

A Unified Theoretical Treatment on Statistical Properties of the Semi-batch Self-condensing Vinyl Polymerization System

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Abstract We present a novel generating function (GF) method for the self-condensing vinyl polymerization (SCVP) system with any initial distribution of preexisted polymers. Such a method was proven to be especially useful to investigate the semi-batch SCVP system allowing a sequence of feeding operations during the polymerization. Consequently, the number-, weight-, and z-average molecular weights as well as dispersity index of hyperbranched polymers can be explicitly given, which are determined by predetermined feeding details and conversions in each polymerization step. These analytical results are further confirmed by the corresponding Monte Carlo simulations. Therefore, the present GF method has provided a unified treatment to the semi-batch SCVP system. Accordingly, hyperbranched polymers with desired properties can be prepared by designing feeding details and presetting conversions at each step based on the present GF method.

Keywords Self-condensing vinyl polymerization; Semi-batch; Generating function; Statistical properties

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INTRODUCTION

Since the pioneering discovery of dendrimers due to Tomalia and coworkers,^[1] dendritic polymers such as dendrimers and hyperbranched polymers have caused particular interest for their special structures and properties.^[2–5] Compared with dendrimers, hyperbranched polymers have imperfect structures, but possess the features of relatively convenient synthesis and low cost,^[4,5] and therefore can be easily industrialized. With the numerous relevant studies, some characteristic properties of hyperbranched polymers have been found such as low viscosity, high solubility, without entanglement, and with a large number of functional terminal groups. So far, hyperbranched polymers have been widely utilized in blending modification, surface modification, coating, catalytic reaction, and drug delivery.^[6,7]

As is well known, there are two representative methods for preparing hyperbranched polymers. One is the polycondensation of AB_g ($g \geq 2$) type monomers proposed initially by Flory,^[8] and realized in the lab by Webster and Kim.^[2] The other is the self-condensing vinyl polymerization (SCVP) of AB^*

type inimers proposed by Fréchet in 1995,^[3] where A denotes a vinyl group and B^* represents an active site capable of initiating a vinyl group A into a new active site A^* . In the light of this synthetic route, a large number of experiments on several typical SCVP systems have been performed, which include SCVP systems of pure inimers,^[9–14] binary copolymerization systems (inimers and core initiators,^[15–19] inimers and monomers^[20–25]), and ternary copolymerization system (inimers, monomers and core initiators).^[26–28] These experiments have manifested that these SCVP systems had an appreciable prospect not only in polymer science but also in industry and chemical engineering.

Following these relevant experiments,^[9–29] some theoretical investigations on SCVP systems have been well presented. In 1997, the SCVP system of pure inimers was investigated for the first time by Müller, Yan and Wulkow.^[30,31] Subsequently, binary and ternary SCVP systems have been extensively studied by various methods.^[32–49] Among these studies, much attention has been paid to the polymerization mechanism, kinetics, size distribution, average molecular weights, dispersity, degree of branching, mean-square radius of gyration, and so forth. These theoretical work has not only offered rich information to learn about various SCVP systems but also inspired some new research interest.

With the rapid developments in both theoretical and experimental studies on different SCVP systems, the semi-batch

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process (known also as the semi-continuous process) has attracted an increasing attention since it is closely related to large-scale applications of hyperbranched polymers in various fields.^[50–58] It is well known that for a polymerization system, the procedure by which a polymerization is carried out can lead to a significant effect on the polymerization kinetics, dynamics and physical properties of resultant polymers. As far as this aspect is concerned, depending on the manner that the reactants are added into the reactor, polymerization processes can be classified into the batch, semi-batch, and continuous processes, respectively.

In a batch process, all the reactants are fed into the reactor at the beginning of a polymerization, and no material is added into or removed from the reactor during the polymerization. A semi-batch process refers to the case that reactants would be added into the reactor during the polymerization, while the products may also be removed from the reactor. In general, only a portion of reactants is initially loaded into the reactor, whereas the remainder would be fed according to a predetermined schedule. Unlike batch and semi-batch processes, a continuous process involves both a feeding of reactants and a removal of products such that there is usually a balance between the input and output streams.

In essence, these three types of feeding operations signify different local reaction conditions such as concentrations of individual species including monomers, initiators, and possible chain transfer agents. As such, polymers produced from the same reactants may possess quite different properties depending on the distinct feeding processes. It is therefore expected that there is an obvious effect of the feeding process on the final properties of polymers such as the average molecular weights, polydispersity, degree of branching and possible copolymer composition.

Experimentally, a batch process needs the modest demanding and the least amount of control, and hence it is mainly used for pure academic interest. A drawback in the batch process is that the drifts of molecular weight distribution and composition distribution are very common because reactant concentrations decrease gradually during the polymerization. In contrast to the batch process, a continuous process tends to be applied when a large volume of polymers is manufactured. In practice, most continuous processes are performed at a relatively steady reaction condition. In this way, the drift of molecular weight distribution can be well inhibited. However, it is inevitable that a high instrumentation cost and a long uninterrupted reaction time are usually involved. By comparison, in a semi-batch process, the corresponding drifts can be substantially reduced since the concentration of reactants can be controlled by an appropriate predetermined feeding schedule. Consequently, a polymerization can even be carried out under starved conditions to prepare polymers with desired properties.

In addition to the above-mentioned features, the versatility of the semi-batch mode is also closely related to the problem of exotherm. As is well known, some living polymerizations are so fast that the released heat due to polymerization becomes a potential hazard. However, controlling the feeding details in the semi-batch process allows a control over the reaction rate, and hence the exotherm. In other words, a low concentration of reactants can be maintained such that the

semi-batch operation is compatible with the safety requirement. Moreover, the semi-batch process can also provide a regulation over the polymer structure and morphology for some polymerization systems.^[50–58] In view of these obvious advantages, the semi-batch process has been widely utilized in both industry and academic interests.

This work is motivated by the use of semi-batch process in the SCVP system consisting of pure inimers. An attempt is made to find how the semi-batch process regulates the average properties of hyperbranched polymers. This idea is based on the fact that a semi-batch process can always be decomposed into a series of time-sequenced feeding and polymerization steps. More importantly, the polymerization occurred between any two nearest neighbor steps is in essence equivalent to a batch process with various preexisted polymers formed by another SCVP system. Therefore, such a goal can be achieved once an average polymeric quantity associated with any two nearest neighbor steps is presented. This signifies that, if an average polymeric quantity for any two nearest neighbor polymerization steps is figured out, one is able to find the effect of the semi-batch process on the SCVP system.

