Continuous Production of Multiblock Copolymers in a Loop Reactor: When Living Polymerization Meets Flow Chemistry

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ABSTRACT: A continuous process for the production of multiblock polymers via living anionic polymerization in a loop reactor is proposed by kinetic modeling. The process utilizes specific configurations of the loop reactors and feed inlets, thus producing multiblock polymers constituted by a blend of chains with varying number of blocks. The dependence of the product molecular parameters, such as length, composition of each block, and the block number distribution, on the residence time and the recirculation fraction is analyzed by numerical integration of differential mass balances. This dependence is subsequently translated into controllability of molecular parameters by changing the operation conditions such as the recirculation and inlet flow rates. In general, higher recirculation flow rate yields products with shorter block length but larger fraction of polymers possessing higher number of blocks and more significant compositional mixing in each block. An increase in the feed flow rates also increases the compositional mixing but gives longer block length with lower fraction of polymers possessing a higher number of blocks. While being discussed in terms of living anionic copolymerization of styrene and butadiene, the present strategy can be extended to any other living copolymerization of suitable monomer pairs, thus highlighting the use of reaction engineering to control the polymer structures.

INTRODUCTION

Block polymers continue to draw significant research interest owing to their unique interfacial properties, self-assembly behavior, and microphase separation ability. These properties endow block polymers with applicability in manifold materials ranging from thermoplastic elastomer to self-assembler to photolithography, depending on the molecular structures of block polymers.1−8 Numerous efforts have been devoted to control the molecular structure of block polymers such as chain architecture (linear, branched, or dendritic), composition, molecular weight, and molecular weight distribution as well as end-functionality in order to obtain products with desired properties.1−5 Multiblock polymers exhibit distinct properties in comparison to those of di- or triblock polymers.6−14 For example, it was reported that multiblock polymers of 1,3-butadiene and styrene or lactide exhibited significant improvement on the mechanical properties as compared to the corresponding triblock polymers.5,10 Simulation results based on density functional theory and lattice spring model show an increase in the fracture strain with increasing number of blocks, from diblock to hexablock polymers.11 Tri- and pentablock poly(styrene-b-butadiene) polymers were found to be better compatibilizers of polystyrene/polypropylene blends than the di- and heptablock polymers.12 Multiblock polymers of poly(caprolactone-b-ethylene glycol) were found to have better sol phase stability than the triblock polymers at room temperature.13 The investigation on the micellization process of multiblock polymers have revealed that tri-, tetra-, and pentablock polymers exhibit similar micelles radii, while the hexablock polymers form larger micelles.14

The synthesis of di- and triblock and multiblock polymers is made possible by the advent of living polymerization and reversible deactivation mediated radical polymerization, utilizing either noncontinuous or continuous strategy.15−21 Both approaches may involve sequential chain extension polymerization or coupling reaction of the end-functionalized precursor. Sequential chain extension polymerization is a classic straightforward method to prepare di- and triblock polymers based on the living chain ends.3 In recent progress, multiblock polymers consisting of up to 21 short blocks in specific order were synthesized in one-pot batch mode without intermediate purification steps, taking the advantages of elegant controllability in Cu and thiocarbonylthio compound mediated radical polymerizations.14,22−39 The noncontinuous approach was also applied in the synthesis of multiblock polymers by coupling of the telechelic precursors in a polycondensation manner, with the end product being a mixture of chains with different...
number of blocks, connected in either an alternating or a random fashion. 4,9,10,40−45

Continuous strategy is an attractive alternative for block polymer syntheses, since batch and semibatch polymerization may suffer from product inconsistencies and often very laborious. The continuous production of block polymer using various living polymerization reported thus far generally focuses on di- or triblock polymers in a series of tubular reactors. 46−64 or in a series of continuous stirred tank reactors (CSTRs). 65,66

The continuous synthesis of multiblock polymers has also been reported by alternating monomer feed in a CSTR. 87,68 The use of a series of straight tubular reactors is analogous to the sequential batch polymerization, with potentially better heat transfer, materials mixing, and product consistency. Recently, a number of studies reported the use of microflow reactors for continuous syntheses of diblock and triblock polymers using living anionic polymerization. 46−54 The use of microflow reactor allows fast heat dissipation, which is especially advantageous for fast exothermic reaction such as anionic polymerization. This method has been used to estimate the reaction rate constants in system with very fast kinetics and was also used to employ reaction condition that may not be well-controlled in batch, for example, anionic polymerization of styrene in THF at room temperature. 57−59,69−74

Investigation on block polymer formation using reversible deactivation radical polymerization (RDRP) has also been reported in a series of tubular reactors 56−63 or semicontinuous microreactor. 75

Another type of tubular reactor often used in chemical engineering is loop reactor which can be operated in a continuous or a batch mode to enhance mixing. 76 Continuous loop reactor can be viewed as a middle ground between CSTR and straight tubular reactor, and it is often modeled as a tubular reactor with recycle. The recirculation flow rate, \( Q_{\text{in}} \), and the inlet or feeding flow rate, \( Q_{\text{out}} \), can be controlled independently from one another by adjusting the power of the corresponding pump, thus allowing for versatile operation on a wide range of operating parameters. At a high recirculation ratio (\( f_R \equiv Q_{\text{in}} / Q_{\text{out}} \) where \( Q_{\text{in}} \) is the flow rate exiting the reactor), loop reactor approximates the behavior of CSTR, while at a low recirculation ratio it approaches tubular reactor behavior. 76−78

