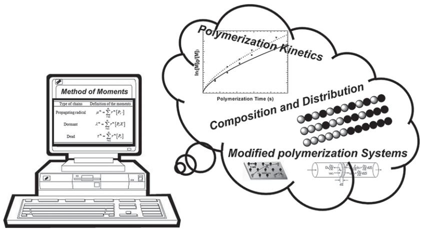
State-of-the-Art and Progress in Method of Moments for the Model-Based Reversible-Deactivation Radical Polymerization

Yin-Ning Zhou, Zheng-Hong Luo*

Reversible-deactivation radical polymerization (RDRP) techniques have received lots of interest for the past 20 years, not only owing to their simple, mild reaction conditions and broad applicability, but also their accessibility to produce polymeric materials with well-defined structures. Modeling is widely applied to optimize the polymerization conditions and processes. In addition, there are numerous literatures on the kinetic and reactor models for RDRP processes, which show the accessibility on polymerization kinetics insight, process optimization, and controlling over chain microstructure with predetermined molecular weight and low dispersity, copolymer composition distribution, and sequence distribution. This review highlights the facility of the method of moments in the modeling field and presents a summary of the present state-of-the-art and future perspectives focusing on the model-based RDRP processes based on the method of moments. Summary on the current status and challenges is discussed briefly.



1. Introduction

Macromolecular reaction engineering, as a well-established branch of chemical engineering, comprises polymerization kinetics, reactor design, and analysis and plays an important role in industrial fields.[1–3] For example, the selection of a reaction system that operates in the safest and most efficient manner can be the key to produce the most economical and high-quality products in polymer industries. In the past century, industrial polymer productions, including poly(methyl methacrylate), polystyrene, low-density polyethylene, polypropylene, and so on, have made great contributions for our society. A large proportion of commodity polymeric materials are produced by conventional free radical polymerization (FRP). However, because of the slow initiation, rapid propagation, and termination involving many different chain lengths, FRP is difficult to control over the polymer architectures and the minimum dispersity of the molar mass distribution is 2.[4,5] What's exciting is that controlled radical polymerization (also termed as reversible-deactivation radical polymerization (RDRP)) was discovered about two decades ago.[6,7] In most of RDRP systems, the initiation or degeneratively exchange is fast, propagation is relatively slow, and termination is suppressed per present chain, referring to the dominance of dormant chains in the final mixture. As a result, polymerization proceeds in a controlled manner, allowing one to prepare various well-defined block copolymers, stars, bottlebrushes, and hybrid materials.[6] Therefore, RDRP has attracted increasing interest from both academic and industrial fields.[8–10]

Facing the increasing demand on high qualified and tailor-made polymeric materials, despite the technological promise, there are only limited products and investigations based on RDRP techniques at industrial scale. This can be attributed to the limited commercial RDRP agents

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in large quantities at reasonable costs and the extra cost of the polymer purification processes.[10] From the view point of chemical engineering, the productivity and quality of the polymer products, as well as the polymer chain composition and chain topology, are largely influenced by the engineering problems, such as micromixing, residence time distribution of reactor, mass and heat transfers. It normally takes a long time to obtain an optimized operation condition and products only through practices. The ongoing paradigm of polymerization processes begins to shift from process design and operation by experiments and empirical methods to one by the combination of experiments and mathematical models.[11,12] In order to speed up the industrialization of RDRP techniques, the polymerization engineers can take advantage of their knowledge in both polymer chemistry and engineering for scaling up the production and optimizing operational conditions through constructing the sound mathematical models.[3]

The modeling investigations of various RDRP systems were carried out through two methods, namely, statistical and deterministic methods.[13] Monte Carlo simulation is a classical approach belonging to the statistical method, and it has the advantage in the prediction of full chain length distribution (CLD) in RDRP systems.[14–36] Modified Monte Carlo simulations were also presented for controlling the comonomer sequence in polymer chains,[16,19,21–24,31,32] reducing the computational time,[26,28] and capturing the low radical concentration.[29] Compared to the stochastic-based method, the core of deterministic approaches (e.g., Predici software and the method of moments) is the solution of a set of mass balance equations derived from reactions.[13,37,38] Predici software served as a ready-made solution tool and has been commonly used in RDRP systems, for example, atom transfer radical polymerization (ATRP),[39–46] nitroxide-mediated polymerization (NMP),[47–50] and reversible addition–fragmentation chain transfer (RAFT) polymerization.[51–55]

To date, modeling of RDRP has made some achievements, and some review articles provided already part of the progress in the field. Zhu and co-workers introduced a comprehensive overview on the modeling and theoretical development in controlled radical polymerization, demonstrating the importance of RDRP modeling. Particular attention was paid to the description of polymerization kinetics and average chain properties through analytical modeling and the modeling of homogeneous and heterogeneous RDRP systems.[13] Subsequently, Zhu and co-workers captured the research progresses in the design and synthesis of gradient polymer chain composition and chain topology distributions, as well as the research activities in semibatch reactors, tubular reactors, and continuous stirred-tank reactors (CSTRs) of both homogeneous and heterogeneous RDRP systems.[56,57] D'hooge et al. gave a review on the model-based design and synthesis of polymeric materials, highlighting the synergetic efforts of experimental and theoretical researches.[58] As a complementary part with Zhu's work,[38] this review is not a walkthrough on the use of method of moments, while our purpose is to present the state-of-the-art and future perspectives focusing on the modeling and simulation of RDRP processes based on the method of moments. Examples on the controllable synthesis of polymer products and process optimization are addressed. Highlighting the facility of the method of moments in modeling field is therefore presented.

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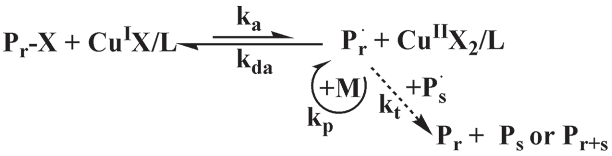
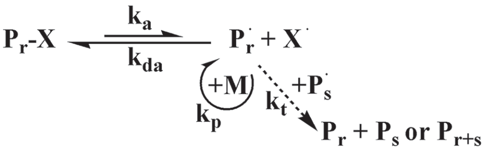
We start by the brief introduction of reversible-deactivation radical polymerization systems, followed by a discussion of the method of moments. In the next part, the progresses of modeling work on the basis of the method of moments for the three most studied RDRP techniques (i.e., ATRP, NMP, and RAFT polymerization) are summarized and discussed. Specifically, this part is classified into polymerization rate and average chain properties, copolymer composition distribution (CCD), copolymer sequence distribution, and modified polymerization systems. Finally, conclusions and future perspectives are addressed briefly.

2. Reversible-Deactivation Radical Polymerization

On the basis of the different reaction mechanisms, there are three well-known approaches for the establishment of dynamic equilibrium in RDRP, namely, reversible



Scheme 1. General ATRP mechanism (X = halogen atom; L = ligand).



Scheme 2. General NMP mechanism (X = nitroxides).

deactivation by atom transfer, reversible deactivation by radical trapping, and reversible deactivation by degenerative transfer.[6] Following these mechanisms, ATRP,[59–62] stable free-radical polymerization (SFRP, also called NMP),[63,64] and RAFT polymerization[65–67] are three known powerful RDRP techniques for preparing polymers with well-defined structures and low dispersities. The key here is that the lifetime of a propagating radical in RDRP is increased from a matter of seconds (typical in FRP) to several hours through the introduction of a dynamic equilibrium between activation and deactivation.[5,6] It is noted that the lifetime of a propagating radical is a cumulative lifetime as a consequence of consecutive activation–growth–deactivation cycles.

2.1. Atom Transfer Radical Polymerization

ATRP as a convenient RDRP method is widely used for designing and preparing functional polymer materials.[61,62]

Scheme 1 illustrates the general mechanism of ATRP, which is mediated by transition metal complex (normally Cu salt). The controllability of ATRP is governed by the equilibrium between dormant and propagating radical chains.[59] In the activation step, the growth of chain is initiated through the abstraction of halogen from organic initiator to lower-oxidation-state transition metal/ligand catalyst. At the early stage of the polymerization, the unavoidable bimolecular radical termination leads to accumulation of the persistent deactivator ($Cu^{II}X_2/L$). As a result, the propagating radical chains are deactivated reversely by the reduction of the higher-oxidation-state transition metal complex. Furthermore, the irreversible termination is suppressed. This kinetic characteristic is known as persistent radical effect (PRE) as proposed by Fischer.[68] In order to fully exploit the potential of the polymerization process and better understand the mechanism, modeling work based on the general or improved ATRP mechanism is imperative.