For this purpose, our discussions will be firstly focused on the two nearest neighbor feedings, and then we generalize it to the whole feeding sequence. As usual, the number-, weight-, and z-average molecular weights denoted by M_n , M_w and M_z as well as dispersity index (\mathcal{D}) would be investigated. Although the semi-batch SCVP system is very complicated, these average physical quantities can still be obtained in a straightforward manner. Throughout the study the following classical assumptions of ideal polymerization were adopted: (1) two types of active sites B^* and A^* have the same reactivity; (2) all the vinyl group A react independently one another; (3) no intramolecular reaction takes place in the system. These approximations have been used in previous studies.^[30–36] For simplicity, the mass of an inimer has been taken as the unit mass.

This article is organized as follows. Firstly, an explicit generating function (GF) is proposed to calculate some average properties of the SCVP system with any initial distribution of preexisted polymers. Upon applying the GF method to the batch SCVP system of pure inimers, it reproduces identical results as given by previous studies, thereby validating the present GF method. Secondly, we generalized the present GF method to the semi-batch SCVP system, and investigated M_n , M_w , M_z , and \mathcal{D} of hyperbranched polymers. This is based on the fact that an SCVP system with preexisted polymers corresponds to two nearest neighbor steps in the semi-batch SCVP system. Meanwhile, two typical feeding processes are taken to illustrate the effect of the semi-batch process on these average polymeric quantities. Thirdly, a Monte Carlo (MC) simulation is performed for the semi-batch SCVP system to confirm the present GF method. As expected, an excellent agreement between analytical and simulation results is observed. Finally, we summarize some relevant results and discuss some limitations of the present work.

MODEL AND THEORY METHOD

Generating Function Method for an SCVP System with Any Initial Distribution of Polymers

As stated above, the effect of the semi-batch process on an

SCVP system can be presented as long as the relationship of an averaged polymeric quantity associated with any two nearest neighbor feedings is obtained. In this section, a novel GF method will be proposed to achieve such a goal. Without loss of generality, we suppose that there have preexisted some polymers at the beginning of the SCVP system under consideration. This could correspond to two nearest neighbor polymerization steps, where the preexisted polymers come from either a previous polymerization step or a feeding operation, or from both them. In this way, an explicit GF will be employed to study such an SCVP system, which enables us to find how an average polymeric quantity depends on these preexisted polymers.

To proceed, we suppose that, for the present SCVP system, the number of preexisted polymers of m -mer ($m=1,2,3,\dots$) in the initial stage is $P_m(x=0)$, where the symbol x denotes the conversion of vinyl groups A. According to the reaction mechanism of the SCVP,^[3,30,31] an active site B* or A* can initiate a vinyl group A of another molecule to form a new molecule and generate a new active site A*. Clearly, the consumption of an old active center (A* or B*) always leads to a new active center A*. This means that the number of active sites remains unchanged during the polymerization. It is also evident that there exist m active sites and only one vinyl group A in an m -mer is in accordance with the assumption of neglecting intramolecular reaction. Thus, the total number of active sites $N_* = \sum_m mP_m(x=0)$, while the total number of vinyl groups A is $N = \sum_m P_m(x=0)$. This is the initial condition of the present SCVP system.

Through successive reactions, molecules in the system can be linked together to form hyperbranched polymers of various sizes. As proposed by Müller, Yan and Wulkow, the evolution of the size distribution of polymers with time t in such an SCVP system is governed by the following kinetic equation:^[30]

$$\frac{dP_m(x)}{dt} = R \left[\frac{1}{2} \sum_{n=1}^{m-1} mP_n(x)P_{m-n}(x) - \sum_{n=1}^{\infty} (n+m)P_n(x)P_m(x) \right] \quad (1)$$

where $P_m(x)$ denotes the number of polymers of m -mer at conversion x , and R is rate constant for the polymerization. As usual, the same rate constants of A* and B* reacting with vinyl group A have been used under the assumption of equal reactivity.

Considering that the initial conversion of vinyl groups A has been arranged to be zero, then there would be $N(1-x)$ free vinyl groups A in the system at a conversion x . According to the reaction mechanism, upon considering the change of free vinyl groups A during the polymerization, one can find that the variation of the conversion x in time t is subject to the equation:^[30]

$$\frac{dx}{dt} = R \left[\sum_{m=1}^{\infty} mP_m(x=0) \right] (1-x) = RN_*(1-x) \quad (2)$$

where the number of active sites N_* keeps a constant. Solving this equation yields

$$x(t) = 1 - \exp(-RN_*t) \quad (3)$$

This is an explicit relationship between the conversion $x(t)$ and time t . The combination of Eqs. (1) and (2) enables one to obtain the following equation:

$$\frac{dP_m(x)}{dx} = \frac{1}{r} \left[\frac{m}{2N(1-x)} \sum_{n=1}^{m-1} P_n(x)P_{m-n}(x) - \left(m + \frac{r}{1-x} \right) P_m(x) \right] \quad (4)$$

in which $r = N_*/N$, denotes the molar ratio of active sites to free vinyl groups at the beginning of the present SCVP system. As $r=1$ (this signifies that no polymer is preexisted), this equation is identical with that given by Müller, Yan and Wulkow.^[30]

Note that there are N free vinyl groups A at the beginning of the system, therefore the total number of molecules would be $N(1-x)$ when the conversion of vinyl groups A is x . This means that $N(1-x) = \sum_m P_m(x)$. Furthermore, $P_m(x)$ can be rewritten as $P_m(x) = N(1-x)c_m(x)$ since each molecule possesses only one free vinyl group A, in which $c_m(x)$ denotes the number fraction of polymers of m -mer at a conversion x . This results in the following identity:

$$\sum_m c_m(x) \equiv 1 \quad (5)$$

Substituting $P_m(x) = N(1-x)c_m(x)$ into Eq. (4) yields the differential equation satisfied by $c_m(x)$:

$$\frac{dc_m(x)}{dx} = \frac{m}{r} \left[\frac{1}{2} \sum_{n=1}^{m-1} c_n(x)c_{m-n}(x) - c_m(x) \right] \quad (6)$$

In order to determine $c_m(x)$, a GF denoted by $G(x, \theta)$ can be introduced as follows:

$$G(x, \theta) = \sum_{m=1}^{\infty} c_m(x) \exp(m\theta) \quad (7)$$

where θ is an auxiliary variable. Such a GF signifies that $c_m(x)$ can be obtained by expanding $G(x, \theta)$ in the series of $\exp(\theta)$ provided that the GF is explicitly given. It is therefore necessary to derive an explicit expression of $G(x, \theta)$ for further investigations. To this end, through Eqs. (6) and (7), one can obtain a partial differential equation satisfied by $G(x, \theta)$, namely

$$[1 - G(x, \theta)] \frac{\partial}{\partial \theta} G(x, \theta) + r \frac{\partial}{\partial x} G(x, \theta) = 0 \quad (8)$$

It is obvious that through the initial conditions of the system, solving this equation will enable us to obtain $G(x, \theta)$, and hence $c_m(x)$ and $P_m(x)$.