Loop reactor is commonly used for solution and slurry homo- and copolymerization of olefins. 77−80 Similar to a tubular reactor, the loop reactor also offers higher surface-to-volume ratio, hence offering better heat transfer than a batch or a tank reactor. A recent study demonstrated how a loop reactor can be used to tailor the molecular weight distribution of polymers for a RAFT polymerization system. 81,82

Anionic homopolymerization of styrene in a loop reactor was reported at different recirculation ratio (\( Q_{\text{in}} / Q_{\text{out}} \)) of 8 and 100. 83−85 When the recirculation ratio of 8 was used, the dispersity of polystyrene obtained is in-between those of polymers synthesized in a CSTR and in a straight tubular reactor. 85 Another study proposed the use of a loop reactor with two feed streams and a recirculation ratio of 8 to 15 for the anionic homopolymerization of styrene or acrylonitrile. 86 The author mentioned the possible synthesis of block polymers by replacing one of the monomer feeds with a comonomer and also proposed creating multimodal molecular weight distribution by dividing the initiator between the two feed streams. A loop reactor in series with a tubular reactor was used to improve the space-time yield of anionic polymerization of styrene. 87 Anionic statistical copolymerization of styrene with α-methylstyrene, 88 p-methylstyrene 89 and butadiene 89 has also been investigated in a loop reactor.

Considering the living character of anionic polymerization and the operation capability of continuous loop reactors, we propose a production strategy for multiblock polymers using loop reactor for organolithium initiated copolymerization of styrene and butadiene. In the present modeling work, we investigate the effect of fundamental parameters on the structure and composition of multiblock polymer product. This strategy offers two main advantages over the sequential batch and straight tubular reactors. First, it is a continuous process and thus easier to automate with no batch-to-batch inconsistencies. Second, fewer feeding points and smaller volume are required in a loop reactor than in a series of straight tubular reactors. The polymers produced consist of chains possessing different numbers of blocks and expected to exhibit high regularity, in terms of repeating block structure, due to the narrow molecular weight distribution of each block and the repetitive nature of the blocks formed. To the best of our knowledge, this is the first report of in-depth investigation on the use of a loop reactor with multiple inlet streams to synthesize multiblock polymers using living anionic polymerization. This strategy can also be extended to other living copolymerization systems. However, it should be noted that for systems involving the formation of dead chains (such as reversible deactivation radical polymerization) the chain length, segment length, and block number distributions may be broader than what are calculated here.

### MATHEMATICAL FORMULATIONS

Different reactor configurations will result in a blend of polymers possessing different number of blocks. Several examples of the reactor configurations and the block polymer blends expected are shown in Table 1. The block numbers are calculated by assuming that all chains undergo at least one propagation in each reactor part. The block discussed here may be a pure homopolymer block or a copolymer block.

Since our objective in this study is to demonstrate the use of a loop reactor to synthesize multiblock polymer and to investigate the effect of different parameters, the configurations considered (Table 1) only involve one initiator inlet stream and only one type of monomer in each inlet stream. The present feeding scheme can, however, be modified depending on the intended chain properties, e.g., initiator may be fed in multiple streams and some or all of the inlets can contain both monomers. In addition, postpolymerization functionalization or termination of active ends can be done downstream of the loop reactor in a continuous fashion.

We use multiblock copolymerization of styrene and butadiene to elucidate our point, owing to its importance in
industry. Loop reactor with two monomer inlet streams (entry 1 in Table 1, Figure 1) will first be investigated. We consider the polymerization in the presence of polar modifier, tetramethylethylenediamine (TMEDA), which has been reported to promote the dissociation of chain ends in living anionic polymerization.\(^9\) Therefore, this simplifies the polymerization mechanism as shown in eqs 1 and 2, i.e., without association and dissociation reactions. I denotes the initiator, while \(M_i\) is the chain length, segment length, and segment number calculations are included in the Supporting Information. We modeled the loop reactor shown in Figure 1 by treating it as two tubular reactors, separated by the two inlet streams. For the differential equations, we chose relative volume, \(\delta_i\), as the independent variable. The relative volume is defined as 0 at the first feeding point and 1 just before the mixing junction of the first feeding point and the recycle stream. For this configuration, we assume the volume between the outlet and the mixing junction is negligible compared to the total volume of the loop reactor.

In a loop reactor, the exiting polymer chains can be characterized by its recirculation ratio, \(f_R\), which is the ratio between recirculated and exiting flow (eq 5). The two variables can be correlated to each other according to eqs 4 and 5.

\[
\tau_{\text{loop}} = V \sum_{i=1}^{2} \frac{\delta_i}{\dot{Q}_i}
\]

\[
\phi_R \equiv \frac{\dot{Q}_R}{\dot{Q}_{\text{out}}} = \frac{f_R}{1 + f_R}
\]

\[
f_R \equiv \frac{\dot{Q}_R}{\dot{Q}_{\text{out}}} = \frac{\phi_R}{1 - \phi_R}
\]

where \(\dot{Q}_i\) is the flow rate in the \(i\)th reactor.