2.2. Nitroxide-Mediated Polymerization

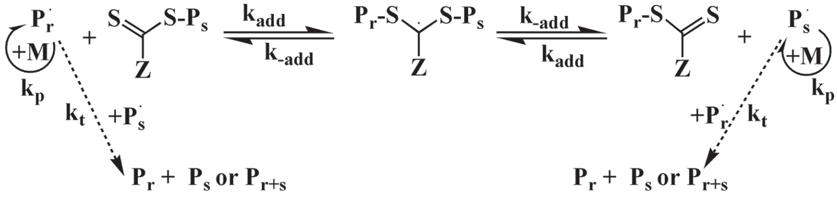
Since the advent of SFRP or NMP in 1993, many efforts have been devoted into the development of NMP, including the synthesis of nitroxides and alkoxyamines, kinetic study, and the usage for preparing functional materials.[63,64]

A robust NMP is controlled by a rapid dynamic equilibrium between a small amount of radicals and a large amount of dormant species as shown in Scheme 2. The kinetics of NMP are governed by both this activation–deactivation equilibrium and the PRE.[68] The reaction is started through the homolytic dissociation of alkoxyamine initiator at an elevated temperature depending on the type of initiator. The propagating radicals can not only propagate with monomers to form propagating polymer chains but also recombine with stable nitroxide radicals to form macroalkoxyamine species. In this system, the stable nitroxide radical acts as a control agent that cannot react with monomers or take part in side reactions under ideal conditions.[69] It should be noted that the concentration of propagating radical species is reduced to an extremely low level due to the PRE (accumulation of the persistent radical), and thus the bimolecular radical termination is suppressed. For more information, readers can refer to an in-depth review of NMP from its emergence to the recent advances reported by Nicolas and Guillaneuf.[64]

2.3. RAFT Polymerization

RAFT polymerization is another versatile RDRP method for preparing polymer materials with various structures and becomes one of the most successful RDRP techniques.[65–67]

The general mechanism depicted in Scheme 3 shows that RAFT process is mediated by dithioester (thiocarbonylthio compound is commonly used). RAFT polymerization is initiated through the interaction between initial radicals generated by the thermal decomposition of conventional free-radical initiator and monomer. Subsequently, this propagating radical chain reacts with a RAFT agent to form an intermediate radical chain, which can reversibly fragment back to the propagating



Scheme 3. General RAFT polymerization mechanism.

radical chain or toward release a new initial radical from RAFT agent. This new initial radical can re-initiate polymerization or react back to intermediate species. Until the entirely consumption of initial RAFT agent, a reversible addition and fragmentation equilibrium can be established between propagating radical chains and dormant chains mediated by macrointermediate radical chains. Fast exchange reactions are required to maintain low concentration of propagating radical species and high concentration of dormant species, which ensure control and limited termination.[67] In should be noted that for ideal RAFT polymerization systems no kinetically significant side reactions with the intermediate radical are taking place. In addition to a plenty of experimental studies, modeling of RAFT polymerization is also a powerful tool for investigating process development and optimizing operation conditions.

Each RDRP technique has its own comparative advantages and shortcomings. For example, ATRP can be carried out at a large range of temperatures using inexpensive and commercially available initiators and ligands. And also, the end-functionalization is relative facile and simple. However, the biggest limitation of ATRP is the requirement of transition metal catalyst removal and less effective for acidic monomers.[6,62,70] By contrast, the advantages of NMP include purely organic system and suitable for polymerization of acidic monomers (e.g., acrylic acid, meth acrylic acid),[71,72] but the mediated reagent used in NMP is relatively expensive and the reaction is normally carried out at elevated temperature and is not efficient controlling the polymerization of methacrylates.[64,73] Similar to NMP system, RAFT is usually a purely organic system. Nevertheless, several transfer agents are not commercially available and the dithioester end group requires to be removed because of their toxicity and odor in some specific fields.[6,74] Overall, it is not essential to point out which one is the best. With the mechanistic development of RDRP techniques, some disadvantages have been overcome, they all serve human beings in preparing the polymers with controlled structures.

3. Method of Moments

The aim of modeling and simulation is to better understand and optimize RDRP processes. Compared with the relatively complex and time-consuming of Monte Carlo simulation and the extra cost associated with the purchase of Predici software, the method of moments is a relatively simple, convenient, and low-cost approach for simulating the monomer conversion and the average properties of resulting polymers. The method of moments as a commonly used kinetic-based method in modeling polymerization systems was proposed as early as 1953 by Bamford and Tompa.[75]

In a polymerization system, a set of differential equations of mass balances with infinite number is required, because the length of polymer chain can be theoretically infinity (in practice this is not the case, but it still involves a plenty of monomeric units). To solve the huge number of differential equations through a straightforward integration method should be a very time-consuming process, particularly the case if also chain length dependencies of rate coefficients need to be taken into account. According to the definition of nth order moment (Q_n), as expressed by Equation (1), the method of moments can significantly simplify the calculation complexity when solving the mass balance equations. That is to say, the infinite number of differential equations of mass balance can be transferred into a finite number of differential equations of moment balance

$$Q_n = \sum_{r=0}^{\infty} r^n \left[P_r\right] \tag{1}$$

where r represents the length of polymer chain, P_r is the polymer with length r, and [] is the concentration of species.

Based on the definitions of the number-average chain length (r_n), the weight-average chain length (r_w), and dispersity ($Đ$, also known as polydispersity index (PDI)), one can express them using the moments, as shown in Equations (2)–(4), respectively

$$r_n = \frac{\sum_{r=0}^{\infty} r\left[P_r\right]}{\sum_{r=0}^{\infty}\left[P_r\right]} = \frac{Q_1}{Q_0}, \tag{2}$$

$$r_w = \frac{\sum_{r=0}^{\infty} r^2\left[P_r\right]}{\sum_{r=0}^{\infty} r\left[P_r\right]} = \frac{Q_2}{Q_1}, \tag{3}$$

$$Đ = \frac{r_w}{r_n} = \frac{Q_2 Q_0}{\left(Q_1\right)^2} \tag{4}$$

From the definition of moments, one can know that the "moment" represents a series of one type of polymer chains (e.g., propagating chains, dormant chains, dead chains, etc.) with different lengths. In other words, the information of the individual chain is sacrificed and one type of polymer chains is considered as an integrate unit in this method. As a consequence, the modeling results based on the method of moments can strictly not capture the full chain length distribution without extensive additional calculations and only predict the average properties of the polymer chains. However, these average properties are enough to meet the general demand for industrial production in most cases.

If needed, inversion method can be applied to construct the full CLD based on the premise that the distribution type is known. Furthermore, Mastan et al. recently proposed a novel method for the description of full molar mass distribution of polymer synthesized by ATRP.[76–78] The novelty of that work lies in analogously relating the activation–deactivation cycles in ATRP to a series of CSTRs. By using the concept of by-product streams to simulate the formation of dead chains (both of which did not participate in further reactions), the authors derived a termination that involved full molar mass distribution expression for ATRP-based polymers.[76] In this work, diffusional limitations on termination were ignored for simplicity. Subsequently, a modified model for monomer conversion dependent PDI and a new polydispersity expression including effects of the monomer conversion, monomer addition per activation/deactivation cycle, and amount of dead chains were introduced for ATRP systems.[77,78] Saldívar-Guerra et al. showed that direct integration of the equation can be used to predict the CLD for NMP and RAFT polymerization systems.[79,80]

By the merit of such simplification, investigations on kinetics of conventional free radical polymerization, coordination polymerization, RDRP, and other polymerization systems (e.g., continuous processes, surface polymerization, branching/crosslinking) have been studied extensively.[3,13,81–97] For the details of mathematical formulations in a given system, one can refer to the recent tutorial article on the method of moments.[38]

4. Batch Polymerization Rate and Average Chain Properties

4.1. ATRP Systems

4.1.1. Normal ATRP

In 1999, Zhu gave a pioneer work on modeling of ATRP process based on the method of moments, which was used for estimating rate coefficients, designing new experiments, and elucidating the underlying mechanism.[98] Results showed that a too high propagation rate led to the evolution of molecular weight deviating from theoretical value and a higher dispersity. For a slow initiation system, delaying monomer addition helped to lower the dispersity. However, diffusion-controlled reactions were not considered in that work, which is a commonly important phenomenon in radical polymerization. Inspired by its importance, Delgadillo-Velazquez et al. evaluated the effect of diffusional limitation on bulk and solution ATRP of styrene, methyl methacrylate (MMA), and methyl acrylate on the basis of kinetic modeling.[99] Simulations showed that diffusion-controlled propagation reduced the “living” behavior of the system, whereas a diffusion-controlled termination enhanced its livingness. However, it is worth noting that diffusion-controlled propagation implicitly assumes a rather low polymerization temperature to ensure a possible glass effect.

