Optimization of living polymerization through distributed control of a nitroxide radical

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Abstract

An optimal control methodology is applied to the goal of lowering the reaction time while maintaining low polydispersity in living free-radical polymerization. An illustration using a nitroxide radical profile for living free-radical polymerization of styrene in a plug flow reactor is provided. The reactor designs show that a distributed nitroxide radical flux along the length of the reactor can reduce the reaction time significantly for a given conversion. The reduction in residence time comes at the expense of a modest increase in polydispersity. A reference simulation with no optimization shows a conversion of 85% after 70 h and a final polydispersity of 1.31. Optimization of a 2,2,6,6-tetramethyl-1-piperidinyloxy flux results in a conversion of 90% after only 46 h while the polydispersity rises slightly to 1.42. The majority of the conversion takes place in the first 35 h. The theoretical designs, although not proven to be globally optimal, are of high quality. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Living free-radical polymerization is an attractive process because it offers controlled end-functionality, chain topology and composition, preparation of block copolymers, etc. In particular, it may avoid the high polydispersity associated with conventional free-radical polymerization as well as the shortcomings of ionic polymerization, in which high purity monomers and solvents and anhydrous conditions are often demanded. Despite the debate on the terminology [1], low polydispersity in living or controlled free-radical polymerization is achieved by using reversible capping of growing polymer chains in a free-radical polymerization resulting in a *pseudo-living* polymer that is capable of chain growth [2].

Living polymerizations most frequently proceed with polar growing species such as ions or organometallic compounds [3]. In such systems, the active chains interact with the monomer and may sometimes terminate in reactions with impurities or terminators that are added to the system. Chain ends, however, do not interact with each other due to electrostatic repulsions. In free-radical polymerization, however, the growing species are free radicals that can easily interact with each other via coupling or disproportionation leading to broad polydispersities. It is thus inherently difficult to achieve a true living radical polymerization in the same sense as living ionic polymerization. It is possible, by careful adjustment of the reaction conditions, to prepare a controlled system where interactions between growing chains are limited.

Several studies have succeeded in creating these controlled systems where a stable free radical that can reversibly terminate a growing chain is added to a free-radical system [2–5]. Polymers with narrow molecular weight distributions have been synthesized with the use of the stable free radical 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). Such nitroxides react with growing free-radical polymer chains, acting as strong polymerization inhibitors [6]. The reaction of nitroxides with carbon-centered radicals proceeds at nearly diffusion-controlled rates [7]. This living free-radical polymerization results in polydispersities comparable to those obtained by anionic polymerizations and below the theoretical limiting polydispersity of 1.5 for conventional free-radical polymerization [8]. However, the

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polymerization often requires a very long reaction time to achieve reasonably high yields, which hinders its industrial applications. There have been several methods for lowering the reaction time while maintaining low dispersity [9–14].

None of these efforts, however, have attempted to optimize the distribution of mass (e.g. stable free radical) along the reactor length. Consequently, the polymer yields from any particular reactor design represent a lower bound on what may be achieved. Thus, it is desirable to explore the improved polymer yields from an optimal design of distributed chemical flux along the length of the reactor. In particular, the long reaction times of living free-radical polymerization may be shortened significantly by an optimal chemical flux.

The aim of this paper is to show that a special design of a TEMPO flux along the side of a tubular plug flow reactor (PFR) may produce a polymer of a desired average molecular weight with as narrow a molecular weight distribution as possible while maintaining the highest possible conversion. Here, we apply a previously developed optimal control methodology for a PFR with a variable mass flux along the reactor's length [15]. This methodology has been applied to complex reaction mechanisms and high quality solutions were obtained [15]. While the reactor model is similar to the one in that paper, the chemical model has been replaced with a styrene living polymerization mechanism.

In this article, the reactor model is presented and an optimal control design is demonstrated to improve upon a simulation that does not incorporate distributed control. The applicability of the process for laboratory implementation is also discussed.

2. Modeling

2.1. Physical formulation of the flow reactor

A PFR was chosen as the basic reactor configuration. The PFR is a cylinder with constant cross-sectional area and length L. Control is implemented through chemical and/or heat flux through the sidewall of the reactor as a function of the position l along its length. The reactions are described by the production rate w_i of the i-th species, $i = 1, 2, ..., n$. The control variables are the fluxes of species i, denoted as j_i (mass/length-time), and the heat flux, q (energy/length-time), as a function of position l. The mass fraction of species i in the reactor is denoted as $x_i(l)$, and the total mass flow rate is $F(l)$.

The following assumptions were made in modeling the PFR: (i) steady one-dimensional plug flow; (ii) instantaneous radial mixing; (iii) no diffusion along the axis of the reactor; and (iv) adiabatic reaction conditions. To make the assumptions realistic, the ratio of the length of the reactor to its radius was chosen to be greater than 25.