In a loop reactor, the exiting polymer chains can be differentiated based on how many cycles they experienced. It can be shown through simple mass balance that the distribution of chains undergoing different loop cycles, i.e., loop cycle distribution, follows the most probable distribution (Schulz–Flory distribution). The loop cycle distribution is shown in eqs 6 and 7 for the number and weight fraction of chains undergoing \(i\) loop cycles, respectively. The number-average loop cycles, \(n_{\text{loop}}\), can be calculated by eq 8, indicating the number of loop cycles that polymer undergoes on average prior to exiting the reactor.

\[
\lambda_n(i) = (1 - \phi_R)^{i - 1}
\]

\[
\lambda_w(i) = i(1 - \phi_R)^2(\phi_R)^{i - 1}
\]

\[
r_{\text{loop}} = (1 - \phi_R)^{-1}
\]
The number-average chain length \((r_N)\) in living polymerization can be calculated by simply taking the ratio of monomer consumed to the amount of initiator present. This is also applicable for the overall chain length produced in a loop reactor, which is not dependent on the recirculation fraction for cases with complete conversion. However, the number-average length of the repeating block \((r_{N,1})\) depends on the recirculation fraction and the overall number-average chain length, as shown by eq 9.

\[
r_{N,1} = r_N(1 - \phi_R)
\]  
(9)

The fraction of \(M_1-M_2\) bonds (heterodyads), \(Z\), in the polymers can be used as an indicator to quantify the composition mixing of the product.\(^9\) A higher ratio indicates the tendency to alternate between monomers. Equation 10 calculates the heterodyads fraction using the number-average segment number.

\[
Z = \frac{r_{SN} - 1}{r_N - 1}
\]  
(10)

where \(Z\) is fraction of heterodyads \((M_2-M_2\) dyad) in the copolymers, \(r_N\) is number-average chain length, and \(r_{SN}\) is number-average segment number.

The operating and the reaction kinetic parameters used in the calculations presented in this study are listed in Table 2.

### Table 2. Operating and Kinetic Parameters Used for the Production of Styrene–Butadiene Multiblock Copolymers with 30 wt % Styrene in a Loop Reactor

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Operating parameter</th>
<th>Value (range considered)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([1_{in,1}]) (mol/L)</td>
<td>9.6</td>
<td>temp (°C)</td>
<td>50</td>
</tr>
<tr>
<td>([M_1]_{in,1}) (mol/L)</td>
<td>2.8</td>
<td>(V) (L)</td>
<td>3.5 (1–20)</td>
</tr>
<tr>
<td>([M_2]_{in,2}) (mol/L)</td>
<td>3.0</td>
<td>(Q_{n,1,0}) (mL/min)</td>
<td>3.6 (1.8–42)</td>
</tr>
<tr>
<td>(\delta_1)</td>
<td>0</td>
<td>(Q_{n,2,0}) (mL/min)</td>
<td>15.0 (7.5–175)</td>
</tr>
<tr>
<td>(\delta_2)</td>
<td>0.45</td>
<td>(Q_{p,0}) (mL/min)</td>
<td>8.0 (5–45)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Kinetic parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_{11}) (= k_{p,11}) (M(^{-1}) s(^{-1}))</td>
<td>0.42</td>
</tr>
<tr>
<td>(k_{12}) (= k_{p,22}) (M(^{-1}) s(^{-1}))</td>
<td>1.20</td>
</tr>
<tr>
<td>reactivity ratio, (r_1) ((r_1 \equiv k_{p,11}/k_{p,12}))</td>
<td>1.53</td>
</tr>
<tr>
<td>reactivity ratio, (r_2) ((r_2 \equiv k_{p,22}/k_{p,21}))</td>
<td>1.97</td>
</tr>
</tbody>
</table>

The polymerization recipe is based on the production of 100 kDa styrene–butadiene multiblock copolymer with 30 wt % styrene content in the copolymer. The reaction rate parameters and reactivity ratios are based on the reported values for the fully modified living anionic copolymerization of styrene and butadiene in hexane under the presence of polar modifier, TMEDA (with [TMEDA]:[initiator] > 2).\(^9\)

As the reactivity of living ends in anionic polymerization depends heavily on the solvent, care must be taken in choosing the solvent so that the cross propagation rate is not much slower than the propagation rate for homopolymer blocks. Otherwise, polymers possessing less blocks than expected may be present, thus broadening the block number distribution. In addition, the feeding point location can be optimized to allow for smaller reactor to be used for different operating parameters. However, as our objective in this work is to elucidate the concept, we opted to use the same relative location in all calculations for simplicity purposes.

### RESULTS AND DISCUSSION

In a loop reactor system operating at steady state, a loop segment between two feeding points produces one polymer block with the same composition and length. Therefore, when a loop reactor with two feeding points (Figure 1) is considered, every cycle will produce two blocks, one of styrene and one of butadiene, i.e., PS-b-PB. Each block may contain the other monomer type, depending on its conversion at the subsequent feeding point. These two blocks are the repeating block, which forms the multiblock polymer product, \((PS-b-PB)_n\), as they undergo various number of loop cycles, \(i\). The product can be characterized in terms of the overall chain length distribution (CLD), the block number distribution \((i.e.,\) the fraction of chains possessing different number of blocks), and the composition of the repeating block. The composition of the repeating block is described by the segment length distributions (SLDs) of styrene and butadiene, the instantaneous copolymer composition, and/or the heterodyads fraction present in the repeating block.