Different from previous work, Al-Harthi et al. investigated kinetics of ATRP with bi-functional initiators through modeling study.[100–103] Their simulation work compared the difference between mono- and bi-functional initiator, as well as the distinction between the polymerization of styrene (solution), methyl methacrylate (solution), and butyl acrylate (bulk) with and without diffusional limitation. Compared with homopolymerization, copolymerization involves more polymerization kinetic steps and requires more complex population balances. The authors presented a comprehensive mathematical model for atom transfer radical copolymerization in a batch reactor using the concept of pseudo-kinetic rate coefficients and the method of moments for the first time.[104] This methodology greatly reduces the model complexity but does not lose the accuracy of model prediction significantly, which is satisfactory for most polymer reaction engineering applications.

D'hooge et al. provided a methodology for the kinetic modeling of solution ATRP based on an extension of the method of moments in combination with the quasi-steady state approximation for intermediate reactive species, which allows accurately describing the molecular weight distribution and the chain length dependence of reaction rate coefficients.[104] Diffusional limitations on all considered reaction steps were also systematically accounted for in the model. In that work, the so-called coupled parallel encounter pair model has been introduced for the first time, which allows a fundamental description of the diffusional limitations on the activation/deactivation process in ATRP without adjustable parameters and taking into account that these reaction are inherently coupled as they are each other reverse reaction, an aspect previously ignored.[104] By the merit of the developed model, the authors investigated the kinetics of solution ATRP of isobornyl acrylate (iBoA) and N-isopropylacrylamide (NiPAAm) in detail.[105,106] For iBoA system, diffusion coefficients and the Williams–Landel–Ferry parameters for poly(iBoA) are first provided through rheological measurements. Results showed that βC-scission reactions were insignificant in the investigated temperature range (323–348 K), and the importance of backbiting reactions was limited to high conversions. Additionally, diffusional limitation had great effects on the ATRP of iBoA.[105] As illustrated in Figure 1a–c, the evolutions of apparent rate coefficients for termination by recombination between

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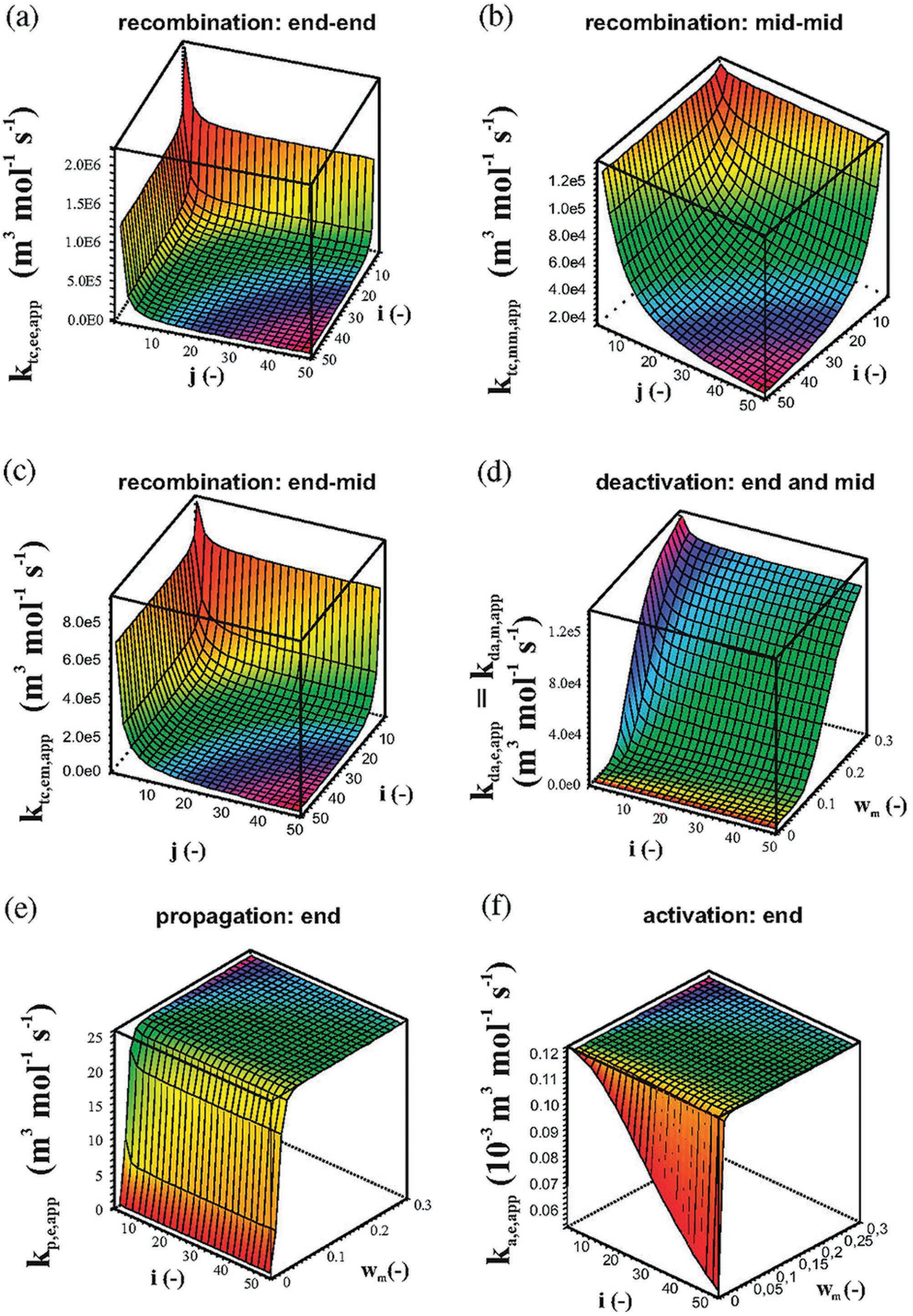

Figure 1. Apparent rate coefficients for termination by recombination between a) end-chain macroradicals ($k_{tc,ee,app}$), b) mid-chain macroradicals ($k_{tc,mm,app}$), and c) their cross-termination ($k_{tc,em,app}$); d) for deactivation with end- and mid-chain macroradicals ($k_{da,e,app}$ and $k_{da,m,app}$) and e) for propagation with end-chain macroradicals ($k_{p,e,app}$); f) for activation ($k_{a,e,app}$). (i, j = chain length, w_m = monomer mass fraction). (Reprinted with permission.[105] 2010, American Chemical Society.)

end-chain macroradicals ($k_{tc,ee,app}$) and mid-chain macroradicals($k_{tc,mm,app}$) and for cross-recombination ($k_{tc,em,app}$) all decreased with the increase of chain length. What is more, the decrease of the apparent rate coefficients for deactivation ($k_{da,e,app}$ and $k_{da,m,app}$) with the increase of chain length was observed at high conversions (>70%) in Figure 1d. By comparison, the effect of molecular diffusion phenomena on apparent propagation and activation rate coefficients was not pronounced. $k_{p,e,app}$ and $k_{a,e,app}$ only decreased at extremely high conversion