Since there are two sources of material flowing into the system (a co-feed and an axial mass flux), the total mass balance for the flow rate is

$$F(l) = F(0) + \int_0^l \sum_{i=1}^n j_i \, dl. \tag{1}$$

By taking a differential control volume at position l and balancing the input and output mass and energy, we can arrive at the equations governing the composition in the reactor [15]:

$$\frac{dx_i}{dl} = \frac{1}{F}\left(w_i - x_i \sum_{k=1}^n j_k + j_i\right), \tag{2}$$

$$\frac{dT}{dl} = \frac{1}{F \sum_{i=1}^n C_{pi} x_i}$$

$$\times \left((T_0 - T)\sum_{i=1}^n C_{pi} j_i - \sum_{i=1}^n H_{fi} w_i - T \sum_{i=1}^n C_{pi} w_i + q\right), \tag{3}$$

where q is the heat influx, H_{fi} the heat of formation of species i, and C_{pi} the corresponding specific heat. T_0 is the temperature of the influxed species.

The optimal control methodology is described in Rojnuckarin et al. [15,16]. In the calculations, the CONMIN [17] code was used as the conjugate gradient minimizer; the chemical kinetics package CHEMKIN-II [18] was employed to interface the thermodynamic and kinetics data, and LSODA [19] was used as a differential equation integrator.

2.2. Polymerization model

The free-radical polymerization mechanism [2,20–23] consisted of the following key steps that were considered in this modeling work:
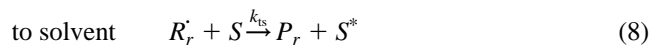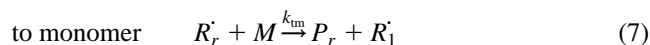
Initiation

$$I \xrightarrow{k_d} 2R_c \tag{4}$$

$$R_c + M \xrightarrow{k_{p1}} R_1^{\cdot} \tag{5}$$

Propagation

$$R_r^{\cdot} + M \xrightarrow{k_p} R_{r+1}^{\cdot} \tag{6}$$

Chain transfer

to monomer $\quad R_r^{\cdot} + M \xrightarrow{k_{tm}} P_r + R_1^{\cdot} \tag{7}$

to solvent $\quad R_r^{\cdot} + S \xrightarrow{k_{ts}} P_r + S^* \tag{8}$

Termination

combination $\quad R_r^{\cdot} + R_s^{\cdot} \xrightarrow{k_{tc}} P_{r+s} \tag{9}$

disproportionation $\quad R_r^{\cdot} + R_s^{\cdot} \xrightarrow{k_{td}} P_r + P_s. \tag{10}$
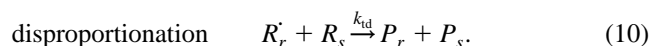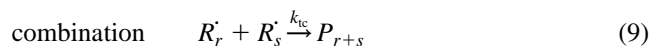
Table 1
Rate parameters (rate constant units not shown are $l\,s^{-1}\,mol^{-1}$, activation energies are in calories)

$k_d = 6 \times 10^{-4}\,s^{-1}$
$k_{p1} = 1.255 \times 10^9\,\exp[-1680/RT]$
$k_p = 1.051 \times 10^7\,\exp[-7060/RT]$
$k_{tm} = 2.31 \times 10^6\,\exp[-12670/RT]$
$k_{ts} = 5.92 \times 10^8\,\exp[-17210/RT]$
$k_{tc} = 9.98 \times 10^5$
$k_{td} = 1.10 \times 10^7\,\exp[-3750/RT]$

Here, I represents the initiator, M is the monomer (styrene, in this study), S is the solvent, $R_r^{\cdot}$ is a growing polymer of length r, and P_r is a dead polymer of length r. R_c is a radical that is formed from the initiator and S^* is a radical fragment of the solvent. The rate constants used are given in Table 1 [2,20–23].

Yamada et al. [22,24] have shown that the rate of propagation for polystyrene radicals remains constant over the degree of polymerization range $40 \leq r \leq 410$. In addition, they have also demonstrated [22,25] that the propagation rate remains constant at higher conversion. Due to the gel effect, the termination rate does not remain constant, but decreases because of the increased viscosity that results from increases in the molecular weight of the polymer chains. The gel effect has been incorporated into the mechanism by considering the effective rate of termination, k_t as a function of monomer conversion, m:

$$k_t = k_{tc} + k_{td} = A_t\,\exp[-Ea/RT]g^2(m), \tag{11}$$

where k_{tc} and k_{td} are the recombination and disproportionation termination constants, respectively, and,

$$g(m) = \begin{cases} 1 & \text{as } 0 \leq m \leq m_1 \\ 0.5093 + 2.4645m - 3.7473m^2 & \text{as } m \geq m_1 \end{cases} \tag{12}$$

where m_1 is the monomer conversion at which the gel effect is appreciable, and is equal to 0.3 in our model [23,26].