We investigate the effect of two fundamental parameters that affect the structure and composition of the resulting copolymers in a loop reactor, namely, the recirculation fraction \((\phi_R)\) and the residence time of a loop cycle \((\tau_{loop})\). For

![Figure 2](image-url)
simplicity purposes, the residence time is varied by changing the volume of the reactor to avoid a effect on recirculation fraction. In reality, it may not be practical to vary the volume of the reactor. Additionally, we also discussed the reactor operating guideline to control the resulting multiblock polymer chain properties by controlling recirculation and inlet flow rates. These flow rates, which can be adjusted independently from one another, affect both the recirculation fraction and the residence time per loop cycle.

In this study, the $\phi_R$ chosen is lower than those generally reported as the "low recirculation ratio" case in the literature for anionic polymerization ($f_R = 8$, which translates to $\phi_R = 0.89$). High recirculation is usually employed to aid in mixing. However, our goal is to use the recirculation as means to create multiblock polymers, thus not requiring such high $\phi_R$.

Effect of Recirculation Fraction ($\phi_R$). We first demonstrate the effect of recirculation fraction ($\phi_R$) on the resulting CLD and block number distribution of the multiblock polymers, while fixing the total volume of the loop reactor and inlet flow rates. Increasing the recirculation fraction by increasing the recirculation flow rate results in a decrease of residence time. On the other hand, when the recirculation fraction is increased by lowering the feed flow rates, the residence time is increased. In order to isolate the effect of the recirculation fraction from that of residence time, which affects the composition of the polymers, near complete conversion of monomer (>99.5%) before the next feeding point is considered. This can be achieved in practice by using either a large reactor and/or slow feeding flow rates (i.e., long residence time). Therefore, the blocks formed consist of predominantly homopolymer, with insignificant amount of other monomer present in that block (i.e., only a slight compositional mixing).

The number and weight distributions of chains undergoing different loop cycles are calculated according to eqs 6 and 7 and illustrated in Figure 2 for various $\phi_R$. As shown in Figure 2a, the number fraction of diblock polymers (i.e., polymers that only went through one loop cycle before exiting the reactor) decreases with increasing $\phi_R$. However, it is always the highest regardless of the $\phi_R$. On the other hand, its weight fraction quickly diminishes as chains with more blocks are formed (Figure 2b). Therefore, eq 6 or 7 can be used to tailor the product on demand, e.g., to calculate the $\phi_R$ needed to obtain a targeted percentage of diblock polymer content in the population.

The overall CLD and SLDs of PS and PB composing the multiblock at the outlet are shown in Figure 3, which were calculated for a 20 L reactor with inlet flow rates of 1.8 and 7.5 mL/min, respectively for styrene and butadiene, to ensure near complete conversion, with other conditions as listed in Table 2. The CLDs produced in a loop reactor are multimodal.
distributions, where each discrete peak can be attributed to polymers possessing different number of blocks (i.e., undergo different cycles). We elucidate this further for the case with recirculation fraction of 0.5, as shown in Figure 3b. The first peak corresponds to the diblock polymer population, PS-b-PB (i.e., the polymer species that only went through one loop cycle), the second corresponds to the tetrablock, (PS-b-PB)₂, and so forth. The area under each peak equals the number fraction of the subpopulation with corresponding i, which agrees with the fraction value in Figure 2. It can also be seen that an increase in the $\varphi_R$ results in an increase in modality of CLD, i.e., producing polymer with more blocks, with shorter

![Figure 4](image1.png) ![Figure 5](image2.png)

**Figure 4.** Concentration profiles of (a) styrene monomer and (b) butadiene monomer along the reactor at steady state. (c) Mole fraction of styrene along the repeating block of multiblock polymers, where the length of the repeating blocks are normalized to 1 in order to keep a uniform appearance between different residence times per cycle. (d) Schematic diagram showing the structure of multiblock polymers produced at a residence time per cycle of 30 min. The subscripts in (c) and (d) refer to segment length, or degree of polymerization, obtained by the integration of the first peak of Figure 5a. These distributions are calculated for residence time per cycle of 30, 150, and 270 min, with other parameters as listed in Table 2.

**Figure 5.** (a) Overall chain length distribution (CLD) and (b) segment length distribution (SLD) of PS segment for different residence time per loop cycle (varied through volume). Both chain length and segment length refer to the degree of polymerization. Other parameters are listed in Table 2.
length for each repeating block, PS-b-PB, while maintaining similar overall number-average chain length, \(r_N\).

The SLDs of styrene and butadiene are unimodal (Figure 3c,d), indicating length homogeneity of each of the PS and PB segments. As the SLDs are calculated based on the number of chains, the area under the curve of Figure 3c,d corresponds to the number of segments per chain. Hence, it is evident that higher \(\phi_R\) results in more segments of styrene and butadiene as they have larger areas.

Figure 3c indicates the presence of lone styrenic units at \(\phi_R\) of 0.9, demonstrating the contamination in butadiene block by leftover styrene. This demonstrates that for high \(\phi_R\) case styrene was not fully converted at the butadiene feeding point. This is also evident from the SLD of butadiene in Figure 3d, where the tailing at low segment length indicated the random placement of the lone styrene unit along the butadiene block. While the contamination is observable in the SLDs, it should be noted that the compositional mixing is negligible, with styrene accounting only for 0.10 mol % of the butadiene block content.