The partial differential equation given by Eq. (8) is known as Burgers equation,^[59,60] and the corresponding characteristics of $G(x, \theta)$ through the point $(0, \phi)$ on the $x - \theta$ plane satisfies the following equation:

$$\theta - \phi = \frac{1}{r} [1 - G(0, \phi)]x \quad (9)$$

where ϕ is a function of x and θ by writing $\phi(x, \theta)$ to be determined. Clearly, the term $\frac{1}{r} [1 - G(0, \phi)]$ plays the role of slope of the characteristic line, and thus we have $G(x, \theta) = G[0, \phi(x, \theta)]$ from Eq. (8). This signifies that $G(x, \theta)$ can be derived once the dependence of $\phi(x, \theta)$ on variables x and θ is figured out. Making use of $G(x, \theta) = G[0, \phi(x, \theta)]$ together with Eqs. (7) and (9), we have

$$G(x, \theta) = \sum_{m=1}^{\infty} c_m(0) \exp(m\theta) \exp \left\{ -\frac{mx}{r} [1 - G(x, \theta)] \right\} \quad (10)$$

From the definition of the GF given in Eq. (7), the explicit expressions of $G(x, \theta)$ and $c_m(x)$ could be directly calculated through the initial conditions given by $c_m(0)$.

The derivation of $G(x, \theta)$ is especially useful for the evalu-

ation of average polymeric quantities of the system. For instance, upon introducing the k^{th} ($k = 0, 1, 2, \dots$) polymer moments, $M_k(x)$ defined by $M_k(x) = \sum_{m=1}^{\infty} m^k P_m(x)$, and then taking into account $P_m(x) = N(1-x)c_m(x)$ together with Eq. (7) follows that

$$M_k(x) = N(1-x) \frac{\partial^k}{\partial \theta^k} G(x, \theta) |_{\theta=0} \quad (11)$$

where $\frac{\partial^k}{\partial \theta^k} G(x, \theta)$ denotes the k^{th} partial derivatives of $G(x, \theta)$ with respect to the variable θ , and $\frac{\partial^k}{\partial \theta^k} G(x, \theta) |_{\theta=0}$ denotes its value evaluated at $\theta=0$.

Bear in mind that the mass of an inimer has been used as the unit mass, the number-, weight-, and z-average molecular weights, and \mathcal{D} can be calculated from the derived $M_k(x)$ by using

$$\begin{aligned} M_n(x) &= \frac{M_1(x)}{M_0(x)}, \quad M_w(x) = \frac{M_2(x)}{M_1(x)}, \\ M_z(x) &= \frac{M_3(x)}{M_2(x)}, \quad \mathcal{D}(x) = \frac{M_w(x)}{M_n(x)}. \end{aligned} \quad (12)$$

For the system under study, as a consequence of Eqs. (11) and (12), we have

$$\begin{aligned} M_n(x) &= \frac{1}{1-x} M_n(0), \quad M_w(x) = \frac{1}{(1-x)^2} M_w(0), \\ M_z(x) &= \frac{M_z(0)}{1-x} + \frac{3xM_w(0)}{(1-x)^2}, \quad \mathcal{D}(x) = \frac{1}{1-x} \mathcal{D}(0). \end{aligned} \quad (13)$$

where $M_n(0)$, $M_w(0)$, $M_z(0)$, and $\mathcal{D}(0)$ are the number-, weight-, and z-average molecular weights, and \mathcal{D} at $x=0$, respectively. This equation indicates that $M_n(x)$, $M_w(x)$, $M_z(x)$, and $\mathcal{D}(x)$ have been associated with their corresponding initial values at $x=0$. In other words, the effect of preexisted polymers on these average polymeric quantities has been explicitly carried out.

Now a question that arises naturally is whether the present GF method is valid. To demonstrate its validity, the present GF method is applied to the batch SCVP system of pure inimers due to Müller, Yan and Wulkow.^[30] Assume that there exist N inimers in the initial stage of the system, then we have $c_m(0) = \delta_{m,1}$ (δ_{ij} is the Kronecker symbol, which is equal to 1 for $i = j$, and 0 otherwise.). Meanwhile, one can find that $r=1$ and $G(x, \theta) = G[0, \phi(x, \theta)] = \exp[\phi(x, \theta)]$. With the help of Eqs. (7) and (10), we have

$$G(x, \theta) \exp[-xG(x, \theta)] = \exp(\theta - x) \quad (14)$$

Making use of Eq. (11) and differentiating both sides of this equation with respect to θ , the polymer moments $M_0(x) = N(1-x)$, $M_1(x) = N$, $M_2(x) = \frac{N}{(1-x)^2}$ and $M_3(x) = N \frac{1+2x}{(1-x)^4}$ can be easily obtained. Furthermore, a direct calculation from Eq. (12) leads to

$$\begin{aligned} M_n(x) &= \frac{1}{1-x}, \quad M_w(x) = \frac{1}{(1-x)^2} \\ M_z(x) &= \frac{1+2x}{(1-x)^2}, \quad \mathcal{D}(x) = \frac{1}{1-x} \end{aligned} \quad (15)$$

Alternatively, these results can be directly derived by substituting $M_n(0) = M_w(0) = M_z(0) = 1$ into Eq. (13). This signifies that one can obtain these results in terms of the present GF instead of using the size distribution of polymers, and all

we need is merely the initial conditions of the SCVP system.

