each tube is assumed to have a Peclet number of 50. As shown in Figure 10, persistent chain growth with polydispersity of 1.2 is predicted, and the chain composition is essentially uniform. Thus a narrow MWD and a uniform compo-
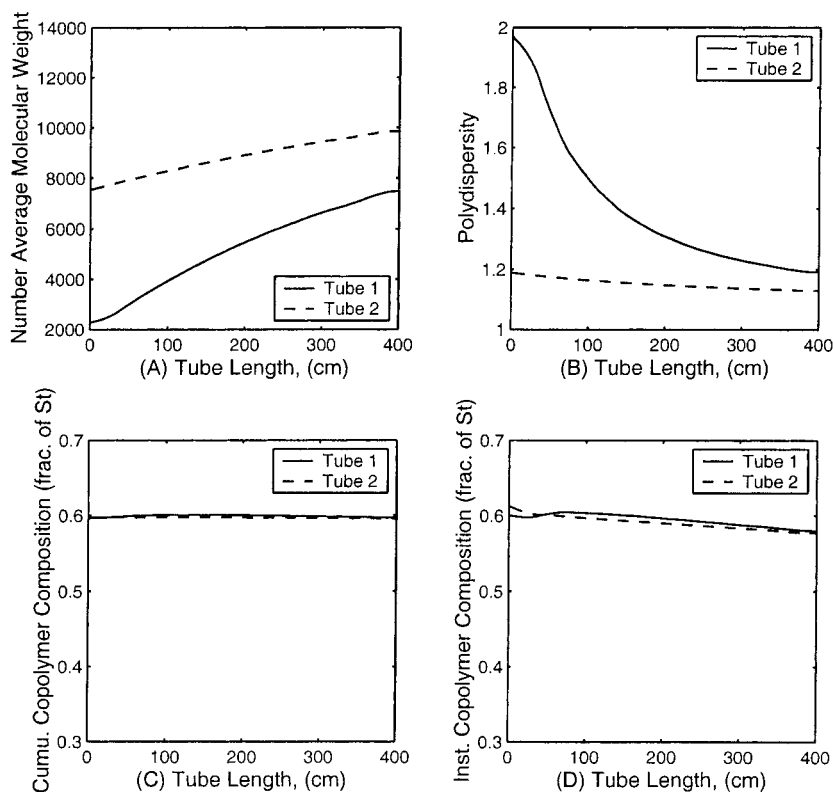

Figure 10 Using interstage feed to prepare polymers with uniform copolymer composition and narrow polydispersity.

sition and chain sequence distribution are possible from this operation.

One might note in Figures 3, 6, and 8–10 that the molecular weight at short times may seem larger than expected. This has nothing to do with tubular reactor behavior; indeed, this effect was seen in Part I for batch reactors in experiments and for reactor model predictions. As explained in Part I, when the initiating species is a dormant species (as is the case here), the rate of reversible formation of growing radicals may be slow enough that it takes some time for all dormant species to have a chance to grow. In this case, at short times a small number of growing radicals are the only ones polymerizing and can grow to significant chain length before being captured by the capping agent. It is this small population that is of a long chain length initially and has a polydispersity close to 2. As time progresses, the rest of the dormant chains have their opportunity to grow and linear chain growth with conversion ensues, with a corresponding drop in polydispersity. Because this initial fraction of polymer is tiny compared to the final amount of polymer produced, there is no significant effect on the final product for sufficiently long chains.

CONCLUSIONS

We have developed a tubular reactor model for "living" free-radical polymerization. The model has been validated at the plug flow reactor limit using batch experimental data for both TEMPO-mediated styrene polymerization and atom transfer radical copolymerization of styrene and n-butyl acrylate. Examples of the production of more complex polymer products such as bimodal polymers and controlled chain composition profile are demonstrated. The effects of resi-

dence time distribution and the effect of Peclet number on reactor operation and polymer properties are also discussed. It is shown that, by using an interstage feed of the more reactive monomer, polymers with a uniform copolymer composition and a narrow MWD can be prepared with tubular reactors.

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