From the above discussion, it is clear that \(\phi_R\) governs the length of the repeating block, PS-b-PB, and the block number distribution, i.e., the fraction of chains possessing different number of blocks. Higher \(\phi_R\) results in more polymers possessing higher number of blocks with shorter block length. The \(\phi_R\) does not affect the overall number-average chain length, but higher \(\phi_R\) requires larger reactor (or slower inlet and recirculation flow rates) for complete conversion of monomer.

**Effect of Residence Time per Cycle \(\tau_{loop}\)**. The residence time per cycle \(\tau_{loop}\) affects the steady-state concentration profiles of the monomers, which in turn affects the composition of the resulting copolymers. It can be adjusted by changing either the reactor volume and/or the flow rates, while keeping the \(\phi_R\) constant (see eq 3). Here, we vary \(\tau_{loop}\) by varying the reactor volume while using the same flow rates; thus, a smaller reactor results in a shorter \(\tau_{loop}\). It should be pointed out that

**Figure 6.** Concentration profiles of (a) styrene monomer and (b) butadiene monomer along the reactor at steady state for different recirculation rates indicated in (a). (c) Mole fraction of styrene along the repeating block of multiblock polymer for various recirculation flow rates, with other parameters as listed in Table 2. The subscripts in (b) refer to the degree of polymerization of corresponding segments and were calculated from the integration of the first peak of Figure 7a.

**Figure 7.** (a) Overall chain length distribution (CLD) and (b) segment length distribution (SLD) of PS segment for polymer at the reactor outlet under various recirculation flow rates. Both chain length and segment length refer to the degree of polymerization. Other parameters are listed in Table 2.
the same effect can be more easily achieved in practice by altering the flow rates.

The effect of $t_{\text{loop}}$ on monomer concentration profiles along the reactor at steady state, as well as that on composition of each repeating segment formed in one cycle, is presented in Figure 4. It is clear from Figure 4a,c that complete monomer conversion is achieved at sufficiently long $t_{\text{loop}}$, such as 150 and 270 min, thus yielding multiblock polymers consisted of homopolymer blocks. On the other hand, shorter $t_{\text{loop}}$ (e.g., 30 min) results in incomplete conversion of monomers at the subsequent feeding point; i.e., there are still styrene monomers remaining unreacted at the butadiene feeding point, and vice versa. This introduces compositional mixing in the resulting blocks, as depicted in Figure 4c, therefore giving us the opportunity to tune the copolymer composition by changing $t_{\text{loop}}$. After normalizing the length of repeating block, which are different due to the incomplete monomer conversion, the system with $t_{\text{loop}}$ of 30 min is found to contain $\sim$74 mol % styrene in the first block, which accounts for $\sim$26% of the

Figure 8. Operating guideline to control the composition and length of the repeating block by changing either fundamental ($\phi_R$ and $t_{\text{loop}}$) or operating ($Q_R$ and $Q_{in}$) parameters. (a) Heterodyads fractions of multiblock polymers ($Z$). (b) Heterodyad fractions formed by composition mixing ($Z'$). (c) The number-average length (in terms of degree of polymerization) of the repeating block ($r_{N,1}$). Calculation are based on a 3.5 L reactor with $Q_{in,1}/Q_{in,2} = 0.24$ and other parameters as listed in Table 2. Constant $Q_R$ lines (white) are calculated for $Q_R = 40, 20$, and 10 mL/min (left to right, respectively), while constant $Q_{in}$ lines (green) are calculated for $Q_{in,1} = 14.4, 7.2$, and 3.6 mL/min (left to right, respectively). $Q_R$ and $Q_{in}$ are related by eq 4, where $Q_{out} = Q_{in,1} + Q_{in,2}$.

Figure 9. Loop reactor system for multiblock polymer synthesis with three inlet streams.

Table 3. Operating Parameters Used in This Study for the Production of Styrene–Butadiene Multiblock Polymers with 30 wt % Styrene in a Loop Reactor with Three Monomer Inlet Streams (Figure 9)

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<th>value</th>
<th>operating parameter</th>
<th>value</th>
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</thead>
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<td>temp (°C)</td>
<td>50</td>
</tr>
<tr>
<td>$[M_1]_{in,1}$ (mol/L)</td>
<td>2.8</td>
<td>V (L)</td>
<td>10</td>
</tr>
<tr>
<td>$[M_2]_{in,2}$ (mol/L)</td>
<td>3.0</td>
<td>$Q_{in,2}$ (mL/min)</td>
<td>1.8</td>
</tr>
<tr>
<td>$[M_3]_{in,3}$ (mol/L)</td>
<td>2.8</td>
<td>$Q_{in,3}$ (mL/min)</td>
<td>15.0</td>
</tr>
<tr>
<td>$\delta_1$</td>
<td>0</td>
<td>$Q_R$ (mL/min)</td>
<td>1.8</td>
</tr>
<tr>
<td>$\delta_2$</td>
<td>0.09</td>
<td>$Q_{in,3}$ (mL/min)</td>
<td>8.0</td>
</tr>
<tr>
<td>$\delta_3$</td>
<td>0.34</td>
<td></td>
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</tr>
</tbody>
</table>

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repeating block length, while the second block is rich in butadiene (∼98 mol % butadiene).