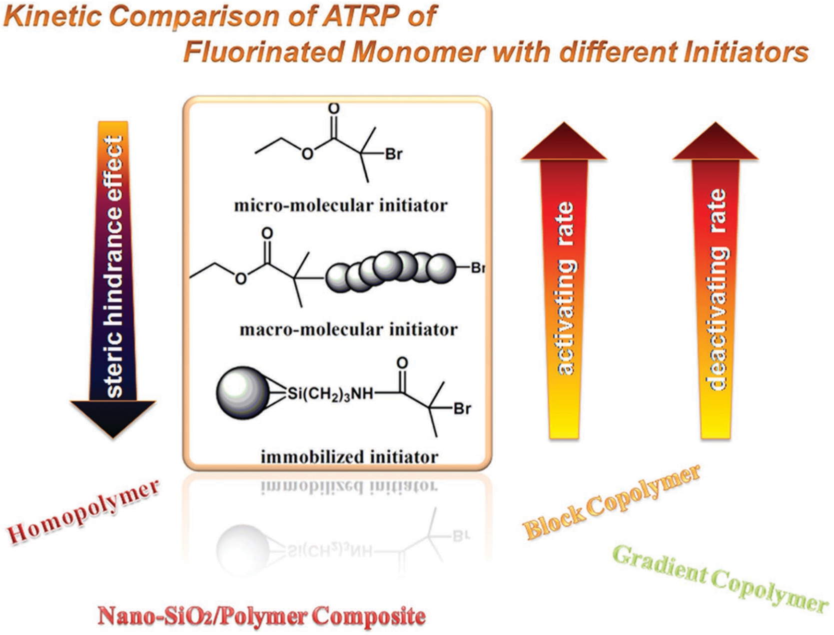

Figure 2. Illustration of the effect of ATRP initiator types on activation and deactivation kinetic coefficients. (Reprinted with permission.[112] 2014, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)

as illustrated in Figure 1e,f. For NiPAAm system, simulations indicated that the importance of cyclization involving dormant species and termination reactions for the loss of end-group functionality (EGF) was limited, and a decrease of EGF caused by cyclization reaction appeared only at very high conversions.[106]

Furthermore, a chain length dependent termination model was incorporated into the kinetic simulation by Johnston-Hall and Monteiro for better understanding the PRE in bulk or solution ATRP system.[107] More recently, Rabea and Zhu investigated the influence of diffusion-controlled reactions on the high conversion bulk ATRP kinetics through model-based approach.[108] Different from the previous works considering diffusion-controlled effect, “residual termination,” relating to a more explicit consideration of reaction diffusion, was introduced following the radical “hopping” mechanism. Simulation results revealed that the “residual termination” does not have much influence on the polymerization kinetics. But the diffusion-controlled deactivation causes auto-acceleration in the rate and loss of control. And diffusion-controlled activation and propagation finally stop the polymerization.[108] Besides, the modeling study on compartmentalization effects on kinetic behaviors in aqueous dispersed phase ATRP system was also carried out.[109]

From previous works, one can know that the effect of diffusional limitation on ATRP was proven to be important and different diffusion models were used to investigate the effect. For example, Delgadillo-Vélazquez et al. used free volume based series encounter pair model,[99] Al-Harthi et al. used empirical average based diffusion model,[102] D’hooge et al. applied free volume based parallel encounter pair model,[104] and Johnston-Hall and Monteiro employed chain length dependent termination model based on the so-called reversible addition–fragmentation chain transfer-chain length dependent-termination (RAFT-CLD-T) technique.[107] A review work of D’hooge et al. compared the aforementioned models and highlighted that a correct diffusion model is very important for the correct optimization of the RDRP process.[110]

There are numerous researches on the preparation of polymeric materials using different ATRP initiators, and the polymerization kinetics are greatly different from each other. Using a developed model, Huang et al. estimated the activation/deactivation rate coefficients of ATRP system involving macroinitiator.[111] In a recent work, the effect of initiator types (i.e., micromolecular, macromolecular, and immobilized initiator) on the ATRP kinetics was studied through a developed mathematical model.[112] Through estimating the activation and deactivation kinetic coefficients in different systems, the results shown in Figure 2 indicated that the activity and deactivity of similar catalytic complex is the highest for microinitiator, lower for macroinitiator, and the lowest for immobilized initiator, which was attributed to the electronic and steric hindrance effect.[112]

4.1.2. Modified ATRP with Low Catalyst Amounts

More recently, kinetic modeling of the initiators for continuous activator regeneration (ICAR) ATRP of MMA and styrene was carried out to determine the effect of reaction conditions and catalyst reactivity on the polymerization process.[113] Subsequently, Toloza Porras et al. applied the model to ICAR ATRP of *n*-butyl acrylate (*n*BuA) and styrene.[114,115] The simulation results shown in Figure 3 clearly provided guidelines for the selection of relevant polymerization conditions for preparing well-defined poly(*n*BuA). To be specific, one can obtain well-defined poly(*n*BuA) with targeted chain length (TCL) lower than 500, EGF higher than 0.9, and PDI between 1.1 and 1.2 by using initial amounts of Cu(II) between 60 and 250 ppm with respect to monomer within 12 h. However, fast polymerizations for higher TCL with very low (<10 ppm) Cu(II) can lead to the reduction of controllability (PDI > 1.3)

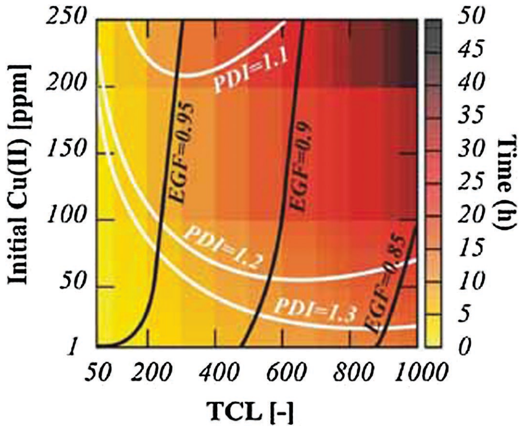

Figure 3. Diagram for the bulk ICAR ATRP of *n*BuA illustrating control over chain length, livingness, and the required polymerization time for a conversion of 0.80 as a function of the initial amount of Cu(II) and TCL; full lines indicate the limits of PDI (1.1, 1.2, and 1.3) and EGF (0.85, 0.9, and 0.95). (Reprinted with permission.[114] 2013, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)

and livingness ($0.85 < \text{EGF} < 0.9$).[114] In addition, by using Arrhenius parameters for ATRP activation/deactivation involving macrospecies obtained via experimental data regression under polymerization conditions, simulations can accurately predict the properties of resulting polymers.[115] The activator-regenerated-by-electron-transfer (ARGET) ATRP as an alternative low-catalyst based technique was also investigated through kinetic modeling by Li et al.[116] Simulations demonstrated that reducing agent with a moderate rate coefficient offered an improved control over ARGET ATRP.

Cu(0)-mediated RDRP received great attention because of its extremely low dissolved copper concentration and reusability of the Cu(0) catalyst. However, two mechanisms are proposed based on the different roles of the Cu species, namely, single electron transfer-living radical polymerization (SET-LRP) proposed by Percec and supplemental activator and a reducing agent (SARA) ATRP denoted by Matyjaszewski and co-workers.[117,118] Monteiro et al. developed a kinetic model based on SET-LRP for the demonstration of experimental results.[119] In our recent study, simulations carried out based on SARA ATRP as shown in Figure 4 indicated that diffusional limitation on termination significantly affected the kinetics of polymerization.[120] Simulations in the presence of diffusional limitation or the chain length dependent termination rate coefficient were in well agreement with the experimental data. The effect of key rate coefficients on kinetics was investigated in detail, which shed light on the underlying mechanism. The optimization of the product quality by experiments was accomplished in MMA and butyl methacrylate systems.[120] Interestingly, photoinitiated ATRP and eATRP as emerging techniques attract increasing interest and have been used to synthesize functional polymers because of the capability of light and electricity in the temporal control of polymerization and their low environmental hazard. The first case study of the kinetics of photoinitiated ATRP and eATRP was carried out based on a newly clarified mechanism using the method of moments by Zhou and Guo, respectively.[121,122] Through the kinetic modeling, the underlying mechanism and the optimization of polymerization condition were demonstrated in detail.