More interestingly, $G(x, \theta)$ can also be employed to derive the size distribution of polymers by starting with Eq. (14) together with the theorem of Lagrange inversion (detailed calculations can be found in the electronic supplementary information, ESI).^[61] For brevity, here we only give the final expression of $G(x, \theta)$:

$$G(x, \theta) = \sum_{m=1}^{\infty} \omega_m x^{m-1} \exp(-mx) \exp(m\theta) \quad (16)$$

where $\omega_m = \frac{m^{m-1}}{m!}$ is rigorously derived from the residue theorem.^[62] Such an explicit expression of $G(x, \theta)$ means that $c_m(x) = \omega_m x^{m-1} \exp(-mx)$, and thus the size distribution $P_m(x)$ can be given by

$$P_m(x) = N(1-x) \omega_m x^{m-1} \exp(-mx) \quad (17)$$

All the results presented in Eqs. (15) and (17) are identical with those obtained in the batch SCVP system,^[30] thereby validating the present GF method. Furthermore, as a direct generalization, the present GF method will be employed to discuss the effect of the semi-batch process on the average polymeric quantities of hyperbranched polymers. This can be carried out by considering the semi-batch process as a series of multi-step processes of feeding and polymerization because any two nearest neighbour steps have been essentially solved by the present GF method.

A Unified Treatment on the Semi-batch SCVP System

For a polymerization system under the semi-batch mode, all the feeding operations are usually performed according to a predetermined schedule. Therefore the whole polymerization is exactly a multi-step process. This means that, at the beginning of each polymerization step, there are always some preexisted polymers resulting either from a previous polymerization or from the present feeding, or from both of them. As done in the previous section, these discrete steps can be further investigated one by one with the aid of the present GF method. Throughout the work, each feeding operation was considered to be instantaneous such that the response of the system during such an infinitesimal time interval can be neglected.

We assume that only inimers are initially loaded into the reactor, which is labeled as the zeroth feeding, for convenience. Subsequently, the first polymerization step begins until the conversion arrives at a predetermined conversion x_1 (or equivalently, at a predetermined reaction time), and then the first feeding is performed. After the first feeding, the second polymerization begins until the conversion arrives at x_2 . The rest steps are repeated in a similar manner until the last step polymerization is completed.

In this way, one can find that a polymerization and a feeding are always involved in each step. For clarity, a sequence of feedings and reactions in an SCVP system can be schematically illustrated in Fig. 1, where the semi-batch process was considered to be an L -step process. This indicates that the semi-batch SCVP system has been divided into an L -step polymerization process, and each step can be studied as we have presented in previous section.

Now the semi-batch SCVP system would be investigated as an application of the present GF method, which enables us to treat the situation that allows polymers of various sizes to be added into the reactor in each feeding. From the results giv-

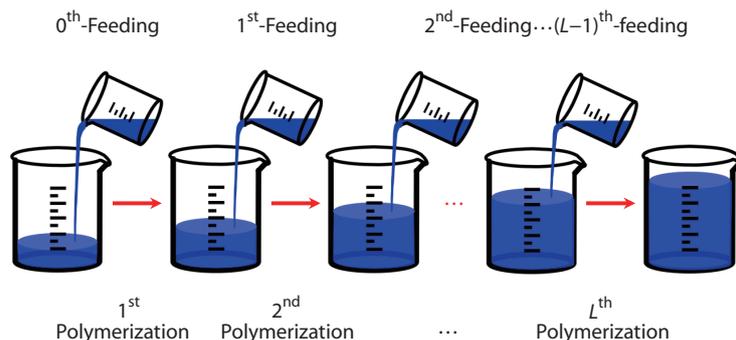


Fig. 1 Schematic illustration of the semi-batch SCVP system, which is thought of as an L -step processes, and each step is comprised of polymerization and feeding.

en in previous section, it has been found that these average polymeric quantities associated with two nearest neighbor steps are closely related to each other. As such, M_n , M_w , M_z , and \mathcal{D} could be readily derived as long as the feeding details are specified.

As schemed in Fig. 1, for any two nearest neighbor steps, for example, the $(i-1)$ th and i th steps, the initial conditions of the i -th step polymerization depend explicitly on the number of polymers coming from the $(i-1)$ th polymerization and feeding. This indicates that the i th polymerization must be affected by the polymerization and feeding in the $(i-1)$ th step, so do the relevant average polymeric quantities.

Note that the $(i-1)$ th feeding was performed when the conversion of vinyl groups A was x_{i-1} , and after this feeding the i th step polymerization takes place. Let $P_m^{(i)}(x_i=0)$ be the number of polymers of m -mer ($m=1,2,3,\dots$) at the beginning of the i th step polymerization, which can be expressed as:

$$P_m^{(i)}(x_i=0) = P_m(x_{i-1}) + F_m^{(i-1)} \quad (18)$$

where $P_m(x_{i-1})$ and $F_m^{(i-1)}$ denote the number of polymers of m -mer due to the $(i-1)$ th polymerization and feeding, respectively. Obviously, now the total number of active sites is $\sum_m m P_m^{(i)}(x_i=0)$, while the number of vinyl groups A is $N^{(i)} = \sum_m P_m^{(i)}(x_i=0)$. This is the initial condition of the i th step polymerization.

In analogy with Eqs. (9) and (10), the most important two equations resulting from the GF method can be found as:

$$r_i [\theta - \phi(x_i, \theta)] = [1 - G(x_i, \theta)] x_i, \quad (19)$$

$$G(x_i, \theta) = \sum_{m=1}^{\infty} c_m^{(i)}(0) \exp[m\phi(x_i, \theta)]$$

where $r_i = \sum_m m P_m^{(i)}(x_i=0) / N^{(i)}$, is the molar ratio of active sites to free vinyl groups in the i -th step, x_i denotes the conversion of vinyl groups A, and $c_m^{(i)}(0)$ is the number fraction of polymers of m -mer at $x_i=0$. In obtaining Eq. (19), the equation $G(x_i, \theta) = G[0, \phi(x_i, \theta)]$ has been used.

Making use of Eq. (19), the k th polymer moment in the i th step polymerization defined by $M_k(x_i) = \sum_{m=1}^{\infty} m^k P_m(x_i)$ can be given by

$$M_k(x_i) = N^{(i)} (1 - x_i) \frac{\partial^k}{\partial \theta^k} G(x_i, \theta) \Big|_{\theta=0} \quad (20)$$