Figure 5 shows the overall CLD and SLD of styrene of the product exiting the reactor for different τ_loop. The consistent modality of overall CLD (Figure 5a) implies that the block number distribution is not affected by τ_loop. The slight shift of CLD to lower chain length for system with shorter τ_loop is caused by the incomplete conversion of monomer at the outlet. The increase in the fraction of comonomer within the blocks can also be observed in Figure 5b, where there are more of short styrene segments formed in system with shorter τ_loop. For the case with τ_loop of 30 min, the chain length of PS-b-PB can be obtained from integration of the first peak of Figure 5, resulting in 932 units in this case. Based on the length and the amount of monomer consumed, the chains that have undergone i cycles possess composition of (S_{183}P_{63}-b-S_{11}P_{675}). Increase in τ_loop leads to longer segment lengths due to less contamination by the comonomer. However, clearly there are upper limits on τ_loop at which complete conversions of monomers are achieved; thus, increasing it further will not affect the products.

Therefore, the dependence of composition and length of the repeating block, PS-b-PB on τ_loop is clear; i.e., shorter τ_loop results in more compositional mixing and shorter PS-b-PB due to incomplete conversion of monomer. This results in shorter overall length of multiblock polymer because τ_loop does not affect the block number distribution. The present system can be used, by changing the value of τ_loop to prepare multiblock copolymer with varying composition of each block in a wide range.

Guideline for the Production of Tailorable Multiblock Copolymer. As described above, recirculation fraction (ϕ_R) and residence time per cycle (τ_loop) are the two fundamental parameters that affect the CLD, block composition, and block number distribution of multiblock polymers in a loop reactor. Adjusting the reactor volume to control these parameters may not be practical in reality; thus, it is preferred to do so by independently regulating the operating parameters such as recirculation and inlet flow rates through adjusting the power of working pumps I and II in Figure 1. A change in any of these flow rates affects both ϕ_R and τ_loop. In this section, we will provide the operating guideline to tailor the multiblock polymer chain properties such as block composition and block length by controlling the recirculation and inlet flow rates.

In spite of the assumption of high monomer conversion monomer at the next feeding point, we are aware that even at high conversion, the residual monomer can interrupt the segment length in each repeating block. Therefore, the composition mixing is investigated by changing the recirculation and inlet flow rates. As shown in Figure 6, higher recirculation flow rate results in more unreacted styrene at the butadiene feeding point, and similarly more unconverted butadiene is present at the subsequent styrene feeding point. A similar trend is observed when higher inlet flow rates is used (Figure S9). The composition mixing in the block is evident from the instantaneous mole fraction of styrene along the polymer (F_1) shown in Figure 6c and Figure S9c for different recirculation and inlet flow rates, respectively. The composition...
mixing can also be observed in Figure 7b or Figure S10b, where more of short styrene segments are present as the recirculation flow rate or inlet flow rates is increased, respectively. The recirculation flow rate also affects the block number distribution, as evident from the modality CLD shown in Figure 7a. The content of multiblock polymer with larger number of blocks in the product stream becomes higher while the fraction of diblock polymers decreases as faster recirculation flow rate is employed. The opposite trend is observed for faster inlet flow rates (Figure S10a).

In general, increasing the recirculation flow rate increases \( \phi_R \) while decreasing \( \tau_{\text{loop}} \). Therefore, faster recirculation flow rate creates chains with more repeating blocks, higher compositional mixing, and shorter length of each repeating block. On the other hand, faster inlet flow rates results in a smaller \( \phi_R \) and shorter \( \tau_{\text{loop}} \) (eq 4). Therefore, faster inlet flow rate decreases the fraction of chains possessing more blocks and increases the composition mixing of each block. The effect of inlet flow rates on the length of repeating block depends on which factor is dominant, \( \tau_{\text{loop}} \) or \( \phi_R \).

A guide to control the composition mixing in the multiblock polymer products is depicted in Figure 8. The composition mixing is expressed by the fraction of heterodyads \( Z \) in the multiblock polymers, which can be calculated from eq 10. This counts, however, overall heterodyads including those connecting blocks of PS and PB. These interblock heterodyads can be extracted by using eq 11, thus obtaining \( Z' \) as pure fraction of heterodyads formed by composition mixing.

\[
Z_{\text{SN},(\text{PS-b-PB})} = \sum_{i=1}^{\infty} [2i \times \lambda_i(i)] = \frac{2}{1 - \phi_R}
\] (11)

for repeating block of PS-b-PB.

Both \( Z \) and \( Z' \) are shown in Figures 8a and 8b, respectively. Only a small difference is observed. Focusing on Figure 8b, the deep blue area is for reaction conditions to prepare multiblock polymer with the lowest composition mixing, while the yellow area is for conditions causing serious composition mixing. Since the conditions are given in the form of either fundamental or operating parameters, Figures 8a and 8b allow tailoring the composition mixing by either specifying the values of \( \phi_R \) and \( \tau_{\text{loop}} \) or the values of \( Q_R \) and \( Q_{\infty} \).