Thermodynamic data for heat capacity and heat of formation of styrene were taken from Gaur and Wunderlich [27], by a fit of the data in Table 3 of their work. The initiation efficiency f, the probability that a primary radical reacts with a monomer, rather than combines with another radical to form a "dead" product [21], is set equal to 0.6.

The presence of TEMPO introduces two more reactions into the mechanism. The first reaction is an additional route to initiating radical formation by a promoted decomposition of the initiator [2]:

$$I + T \rightarrow X + R_c, \qquad k_{pr} = 0.1\,M^{-1}s^{-1}, \tag{13}$$
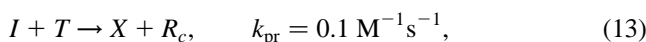
where T is the TEMPO radical and X is the intermediate product. Through a series of steps that have not been fully documented, X would lead to the formation of nitrone and benzoate anion [2].

The second reaction is the reversible termination (or capping–decapping) of a propagating polymer chain by TEMPO [7]:

$$R_r^{\cdot} + T \rightleftharpoons L_n, \quad k_L = 5.03 \times 10^9\,\exp[-3722/RT]\,M^{-1}s^{-1}, \tag{14}$$
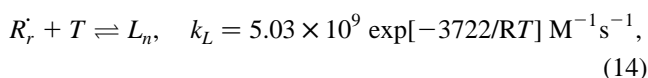
where L_n is the polymer chain that has been reversibly terminated by TEMPO and k_L is the rate constant for the capping reaction.

It is assumed that the presence of the stable free radical does not affect the reaction rates of the propagation and termination steps.

3. Computational studies

The reactor design was applied to a reference case and a test problem where a distributed TEMPO flux was optimized. In the optimization example, an effective strategy was employed for finding a cost functional minimum by making several calculations with increasingly demanding objectives. The flux profiles of the previous simulation were found to be good initial points for subsequent calculations, leading to the optimal solution. The computer code employed for these simulations has performed well in previous applications [15,16,28].

It is important to note that the present work serves to show the general significance of optimally controlling polymer synthesis rather than attempting to corroborate any specific reaction mechanism or experiment. Other possible reactions that are not included in this polymerization model can be readily accommodated, if needed, based on the same principle.

The average iteration took about 42 min of CPU time on an R4000 IRIS Indigo. Although global optimality could not be guaranteed, it is evident that good quality solutions were obtained using the proposed algorithm. In the examples, the length of the PFR in which the polymerization takes place is $L = 100$ cm, with a cross-sectional area of 40 cm^2.

The results for the reference case are shown in Fig. 1. The experimental data shown are from Georges et al. [4]. The initiator used is benzoyl peroxide (BPO) in styrene. Its initial concentration is 0.0125 M. The stable free radical used is TEMPO and its initial concentration is 0.015 M. The temperature is 396 K along the reactor. Both conversion and polydispersity appear to be in close agreement with the experimental data. After 70 h, the reference case results in a conversion of 85% and a polydispersity of 1.31 [4].

Fig. 2 shows the results for an optimized run. The initial concentration of BPO is 0.0125 M but no TEMPO is co-fed. The temperature remains at 396 K. The desired chain length is 75 repeating units and a penalty matrix is used that increases the penalty the further a polymer chain is from that length. The goal is to achieve the desired chain length and maintain high conversion in as short a reaction time as possible. The distributed control of TEMPO results in 90% conversion achieved in 46 h. The significantly lowered
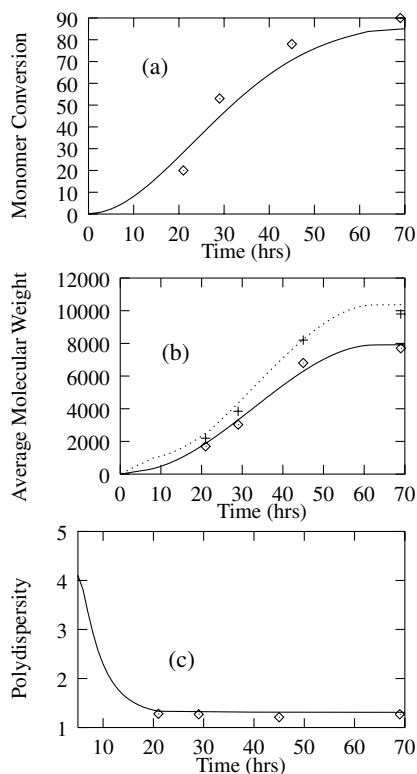
Fig. 1. Results based on experimental conditions with no optimization: (a) monomer conversion as a function of time; (b) M_n (solid line) and M_w (broken line) as a function of time; and (c) polydispersity (M_w/M_n) as a function of time. Solid lines are simulation result and points are experimental data. All experimental data are from Georges et al. [4].

reaction time comes at the price of a moderately higher polydispersity of 1.42.