Likewise, $M_n(x_i)$, $M_w(x_i)$, $M_z(x_i)$, and $\mathcal{D}(x_i)$ in the i th step polymerization can be explicitly derived through the k th polymer moments evaluated by this equation. More specifically, as a consequence of the present GF method, recursion formula (a detailed derivation has been left in ESI) can be obtained as follows:

$$M_n(x_{i+1}) = \frac{1}{(1-x_{i+1})} \frac{f_{1,0}^{(i)} + M_n(x_i)}{1 + f_{0,0}^{(i)}},$$

$$M_w(x_{i+1}) = \frac{1}{(1-x_{i+1})^2} \frac{f_{2,1}^{(i)} + M_w(x_i)}{1 + f_{1,1}^{(i)}}, \quad (21)$$

$$M_z(x_{i+1}) = \frac{f_{3,2}^{(i)} + M_z(x_i)}{(1-x_{i+1})(1+f_{2,2}^{(i)})} + \frac{3x_{i+1}M_w(x_i)}{(1-x_{i+1})^2},$$

$$\mathcal{D}(x_{i+1}) = \frac{1 + f_{0,0}^{(i)} [f_{2,1}^{(i)}/M_n(x_i)] + \mathcal{D}(x_i)}{(1-x_{i+1}) [1 + f_{1,1}^{(i)}]^2},$$

where the quantity $f_{k,k'}^{(i)}$ is defined by

$$f_{k,k'}^{(i)} = \frac{\sum_m m^k F_m^{(i)}}{\sum_m m^{k'} P_m(x_i)}, \quad (k, k' = 0, 1, 2, 3, \dots) \quad (22)$$

which denotes the ratio of the k th polymeric moment due to feeding to the k th polymeric moment due to polymerization in the i th step.

It should be stressed that the quantity $f_{k,k'}^{(i)}$ depends not only on the number of polymers from the i th feeding, but also on those from the i th polymerization. Of course, the removal of polymers can be taken into account by stating in Eqs. (18) and (22) the degree of polymerization and the number of those removed polymers. This indicates that $f_{k,k'}^{(i)}$ is closely related to the feeding details such as species and amount of those fed polymers. For example, $f_{0,0}^{(i)}$ measures the molar ratio of the two types of polymers in the i th step, while $f_{1,1}^{(i)}$ measures the corresponding weight ratio. As such, $f_{k,k'}^{(i)}$ plays a key role in evaluating average polymer quantities in the i th step. In view of the relevance of two nearest neighbour steps, $f_{k,k'}^{(i)}$ becomes the most important factor that determines the average properties of resultant polymers.

RESULTS AND DISCUSSION

In this section, several average polymeric quantities for the semi-batch SCVP system would be calculated. Meanwhile, the MC simulation is also performed to verify the corresponding analytical results. It can be seen from Eq. (21), M_n , M_w , M_z , and \bar{D} involved in two nearest neighbor steps have been connected with each other. In other words, one can find how an average polymeric quantity in the present step is affected by previous steps in terms of the recursion formula. In so doing, we can conclude that these average polymeric quantities have related to all previous steps, and therefore they can be calculated provided that the feeding details and conversions in each step are specified. Furthermore, the effect of the semi-batch process on the SCVP system can be analyzed with the help of Eqs. (21) and (22). As an illustration, we will devote ourself to the most frequently encountered case that only inimers are fed into in each step, which is of particular importance in practice. Specifically, two typical feeding ways would be investigated to calculate M_n and M_w , as shown below.

Case I: Feeding the same amount of inimers in each step

The first feeding way corresponds to the case that the number of fed inimers in each step keeps always the same as each other, which is widely employed in practice and would be referred to as the Case I. This simply means that the number of the fed inimers is equal to that loaded initially (the zero-th feeding in Fig. 1). More precisely, we have for $i \geq 1$:

$$\sum_m m^k F_m^{(i)} = \sum_m m^k F_m^{(0)} \delta_{m,1} = F_1^{(i)} \tag{23}$$

where $\sum_m m F_m^{(i)}$ also denotes the weight of the fed inimers in the i^{th} step since the mass of an inimer has been taken as the unit mass.

Clearly, feeding the same number of inimers in each step signifies that $f_{1,1}^{(i)}$ satisfies the criteria $f_{1,1}^{(i)} = \frac{1}{i}$. This results in the following relationships:

$$f_{2,1}^{(i)} = f_{1,1}^{(i)} = \frac{1}{i}, \quad f_{1,0}^{(i)} = f_{0,0}^{(i)} = \frac{1}{i} M_n(x_i) \tag{24}$$

where $M_n(x_i) = \frac{M_1(x_i)}{M_0(x_i)}$, denotes the number-average molecular weight in the i^{th} step polymerization with the conversion x_i .

According to such a feeding operation, if an SCVP system is eventually terminated at the L^{th} polymerization with the conversion x_L , from Eqs. (21) and (24) we have

$$\frac{1}{M_n(x_L)} = \frac{1}{L} \sum_{j=1}^L \left[\prod_{i=j}^L (1-x_i) \right], \tag{25}$$

$$M_w(x_L) = \frac{1}{L} \sum_{j=1}^L \left[\prod_{i=j}^L \frac{1}{(1-x_i)^2} \right].$$

In obtaining these, $M_n(x_1) = \frac{1}{1-x_1}$ and $M_w(x_1) = \frac{1}{(1-x_1)^2}$ have been used.

The above results manifest that the average properties of resultant polymers would be influenced by all the previous polymerization steps. They can be evaluated in a straightforward manner when the conversions of vinyl groups A and feeding details in each step are specified. Namely, for the Case I, one needs x_i ($i = 1, 2, \dots, L$) to evaluate M_n , M_w , M_z , and \bar{D} . Furthermore, the effect of the semi-batch process on the SCVP system under this feeding way can be found.

As an illustration, M_w and \bar{D} for the semi-batch SCVP system under the Case I have been calculated through Eq. (25), as presented in panels (a) and (b) of Fig. 2, respectively. To reveal the effect of the semi-batch mode, the results of M_w and \bar{D} under the batch mode are also given. In our calculations, the conversions x_i for different L have been listed in Table 1, in which the final conversions of vinyl groups in the batch and semi-batch modes have been designed to be approximately equal to each other. Meanwhile, the conversion at each step has been mapped onto the corresponding conversion to compare with the batch process.