Figure 8c provides guidelines on how to control the length of the repeating block based on the inlet and recirculation flow rates. Generally, decreasing the recirculation flow rate results in a longer repeating block, as the same amount of monomer is divided among less chains circulating in the reactor. On the other hand, decreasing the inlet flow rate at a constant recirculation flow rate generally results in a shorter repeating block. A slight deviation from this trend can be observed at a
very low residence time (very fast recirculation and/or inlet flow rates, at the bottom left corner of Figure 8c) due to incomplete conversion of monomer in the reactor. As each loop cycle produces two blocks in this configuration, the average number of blocks can be calculated from eq 8 to be $2n_{loop}$, which depends solely on the recirculation fraction. In addition, the overall number-average chain length depends on the monomer-to-initiator ratio fed into the system and the overall conversion, as can be expected from living polymerization system.

To illustrate the size of the reactor needed for such system, a rough calculation is presented here for the production rate of 5 kg/day of (PS-b-PB), multiblock polymer having average molecular weight of 100 kDa with 30 wt % styrene content. The minimum volume of the loop reactor needed was estimated based on the operating and kinetic parameters listed in Table 2, with inlet and recirculation flow rates of 3.6, 15, and 8 mL/min ($Q_{in,1}$, $Q_{in,2}$, and $Q_{rec}$, respectively, translating to $\phi_{R}$ of 0.3), to be approximately 1.9 L (based on 99.5% conversion of monomer prior to subsequent feeding point and second feeding point located at 30% of the overall length from the first feeding point, i.e., $\delta_2 = 0.3$). As can be calculated by eq 8, this will result in multiblock polymers having an average block number of 2.9 (70 mol % of diblock, 21 mol % of tetrablock, 6.3 mol % of hexablock, etc.).

The resulting Reynolds number depends on the diameter of the reactor chosen, with a larger diameter resulting in a lower Reynolds number for the same flow rate. Therefore, increasing the Reynolds number can be done by using a smaller diameter reactor, but this comes at the expense of having to use a longer reactor (to maintain the same reactor volume). For loop reactor having 1 cm diameter, the length required would be approximately 24 m. The Reynolds number of such system (for reaction mixture with dynamic viscosity of approximately $5 \times 10^{-3}$ Pa·s and density of hexane of 0.634 g/mL) is about 7.2.

**Loop Reactor with Three Feeding Points.** The presence of a small amount of diblock polymers can be significantly detrimental to the elastic properties of triblock SBS.50 This is attributed to the dilution effect of the diblock polymer caused by the butadiene end-block, thus reducing its elastic response. In the loop reactor presented above, the fraction of diblock polymer can be suppressed by employing high $\phi_{R}$ (number and weight fractions of the diblock polymer in the system are equal to (1 - $\phi_R$) and $(1 - \phi_R)^3$, respectively). This means $\phi_R$ above 0.86 is needed to suppress the amount of diblock polymers to be below 2 wt %. However, the use of such high recirculation ratio results in shorter blocks (eq 9) and requires a larger reactor to avoid compositional mixing in the block. It may be tempting to increase the monomer-to-initiator ratio to obtain longer block length; however, this will increase the overall average chain length.

In this section, we briefly present an alternative approach to mitigate this problem by introducing an additional monomer inlet stream in the loop reactor (Figure 9). This is done to elucidate the viability of using loop reactor to prepare multiblock styrene–butadiene polymer with at least three blocks. The calculations are done with similar approach as the loop reactor with two monomer inlet streams, with operating parameters listed in Table 3.

The volume of reactor is chosen so that the conversion of monomer before each subsequent feeding point is higher than 99.5%. The concentration profiles of styrene and butadiene along the reactor with the copolymer composition profile are shown in Figure 10 for conditions outlined in Table 3. The copolymer composition profile of the repeating block (Figure 10c) indicated the multiblock polymers consists of repeating block of SBS triblock polymer, PS-b-PB-b-PS. In addition, the overall CLD and SLDs of styrene and butadiene are shown in Figure 11. The overall CLD shown in Figure 11a is similar to those found in the loop reactor with two monomer feeding points. However, the first peak now corresponds to a triblock polymer population instead of a diblock polymer population.

The SLD of styrene in Figure 11b shows a bimodal distribution, while that of butadiene stays unimodal, as depicted in in Figure 11c. The bimodality of the styrene segment is because both ends of the repeating blocks are polystyrene, thus creating longer nonterminal blocks. For example, the average composition of polymer experiencing two loop cycles is $S_{101-b-S_{202-b-S_{101}}}$ Thus, the first peak at lower chain length is attributed to the end styrene segments, which is ascertained by its integration to yield the value of 2 (i.e., the number of styrene end-segments per chain). This trend could also be observed by the evolution of the SLDs of styrene and butadiene as the chains grow in the reactor, as shown in Figure 12, in which the SLDs are plotted against normalized length of a repeating block as the indication of the reaction progress. The normalized length of a repeating block is equivalent to or interchangeable with the relative location along the reactor or the flow time. The trend is most clearly visible when using the normalized length of a repeating block as one axis.

It can be seen that the polystyrene blocks may also be tailored to give SLD of styrene with trimodal distribution; however, unimodal SLD is not achievable with this system. Variation of the reactor design could be used to further tailor the modality of SLDs of styrene and butadiene, for example, by the addition of another feeding point to obtain multiblock polymers of (SBS)$_n$, which can be tuned to produce unimodal or bimodal SLDs of styrene and butadiene. If terminal blocks of polystyrenes are preferred, either the location of the outlet stream can be altered or a combination of a loop and tubular reactor(s) can be employed. Several examples of other reactor setup to produce different repeating block types are listed in Table 1 with the modeling results for these reactors are included in the Supporting Information.