4.2. NMP Systems

From the aspect of polymerization kinetics, modeling of SFRP processes at ideal conditions on the basis of the method of moments was initiated by Zhu and Shi in 1999.[123,124] The developed kinetic model was applied

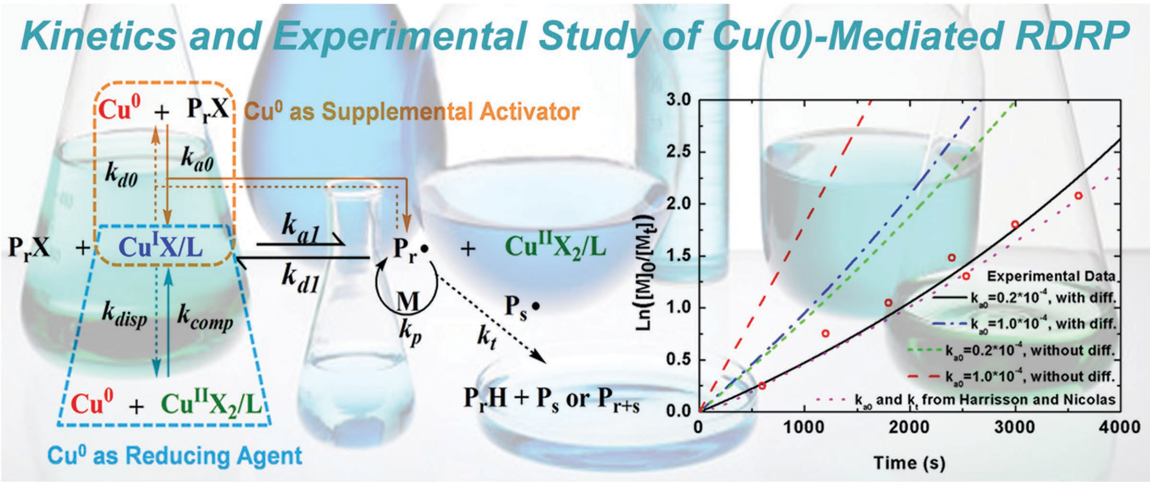

Figure 4. Effect of the diffusional limitation on kinetics of SARA ATRP. (Reprinted with permission.[120] 2014, American Chemical Society.)

to predict monomer conversion, M_n, and PDI in batch process. In the same year, Butte et al. proposed a more systematic modeling approach toward both NMP and ATRP.[125] The simulation results obtained using the method of moments and an empirical expression for diffusion-controlled termination in their work were in good agreement with experimental data, which demonstrated the reliability of developed model. To be sure, these three works presented a precedent that it is expected to have a significant potential in designing and optimizing the operation conditions of NMP based on an appropriate mathematical model.

In 2002, a detailed kinetic model for NMP of styrene was presented by Bonilla et al., which included several side reactions (e.g., chain transfer to monomer and dimer reactions) that were relevant to the result of PDI.[126] Another mechanistic insight into the limitation in the synthesis of high molecular weight polystyrene was carried out by Kruse et al. through modeling study at the mechanistic level using the method of moments.[127] The developed model considering styrene thermal initiation allowed the simulation results to meet experimental data well. On the other hand, chain transfer to polymer and the reaction between a nitroxide radical and a polymeric radical to form a hydroxy amine was shown to be negligible.[127]

By further coupling the model with diffusion-controlled reactions based on free-volume theory, the diffusion-controlled effects on polymerization rate and PDI in NMP of styrene were assessed by Roa-Luna et al.[128] Meanwhile, more experimental data were used for parameter estimation and model validation.[129] The results showed that diffusion-controlled termination improved the “living” feature of polymerization; however, the simulation greatly deviated from the experimental data due to the lack of reliable kinetic parameters. In order to overcome the problem, Belincanta-Ximenes et al. carried out numerous simulations and experimental work covering a wide range of experimental conditions.[130] Particularly, the Arrhenius temperature dependence of activation, deactivation, and other kinetic rate coefficients estimated and used in simulations ensured the accuracy of the results. The simulation results agreed well with experimental data, which provided the confidence in the developed model, and thus it can be used to fully exploit the potential of these polymerization processes. Cho et al. developed a model based on the method of moments to estimate the rate parameters for the reversible nitroxide uncoupling/coupling reactions, thermal initiation, and termination.[131]

Recently, Bentein et al. gave a deep insight into the bulk NMP of styrene.[132] Using the developed model, simulation results showed that the diffusional limitation affected termination greatly. More importantly, the chain transfer to dimer can be suppressed through carefully controlling the polymerization conditions, and thus be able to prepare polystyrenes with high molar mass and high end-group functionality. From the results shown in Figure 5, the kinetic model with transfer reactions gained a broader chain length distribution than that without transfer reactions with the increase of conversion.[132] Additionally, the authors extended the work toward miniemulsion NMP of styrene through coupling 3D Smith–Ewart equations into the above model.[133] Simulations revealed that diffusional limitations on deactivation and on termination became significant for the system with particle diameters at about 40 nm and larger than 70 nm, respectively. Generally, one can obtained polymers with high molecular weight (TCL > 300) and low PDI under optimal conditions with particle diameters up to 50 nm.[133] Quite recently, Van Steenberge et al. presented a 4D deterministic kinetic model for the miniemulsion NMP of acrylates, which allowed the simultaneous calculation of the evolution of the conversion, number-average chain length, PDI, EGF, and short chain branching amount with polymerization time for the first time.[134] Results showed that nitroxide partitioning was an important factor that affected the polymerization rate and polymer average properties greatly. As shown in Figure 6, for the particle diameters lower than 70 nm, the increase in partitioning coefficient (Γ) from 50 (green line) to 5000 (blue line) decreased the polymerization rate and dispersity. Furthermore, the sensitivity of the polymerization rate and dispersity in response to Γ was dependent on the particle diameter.[134] In the very recent work of Fierens et al., the full potential of the

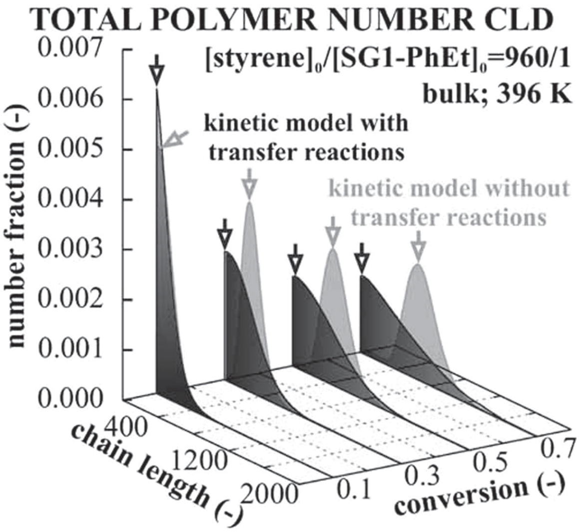

Figure 5. Simulation results with or without the transfer reactions for the polymer number chain length distribution (CLD) at different conversion. (Reprinted with permission.[132] 2011, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)

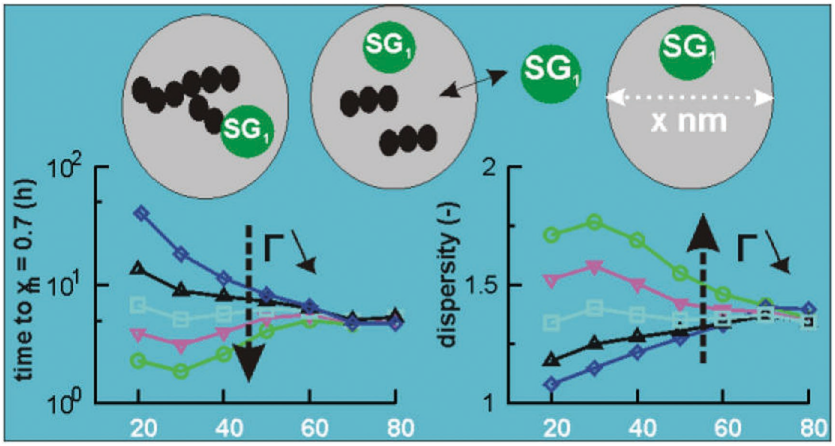

Figure 6. Effect of the nitroxide partition coefficient (Γ) on the polymerization rate and the dispersity as a function of the particle diameter for the miniemulsion NMP. (Reprinted with permission.[134] 2014, American Chemical Society.)