Seen from Fig. 2, we can find the variations of M_w and \bar{D} with the increasing conversion at different L . The feeding operations can be obviously observed through the changes in M_w and \bar{D} since each feeding the inimers always gives rise to an obvious decrease in M_w and an obvious increase in \bar{D} . Compared with that in the batch mode, M_w and \bar{D} in the semi-batch mode can even increase by orders of magnitude. Because both M_w and \bar{D} of polymers play a central role in various fields, one can take advantage of such an ability of the semi-batch process to prepare hyperbranched polymers with

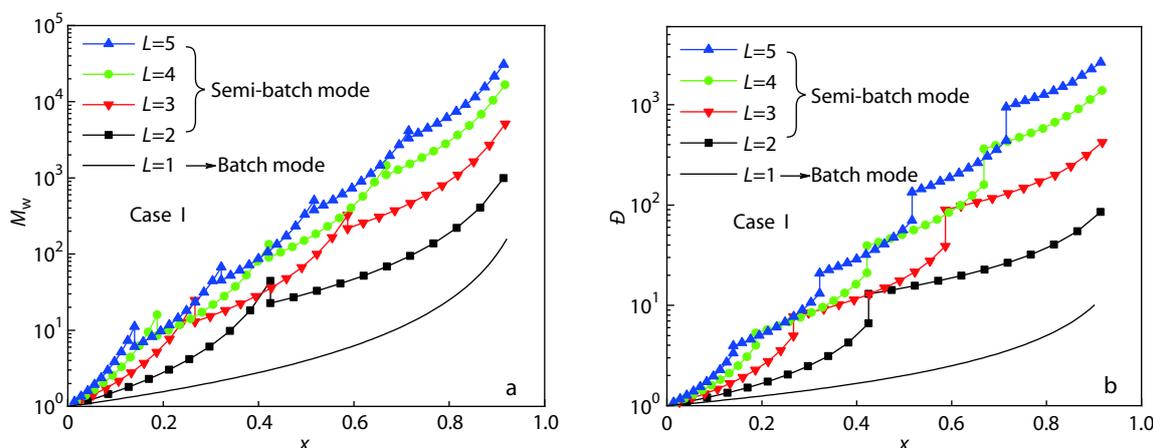


Fig. 2 M_w in panel (a) and \bar{D} in panel (b) for the semi-batch SCVP system under the Case I, where conversions at different L are specified in Table 1, and where the lines are drawn only to guide the eye.

Table 1 Conversions at different L for calculating M_w and \bar{D} under the Case I.

Case I	Conversion
$L=2$	$x_1=x_2=0.85$
$L=3$	$x_1=x_2=x_3=0.83$
$L=4$	$x_i=0.75$ ($i=1, 2, \dots, 4$)
$L=5$	$x_i=0.70$ ($i=1, 2, \dots, 5$)

desired M_w and \bar{D} .

Case II: Feeding inimers to maintain the same number of free vinyl groups in each step

The second case is that feeding inimers is to maintain a fixed initial concentration of free vinyl groups A, which is referred to as the Case II. This kind of feeding implies that the consumption fraction of vinyl groups would be supplied by the feeding operation. In other words, the number of vinyl groups at the beginning of each polymerization step always remains a constant. In a sense, this indicates a steady rate for a polymerization, i.e.:

$$\sum_m m^k F_m^{(i)} \delta_{m,1} = F_1^{(i)} = N^{(i)} x_i \quad (26)$$

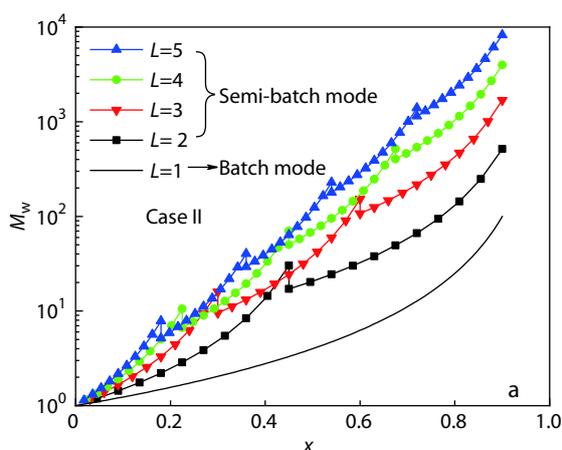
where $N^{(i)}$ denotes the initial number of molecules in the i^{th} step polymerization, and $N^{(i)} x_i$ represents the number of inimers supplied by the i^{th} feeding.

Given that the number of inimers at the initial stage is $N^{(0)}$, thus one can find that $N^{(i)} = N^{(0)}$ ($i=1, 2, \dots, L$) holds true for all the polymerization steps. Through these analysis, we obtain

$$\begin{aligned} f_{1,0}^{(i)} &= f_{0,0}^{(i)} = \frac{x_i}{1-x_i} \\ f_{2,1}^{(i)} &= f_{1,1}^{(i)} = \frac{x_i}{\sum_{j=0}^i x_j} \end{aligned} \quad (27)$$

in which we have arranged $x_0 \equiv 1$, for convenience. If the SCVP system is eventually terminated at the L^{th} polymerization with conversion x_L , making use of Eqs. (21) and (27) leads to

$$\begin{aligned} M_n(x_L) &= \frac{1}{1-x_L} \sum_{i=0}^{L-1} x_i \\ M_w(x_L) &= \frac{1}{\sum_{i=0}^{L-1} x_i} \sum_{j=1}^L \left[\frac{x_{j-1}}{\prod_{i=j}^L (1-x_i)^2} \right] \end{aligned} \quad (28)$$



In obtaining these equations, we have used the results $M_n(x_1) = \frac{1}{1-x_1}$ and $M_w(x_1) = \frac{1}{(1-x_1)^2}$.

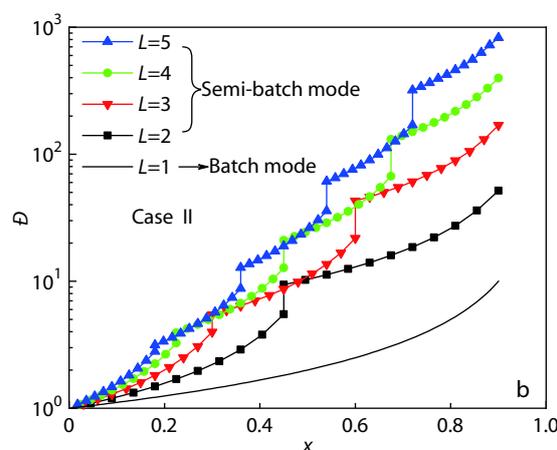
Through Eq. (28), M_n , M_w , and \bar{D} can be evaluated whenever the conversions and feeding details in each step are specified. It is also easy to find that all the previous steps can result in an apparent effect on the average properties of the resultant polymers. Likewise, for the semi-batch SCVP system under the Case II with details given by Table 2, M_w and \bar{D} have been carried out, as presented in panels (a) and (b) of Fig. 3, respectively.

Table 2 Conversions at different L for calculating M_w and \bar{D} under the Case II.