The block number distribution in this work follows the Flory–Schulz distribution (eqs 6 and 7). Strategies to tailor the block number distribution using different reactor setups are currently under investigation. In addition, while we only considered two monomer systems, this reactor can also be potentially used to prepare multiblock polymer with more monomer types, e.g., (ABC), multiblock terpolymers.

### CONCLUSION

In this study, we demonstrated the versatility of using reactor design to produce multiblock polymers. By using loop reactors, multiblock polymers can be prepared in a continuous fashion with fewer feeding streams and smaller volume compared to a straight tubular reactor. The products obtained are a blend of polymers possessing different number of blocks. Under steady-state operation, the blocks formed in one loop cycle can be considered as a repeating block constituting the repetitive multiblock polymer products. The block number distribution, length of the blocks, and the composition of each block can be adjusted by controlling the recirculation and inlet flow rates.
These flow rates are controlled independently from one another, thus allowing for versatile operation.

Two fundamental parameters affecting the polymers produced in a loop reactor system are the recirculation fraction and the residence time per cycle. The composition of the blocks is controlled by the residence time per cycle, while the block number distribution is governed by the recirculation fraction. The length of the blocks can be regulated by both residence time per cycle and recirculation fraction. A longer residence time per cycle decreases the compositional mixing in each block and forms longer blocks by allowing complete conversion of monomer prior to the subsequent feeding point. On the other hand, higher recirculation fraction results in the formation of polymers possessing more blocks but shorter block length. These two parameters can be controlled through the inlet and recirculation flow rates. The residence time per cycle can be increased by reducing either the inlet and/or the recirculation block length. These two parameters can be controlled through the inlet and recirculation flow rates. These two parameters can be controlled through the inlet and recirculation flow rates.

Based on this investigation, loop reactor appears to provide an attractive alternative to continuously produce multiblock polymers with prespecified block number distributions and tailorable composition of each block. The necessary reactor configuration must first be identified depending on the repeating block desired. The recirculation fraction can then be calculated based on the desired average number of blocks for the polymers. Finally, the composition of each block can be tuned without changing the average number of blocks by altering the reactor volume, the position of the inlet streams, the inlet flow rates, and/or the concentration of monomer in the inlet streams, while keeping the recirculation fraction constant.

It should be pointed out that the separation of multiblock polymers to obtain pure multiblock polymers having exact number of blocks may be difficult. Nevertheless, the necessity of purification depends on different purposes and amounts of the samples. On one hand, for the study of the structure–property relationship, a small amount of samples can be obtained through advanced preparative chromatography techniques, such as the field flow fractionation technique (FFFT), temperature gradient interaction chromatography (TGIC), or recirculation preparative chromatography. On the other hand, for application purposes, the product containing different number of blocks may be used in blend form; thus, the purification is not necessary.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.7b01662.

Detailed mathematical formulation, comparison of modeling result with Poisson distribution, results from different reactor configurations, and the effect of inlet flow rates on multiblock chain properties (PDF)

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**SYMBOLS**

- $I$: initiator
- $M_1$: styrene monomer
- $M_2$: butadiene monomer
- $P_r,1$: chains possessing $r$ units of monomer and styrene as terminal unit
- $P_r,2$: chains possessing $r$ units of monomer and butadiene as terminal unit
- $T_{r,1}$: terminated styrene segment possessing $r$ units monomer
- $T_{r,2}$: terminated butadiene segment possessing $r$ units monomer
- $E_{r,1}$: end (growing) styrene segment possessing $r$ units monomer
- $E_{r,2}$: end (growing) butadiene segment possessing $r$ units monomer
- $Q_{in,i}$, $Q_{out,i}$: inlet flow rate of the $i$th feeding point into the reactor, exit flow rate out of the reactor
- $R$: recirculation flow rate
- $\lambda_1,i$: concentration of initiator at feeding point $i$
- $[M_{1,1}]_{in,i}$, $[M_{2,1}]_{in,i}$: concentration of butadiene monomer at feeding point $i$
- $f_R$: recirculation fraction
- $V$: volume of the reactor
- $\phi_R$: recirculation ratio
- $N$: number-average chain length
- $F_1$: instantaneous mole fraction of styrene incorporated into the monomer
- $r_N$: number-average segment number
- $r_{SN}$: degree of polymerization
- $Z$: fraction of heterodyads ($M_1-M_2$ bonds)
- $Z'$: fraction of heterodyads ($M_1-M_2$ bonds) due to composition mixing within the block
- $\lambda_r(i)$: number fraction of chains that underwent $i$ loop cycles
- $\lambda_w(i)$: weight fraction of chains that underwent $i$ loop cycles
- $n(r)$: number fraction of chains possessing $r$ units of monomer

**Notes**

The authors declare no competing financial interest.
$n_{SL,1}(r)$ number fraction of chains possessing styrene segment with $r$ units of styrene

$n_{SL,2}(r)$ number fraction of chains possessing butadiene segment with $r$ units of butadiene

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