NMP technique has been mapped with so-called Pareto-optimal fronts.[135]

4.3. RAFT Polymerization System

For the first time, Wang and co-workers simulated the RAFT process and studied the influence of diffusional limitations on it based on modeling approach using the method of moments.[136,137] The results demonstrated that both diffusion-controlled radical termination and radical addition accelerated the polymerization rate, but the former narrowed and the latter broadened the molar mass distributions of resulting polymers. According to the practicability of the modeling method, Guan and Zhou investigated the effect of initiator concentration, chain transfer agent concentration, and monomer concentration on the RAFT polymerization kinetics.[138,139] In order to provide a quantitative tool for directly analyzing experiment data, Gao and Zhu made efforts to derive analytical equations to calculate the concentration, chain length, and dispersity of various chain species in RAFT system based on an simplified mechanism.[140] It should be noted that the validity of simplifying RAFT process as a degenerative chain transfer process was confirmed at low conversion when side reactions were insignificant.

Using the developed model, Monteiro and co-workers studied the dispersity of block copolymer obtained by RAFT polymerization,[141] predicted the dispersity of polymer prepared by using a single difunctional RAFT agent and a radical initiator,[142] and investigated the kinetics of RAFT process in dilute and gel regimes.[143] The model was validated and used as a predictive tool to generate other desired molar mass distributions. As illustrated in Figure 7, Monteiro's group proposed a novel modeling strategy for accurately predicting the experimental polymerization rates and molecular weight data in RAFT polymerizations under various experimental conditions, as well as in FRP process.[143] This kinetic model comprised of a composite termination model, namely, RAFT-CLD-T.[144] In addition, with the composite termination model using geometric mean "short-long" termination rate coefficient, simulations showed that "short-long" termination was significant in conventional FRP process, while it was little in RAFT process even at very high conversions.[143] However, this model is not able to provide an accurate short-long termination reactivity. In a very recent work, Derboven et al. introduced a generic and flexible protocol based on extended RAFT-CLD-T method for obtaining the short-long termination reactivity precisely.[145]

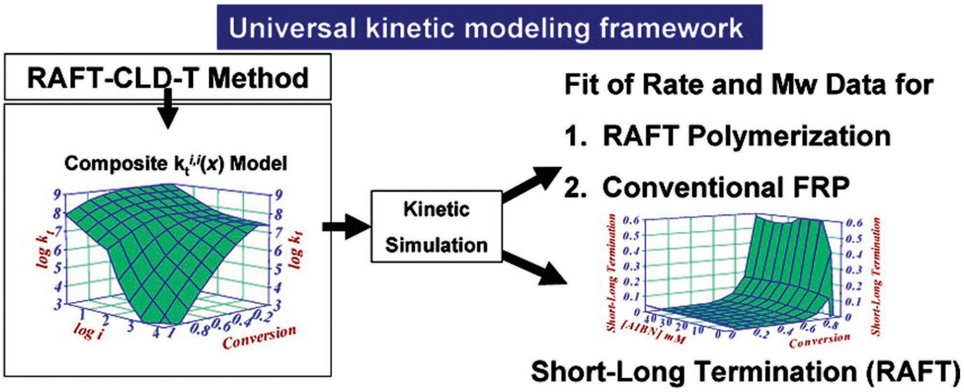

Figure 7. Universal kinetic modeling framework for RAFT polymerization and conventional FRP. (Reprinted with permission.[143] 2007, American Chemical Society.)

5. Composition Distribution and Sequence Distribution of Copolymers

Control of CCD along the chain is an interesting issue in synthetic polymer chemistry, which provides a new route for developing polymer materials with tailor-made properties.

The control of CCD along the chain using model-based synthesis is in fact first achieved through RAFT approach. As early as 2006, Wang et al. theoretically designed a series of copolymer with predetermined CCD using semibatch reactor technologies under programmed monomer feeding rates for the first time.[146] The experimental setup was shown in Figure 8. Based on the theoretical model, a systematic experimental study on the preparation of styrene/butyl acrylate copolymer products with various chain microstructures (e.g., uniform, linear gradient, inverse linear gradient, hyperbolic tangent gradient, and triblock with a linear gradient mid-block profiles) was carried out through programmed semibatch RAFT approach.[147,148] In addition to CCD, monomer sequence length and distribution are also needed to be addressed. Schork and co-workers developed a comprehensive model encompassing a chain model and a sequence model for semibatch RAFT copolymerization, enabling the description of sequence lengths and their distributions in resulting copolymers.[149,150] Simulation results illustrated that controlling a certain number-average sequence length can be accomplished by using an optimized feeding policy. More recently, targeting CCD via model-based monomer feeding policy in semibatch RAFT was extended to miniemulsion system by Li et al.[151] The experimental data of resulting copolymer properties (e.g., particle diameter, M_n, dispersity, and monomer cumulative composition) agreed well with the model prediction, which demonstrated that this approach is effective for precise manufacturing.

In batch ATRP process, composition drift is very common due to the differences in reactivity ratios of monomers, namely, the composition cannot be facilely regulated. However, copolymers with uniform, linear gradient, parabolic gradient, hyperbolic gradient, and di-block and tri-block distributions are available by ATRP based on a semibatch reactor technology with programmed comonomer feeding rates.[152,153] By combining the batch ATRP kinetic model with semibatch reactor model, a comprehensive model can predict polymerization rate, composition distribution, and other polymer properties.

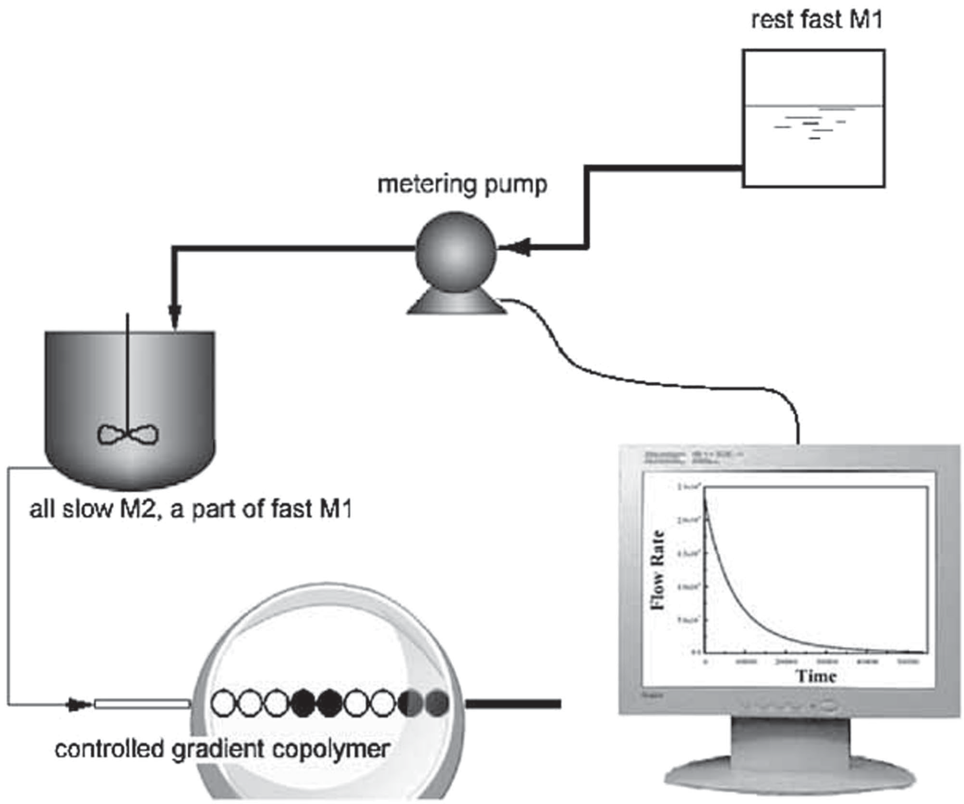

Figure 8. Experimental setup for the semibatch RAFT polymerization. (Reprinted with permission.[146] 2006, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)

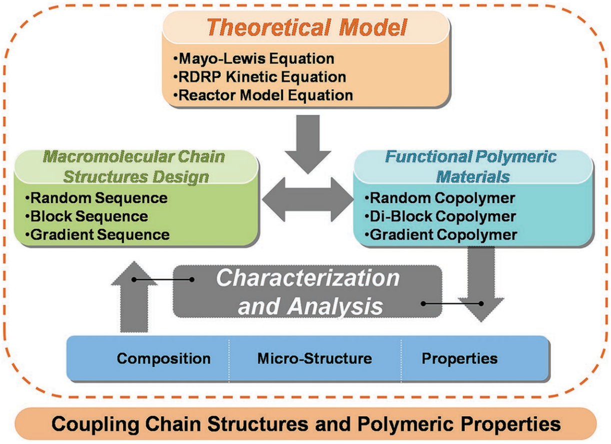

Figure 9. Model-based structure–property relationship for RDRP system.