Case II	Conversion
$L=2$	$x_1=x_2=0.90$
$L=3$	$x_1=x_2=x_3=0.90$
$L=4$	$x_i=0.90$ ($i=1, 2, \dots, 4$)
$L=5$	$x_i=0.90$ ($i=1, 2, \dots, 5$)

Compared with that in the batch mode, M_w and \bar{D} in this case also increase by orders of magnitude, as illustrated. Nevertheless, the difference of the average polymeric quantities between the two cases is rather obvious, as shown in Figs. 2 and 3, respectively. Thus both the two feeding ways can give rise to a significant increase in M_w and \bar{D} . However, the dependence of final average polymeric quantities on conversions of each step is obviously different from each other, which implies a significant effect of the distinct feeding ways on the average properties of hyperbranched polymers.

Note that for the present semi-batch SCVP system, the problem of exotherm could be solved because of its characteristic operation of multiple feedings. In practice, depending on the specific reaction conditions, various species and fed amount can be well designed to control the polymerization. In so doing, the semi-batch mode becomes compatible with the safe requirement. This is, of course, particularly important for applying SCVP method to prepare hyperbranched polymers in industry and chemical engineering.

**Fig. 3** M_w in panel (a) and \bar{D} in panel (b) for the semi-batch SCVP system under the Case II, where conversions at different L are specified in Table 2, where the lines are drawn only to guide the eye.

Monte Carlo Simulation for a Semi-batch SCVP System

In this section, MC simulations on the semi-batch SCVP system would be performed for the case that only inimers are fed into the reactor. In particular, the simulation results for Cases I and II discussed in this work would be compared with the corresponding analytical results. For a stochastic chemical reaction, a set of master equations can be constructed on the basis of the reaction mechanism.^[63,64] In the present SCVP system, the change in size distribution of polymers is subject to the differential kinetic equations given in Eq. (1). Therefore the evolution of MC simulation would be governed by the corresponding master equation. For easy of presentation, here we only outline how to use MC method to simulate a semi-batch SCVP system.

Assume that the system consists of treelike molecules with size distribution $P_n(t)$ at a given time t , and after a time interval t_w a reaction takes place. As a consequence, the system evolves into a new state characterized by a renewed size distribution $P_n(t + t_w)$ of polymers at the time $t + t_w$. The quantity t_w is usually called the waiting time since it denotes a time interval between two successive reactions. It is therefore important for an MC simulation to determine both the waiting time t_w and reaction type (what species are involved in each reaction).

According to the Eqs. (1) and (2), if $\Omega_n(t)$ is the possible reaction rate of forming treelike polymers of n -mer at time t , we have

$$\Omega_n(t) = \frac{R}{2} \sum_{i=1}^{n-1} n P_i(t) [P_{n-i}(t) - \delta_{i,n-i}] \quad (29)$$

where the term with Kronecker symbol δ_{ij} is to avoid repeated counts of reaction ways. The total possible reaction rate as a function of t over all possible n can be written as $\Omega(t) = \sum_n \Omega_n(t)$. Thus, the waiting time, t_w , can be determined by a random number r_1 through the relationship:^[63,64]

$$t_w = \Omega(t)^{-1} \ln r_1^{-1} \quad (30)$$

This indicates that t_w is a stochastic quantity rather than a constant. Subsequently, $q_n(t)$, the probability of generating treelike molecules of n -mer can be expressed as:

$$q_n(t) = \frac{\Omega_n(t)}{\Omega(t)}, \quad (n = 2, 3, \dots) \quad (31)$$

The simulation can be performed by a simple sampling over all reaction events because of the identity of $\sum_n q_n(t) \equiv 1$. In other words, one can sample in the corresponding probability space such that the reaction type associated with a degree of polymerization (index n) could be determined. In such a routine process, two more random numbers would be involved, and the sampling method is available in the literature.^[63,64] In this way, the state characterized by the size distribution of polymers $P_n(t)$ (equivalently, $P_n(x)$) should be renewed after each reaction and feeding, whereby the relevant polymer quantities can be evaluated.

To test the program, we have firstly implemented 100 simulations on the batch SCVP system, where the number of inimers in each was fixed as $N=10^5$. As a consequence of the simulation, M_n and M_w have been presented in Fig. 4, in which $P_n(x)$ at $x=0.97$ is also illustrated in the insert. Meanwhile, a comparison with the corresponding analytic results

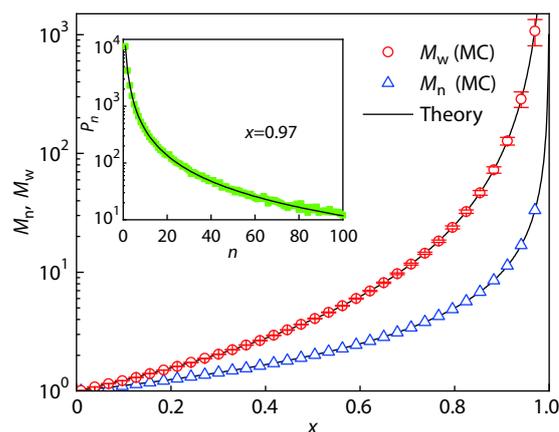


Fig. 4 M_w (with error bar) and M_n against x , and the size distribution $P_n(x=0.97)$ against n (insert) for the batch SCVP system, where the lines and symbols denote the theoretical and simulation results, respectively.

has been made. Clearly, the simulation results of P_n against n , M_n and M_w against x agree well with their analytical results, thereby validating the present MC simulation method. This enables us to simulate a semi-batch SCVP system.

Clearly, the key quantity obtained from the MC simulation is the number distribution of hyperbranched polymers, and hence the molecular weight distribution (MWD). This is measurable in experiments. Interestingly, the variation of MWD with time can be directly carried out provided that the reaction rate R is known. In accordance with the above method, we have implemented 100 simulations on the semi-batch SCVP system for both Case I and Case II. In each simulation, the total number of inimers is fixed as $N=10^6$, while the number of the fed inimers at each step is determined by the conversions specified in the Tables 1 and 2. For brevity, we only take the simulation results of M_w as an example to compare with the corresponding theoretical results, as shown in Figs. 5 and 6, respectively.

An excellent agreement between the theoretical and simulation results can be observed. At a fixed L , there was an obvious increase in M_w whenever a polymerization step is finished. Seen from panels (a) to (d) in Fig. 5, it can be found that M_w increase even by orders of magnitude with the increase of L , so does in Fig. 6. This is a general tendency of the present semi-batch SCVP system. Comparing Fig. 5 with Fig. 6, one can find that the increment of M_w in the Case I is always larger than that in the Case II. Such a tendency depends on the predetermined schedule given in Tables 1 and 2.