The total amount of TEMPO fluxed into the reactor is 1.7 times the TEMPO that is co-fed into the reactor in the reference case. Nitroxide stable free radicals have been shown to promote the dissociation of peroxide initiators [29] and, hence, a significant amount of TEMPO is fluxed into the reactor in the initial stage. The molar ratio of TEMPO to BPO affects both the reaction rate and the poly-dispersity. The higher the ratio, the slower the reaction but the lower the polydispersity. The optimized TEMPO profile helps lower polydispersity by initiating all chains at about the same time with a TEMPO flux in the beginning of the reactor, but this initial amount is smaller than the reference case co-feed and so the reaction is faster.

In the reference case, the large amount of excess TEMPO during the initiation period slows down the polymerization. The large amount of TEMPO is needed since much of it will be used to aid initiation. Once initiation is complete, the TEMPO has reached a lower concentration that remains roughly constant during polymerization. By distributing the TEMPO we avoid the need to co-feed large amounts of TEMPO so that some remains after initiation to trap the growing chains.

It should be noted that the majority of the conversion takes place in the first 30–35 h. After that, the TEMPO flux rises and the increased TEMPO concentration suppresses the polymerization. Thus the effective reaction time needed to achieve high conversion with the distributed control of TEMPO has been cut in half relative to the reference case.

The conversion and chain length criteria that were used in the above cases were chosen arbitrarily to demonstrate the principle of optimal control. Similar results have been
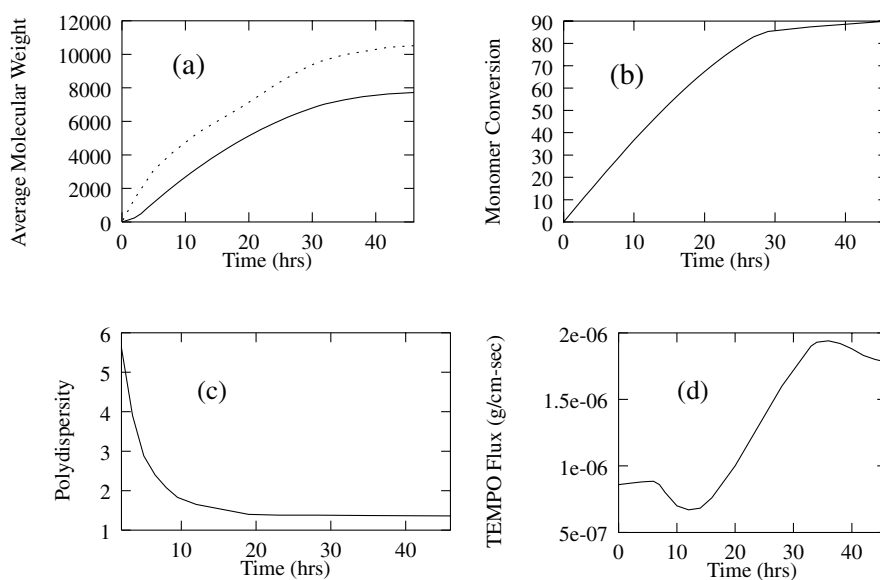

Fig. 2. Results from optimization of TEMPO: (a) M_n (solid line) and M_w (broken line) as well as (b) monomer conversion as a function of time; (c) polydispersity (M_w/M_n) as a function of time; and (d) optimized TEMPO flux as a function of time.

obtained for other conversion values and chain lengths. The resulting TEMPO flux has a similar shape to the optimal flux presented in Fig. 2.

4. Conclusions and remarks

The optimal control of polymer synthesis in a PFR has been demonstrated for the living (or controlled) free-radical polymerization of styrene with TEMPO as the capping agent. An optimally designed TEMPO flux along the length of the reactor can significantly shorten the reaction time without a large increase in polydispersity. This sharp reduction in the reaction time addresses one of the largest obstacles that stand in the way of commercial viability for most living free-radical polymerization processes. Since global optimality was not guaranteed, even better results may be achievable.

The methodology employed in this work is general and may be used in various polymerization processes including catalyzed polymerizations and reactions that do not necessarily involve radicals. Optimal control will yield results that are at least as attractive as those achieved by conventional reactor design.

In the laboratory, the theoretical solutions presented in this paper can serve as starting points for a reactor with feedback control. The output performance of the reactor will be fed to a learning algorithm, to in turn design the next experiment in a repeated sequence. This self-optimization is independent of the model assumptions that were used in the theoretical work and will therefore bring forth the most refined synthesis products.

Acknowledgements

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