Inspired by previous works, attention was paid to the multiscale generalization of the polymeric system through theoretical model and experimental study, namely, the relationship of structures and properties. From Figure 9, one can gain that theoretical models facilitate the identification of optimal reactant ratio and reaction conditions to design and control the synthesis of functional polymers with well-defined microstructure and targeted properties. A preliminary work is on the semibatch controlled synthesis of gradient copolymers with simultaneously tailor-made chain composition and glass transition temperature (T_g) based on a modeling approach using the method of moments.[154] The developed model provided the information about the influence of feeding rate and comonomer activity on the gradient profile and the breadth of T_g. What is more, the authors further extended the idea to design the functional materials with well-defined structures from the perspective of product engineering.[155–161] For fluorinated materials, different properties (e.g., thermal, self-assembly, and surface properties) were investigated and related to their intrinsic structures.[155] For environmental responsive materials, the relationship between backbone molecular structure of brush copolymer and responsive functions, such as pH/Ca^+ responsivity,[156–158] temperature induced self-assembly,[159] and thermal/light responsive surface wettability [160,161] was studied. These case studies provided a general idea that demonstrated the high relevance of polymer chain structures and properties.

In addition, Ye and Schork developed a chain model and a sequence model for NMP in both batch and semibatch reactors to describe the resulting copolymer chain and sequence properties.[162] Employing a combined model including both sequence model and chain model, one can reveal both sequence and chain properties of polymers.

6. Continuous Processes

Continuous processes represent a routinely done in industry. Facing the increasing expectation on the commercialization of RDRP processes, the researches on reactor engineering and industrial aspects (e.g., the effect of feeding policy on polymer properties, backmixing effect, residence time distribution) of RDRP systems have gained a great deal of attention.[163–171]

Zhang and Ray developed a mathematical model for the simulation of RAFT polymerization in different tank reactors (i.e., batch, semibatch, and CSTR).[163] This model provided detailed information for the analysis of process development and design issues. Simulations showed that a series of CSTRs might be appropriate for controlling polymer chain properties as well as for achieving large-scale production of polymer products, while semibatch reactors have the flexibility to prepare well-defined polymers (i.e., producing the desired polymer weight fraction in the reactor or chain copolymer composition and monomer sequence). Additionally, Zhang and Ray subsequently developed a mathematical model for “living” free-radical polymerization (NMP and ATRP) carried out in batch, semibatch, continuous tank reactors, and tubular reactors.[164,165] The simulations showed that semibatch reactor is most flexible for the preparing polymers with controlled chain architecture, which is consistent with those obtained in modeling of NMP and ATRP. For continuous reactors, the residence time distribution has a significant effect on the development of chain architecture and polymer average properties. Their work provided a preliminary investigation on the polymerization process development and design issues.

The work reported by Schork and co-worker showed that the method of moments can be used to produce a mathematical model providing insight into the sequence structure of copolymers in continuous RAFT polymerization.[166] In addition, Bitsch et al. studied the effect of reactor backmixing on RAFT polymerization in plug flow tubular reactor and a series of CSTRs from the viewpoint of chemical engineering.[167] Simulations demonstrated that increasing backmixing effect led to shorter average chain lengths and broader molar mass distributions for the different chain types. Therefore, backmixing should be avoided to show the major advantage of RDRP in continuous processes. Furthermore, the very recent work of Derboven et al. on the modeling of RAFT polymerization of acrylate in microreactors showed that optimized microreactor conditions are ideally suited for improving the degree of livingness and the branching control.[168]

A detailed comparison of ATRP under different feeding policies in stirred-tank reactors was conducted by Wang et al. based on mathematical models.[169] As shown

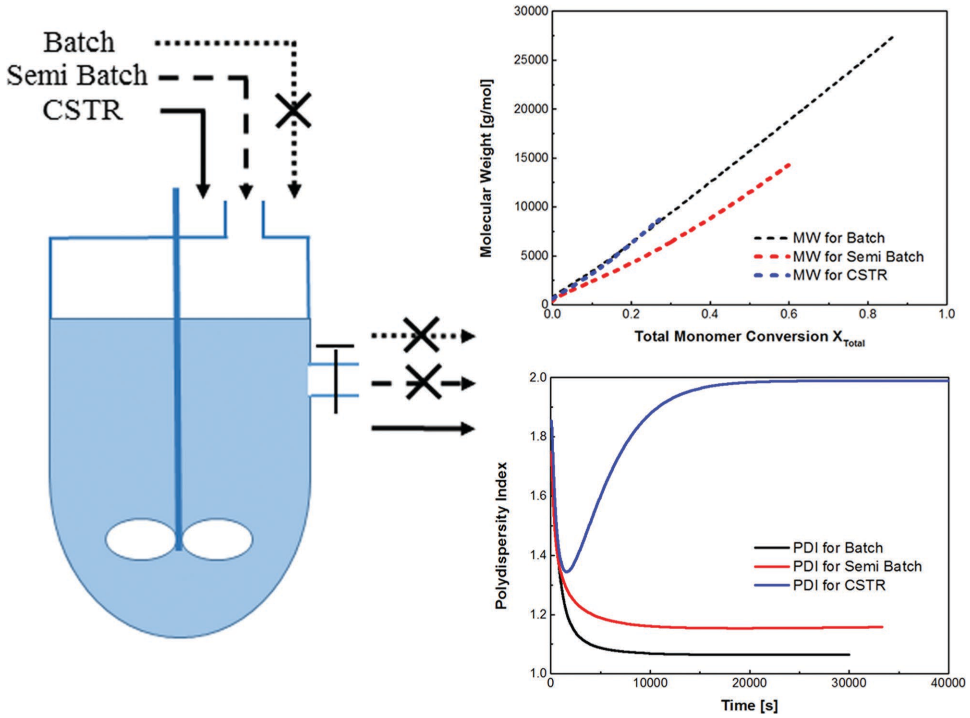

Figure 10. Comparison of product average properties prepared by ATRP under different feeding policies in stirred-tank reactor. (Reprinted with permission.[169] 2014, American Chemical Society.)

in Figure 10, the batch reactor exhibits best capacity of producing copolymers with high molecular weight and low PDI values, but the properties of products may vary from batch to batch. By comparison, the semibatch reactor is powerful in modulating the composition along the copolymer chain as has been illustrated in previous works, but the controllability decreases.[152–155] Compared to batch and semibatch processes, continuous process in single CSTR has advantage of easy operation, higher production efficiency, and consistent product quality; however, the PDI of resulting copolymers is larger than 1.5. Subsequently, the authors carried out the modeling of ATRP in a train of CSTRs. Results showed that the advantages of the CSTRs in series are their enormous potential to continuously produce copolymers with consistent quality and improve the monomer conversion, as well as lower the PDI of resulting copolymers when compared to the copolymers prepared in single CSTR.[170] More recently, the same author extended the copolymerization system in CSTR to a continuous tubular reactor.[171] Results showed that the existence of axial dispersion resulted in the declination of monomer conversion, broadening of dispersity, and decreasing of end functionality (F_t). Besides, the curves of instantaneous copolymer composition (F_i) along the chain for different values of Peclet number (Pe) were overlapped, indicating that the copolymer composition has less relationship to flow pattern of reactants.