The above simulation results manifested that the present GF method can be employed to evaluate M_n , M_w , M_z and \mathcal{D} of polymers by a semi-batch SCVP system. Experimentally, one might be interested in the variations of relevant average physical quantities with time. This can be easily realized in the MC simulation when the reaction rate R is given. Instead of this, in this paper the conversion x is used as the variable to describe the average physical quantities varying in the polymerization process. For a practical polymerization system, one can optimize feeding details to prepare hyperbranched polymers with desired average properties. Consequently, one can choose feeding ways, specify the number of batches, and

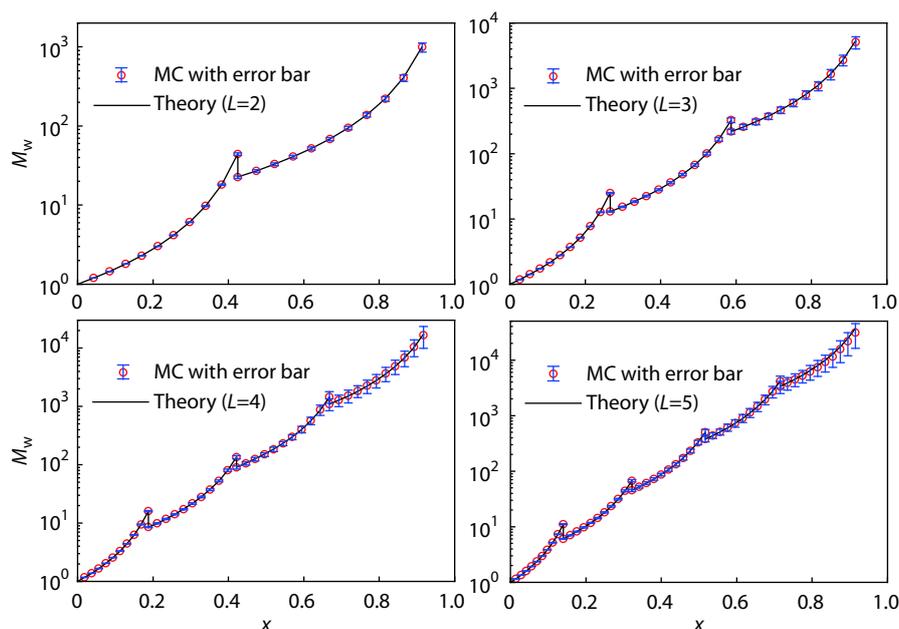


Fig. 5 M_w for the semi-batch SCVP system in the Case I, where lines and symbols denote the results from the GF method and MC simulations, respectively.

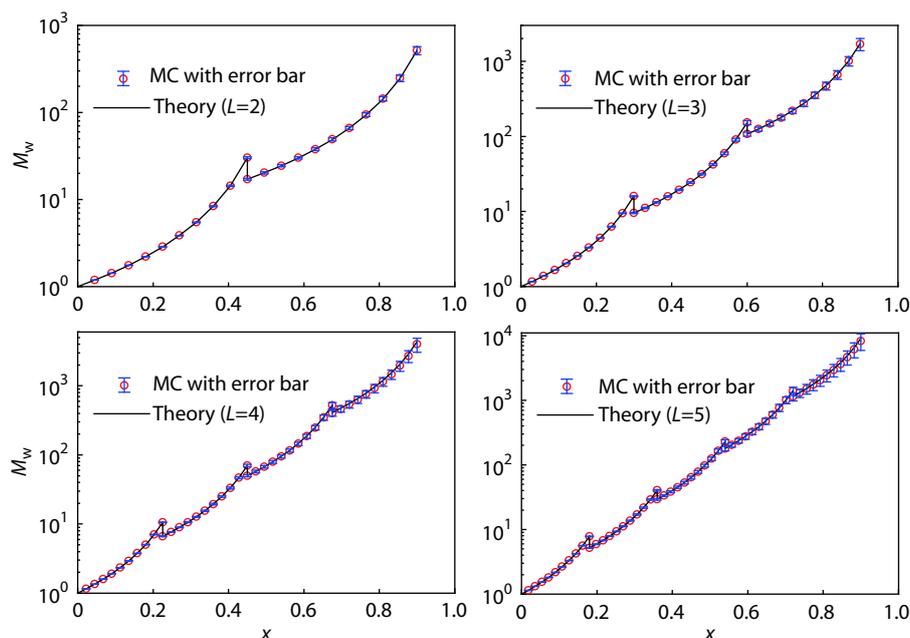


Fig. 6 M_w for the semi-batch SCVP system in the Case II, where lines and symbols denote the results from the GF method and MC simulation, respectively.

predetermine conversions at each step. On the basis of these information, some average polymeric quantities of interest can be obtained by Eq. (21) in a straightforward manner.

CONCLUSIONS

In summary, we presented a GF method for investigating the SCVP system under the semi-batch mode by treating it as an L -step process. In each step the feeding allows various polymers produced from another SCVP system to be added into the

reactor. In this way, the proposed GF method can be employed to calculate some average polymeric quantities such as M_n , M_w , M_z , and \bar{D} when the predetermined details on the polymerization are specified. The relevant results were confirmed by the MC simulation, and therefore a unified treatment on the semi-batch SCVP system of pure inimers has been made.

Clearly, given the predetermined schedule that contains the number of batches L and the feeding details (feeding modes, species and their amounts, and conversions in each

step, and so forth), some average properties of the semi-batch SCVP system can be easily evaluated by the present GF method. In view of the fact that the reactant concentrations in the semi-batch process are controllable, the drifts of molecular weight distribution can be substantially inhibited. Meanwhile, this also reduce the risk of the maximum exotherm, thereby maintaining a stable polymerization condition.

Although the removal of various polymers from the reactor is not yet considered in this work, it is not difficult to generalize the GF method to take into account such operations. This can be realized by adding the corresponding terms in Eqs. (18) and (22) by specifying the degree of polymerization and amount of those removed polymers in each step. Therefore, the effect of the removal operation on the SCVP system can be found.

Note that the present semi-batch SCVP system was treated as an *L*-step process, and a further study on the quasi-continuous process can be performed by increasing *L*. In particular, it is even possible that an SCVP system with a continuous feeding can be investigated for a large *L*, where the feeding rate plays an important role. Meanwhile, the binary SCVP system consisting of inimers and core initiator under the semi-batch mode can be readily studied by the present GF method. The relevant investigations are underway.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-021-2603-2>.

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