7. Other Polymerization Processes

7.1. Surface Initiation Polymerization

As is known, surface-initiated (SI) polymerization is an enabling tool for preparing multifunctional engineered hybrid materials. Recently, Gao and Zhu presented a model for SI ATRP based on a moving-boundary brush model as illustrated in Figure 11.[172] When the free end

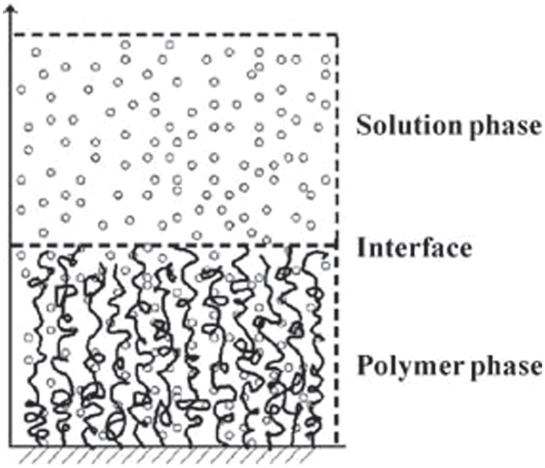

Figure 11. Schematic presentation of the SI ATRP from flat surface. (Reprinted with permission.[172] 2010, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)

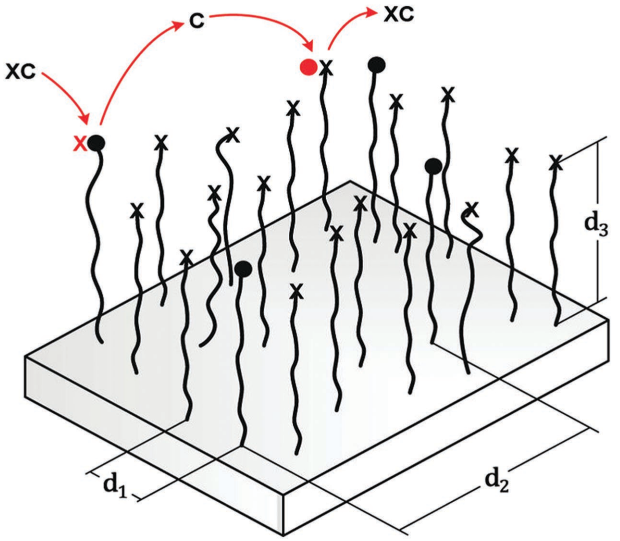

Figure 12. SI ATRP: How surface radicals migrate toward each other and terminate through activation/deactivation cycles ((×) dormant chain ends; (•) radical chain ends). (Reprinted with permission.[173] 2012, American Chemical Society.)

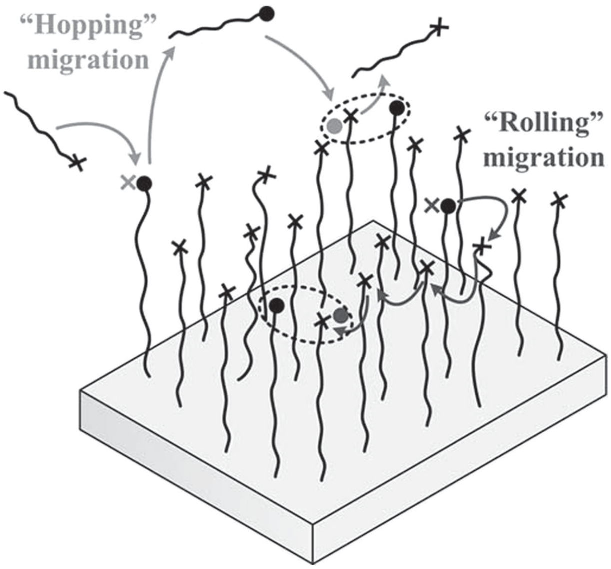

Figure 13. Migration of radical in SI RAFT through "rolling" and "hopping" to promote termination ((×) dormant chain ends; (•) radical chain ends). (Reprinted with permission.[175] 2012, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)

stretches out into the solution and reacts with monomer molecules, the interface moves away from the surface with the increase of polymer chains. In that work, the authors proposed a new mechanism for surface radical termination, termed as "migration-termination," which argued that although polymer chains can be very crowded on surface, radical centers are sparse and are distant from each other. The developed model allows the comparison of the effect of adding free initiator (Method I) and adding excess deactivator (Method II) on kinetics of SI ATRP. Results showed that Method II gave a much better control over molecular weight development of the grafted chains and a thicker grafting layer could be obtained under similar conditions. The advantage of Method II gave rise to further investigations on SI ATRP through developing a simple model in the same group. They proposed a new model providing a deep insight into the termination mechanism happened in this system, which is vividly described as "migration-termination." As shown in Figure 12, the nearby surface radicals terminated through "hopping migration" driven by activation–deactivation equilibrium.[173] But, there are many fundamental questions still remaining to be answered in SI ATRP process, such as: What determines the surface initiator efficiency? How many chains per square nanometer can be fully grown? What limits the chain growth?[174]

Differing from SI ATRP, SI RAFT polymerization has various termination modes in reaction system, namely, termination between solution radicals, termination between surface radicals, and that between solution and surface radicals. Zhou et al. presented a model for the study of SI RAFT polymerization from flat surfaces using the R-group approach.[175] In that work, the surface radical termination was assigned to two mechanisms, namely, "rolling migration" and "hopping migration" as demonstrated in Figure 13. "Rolling" occurred through transferring between surface/surface chains, which was proportional to the grafting density at surface. "Hopping" occurred through activation/deactivation cycles between surface and solution chains, depending on the RAFT agent concentration in solution. In light of both termination mechanisms, simulations provided insights into the kinetics of RAFT process, and showed that termination reduced the average chain length and broadened molar mass distribution of resulting polymers.

7.2. Crosslinking/Branching

Synthesis of copolymer with various polymer chain topologies, such as hyper-branched, star, network, etc., has also attracted much interest in recent years. Crosslinked/(hyper)branched polymers are desirable and would be promising through applying RDRP cross-linking processes. Within the scope of this review, only model-based studies on crosslinking/branching processes using the method of moments are discussed.

The first mathematical model for NMP of vinyl/divinyl monomers has been developed and validated for the case of styrene and divinylbenzene system by Hernandez-Ortiz et al. in 2009.[176] Simulation results showed that adding nitroxide-type controllers to a vinyl/divinyl copolymerization system allows the production of more homogeneous polymer networks.[176] Subsequently, Hernandez-Ortiz et al. developed a mathematical model for ATRP using the case of methyl acrylate and ethylene glycol diacrylate.[177] Both developed models were used to obtain polymerization rate, molecular weight development, gelation point, evolution of sol and gel weight fractions, crosslink density, and copolymer composition, as well as concentrations of the species participating in the reaction mechanism.

Schork and co-workers investigated the effect of chain transfer to polymer on branching in RAFT polymerization of vinyl acetate based on a detailed mathematical model, however, the branching reaction involved in this work was considered as a side reaction.[178] Wang et al. developed a comprehensive kinetic model for describing the RAFT cross-linking process and the structure of network products in batch reactor using the method of moments.[179] Importantly, the gel conversion in the RAFT cross-linking process was analytically expressed based on Flory's criterion, which can estimate the gel point and optimize the cross-linking recipe. In addition, the branching developments also provided a better understanding of the branching process and guidance on the design of hyperbranched materials.

Subsequently, Wang et al. developed an extended kinetic model to provide insight into branching mechanisms and control of gelation in semibatch reactor.[180] Figure 14 schematically shows the batch or semibatch RAFT copolymerization of acrylamide (AM) with *N,N′*-methylenebisacrylamide (BisAM) for producing hyperbranched polyacrylamide (b-PAM). Compared to the gel formation in batch copolymerization at 70% conversion, no gel occurred in the semibatch reactor up to 99% conversion. Increasing the feeding rate of BisAM under semibatch operation made the copolymerization kinetics approach that in batch process. Also, polymer molecular weight, polydispersity, and branching density were well controlled in semibatch mode. The modeling study showed that cyclization reaction is important in both processes which postponed the gelation. More recently, a model-based computer programmed monomer feeding strategy was applied to control of branching density distribution (BDD) in RAFT miniemulsion copolymerization system in semibatch reactor. Using this technique, a series of branched polystyrenes having the uniform BDD was synthesized.[181]

8. Conclusion and Outlook

Impressive progress in RDRP techniques has been made in the past 20 years, which allows scientists to prepare multifarious polymeric materials. However there are some successful examples on commercial products in industrial scale, it remains an arduous task in the industrialization of RDRP techniques. Successful commercial development requires taking in-depth investigation on practical methods of implementing RDRP techniques in different processes. Mathematic models are necessary for people to get insight into the processes under uncommon situations, such as those inconvenient, impractical, or unsafe operations. A large number of researches have proved that modeling is an invaluable tool in polymerization processes study.

In this review, we highlighted the progress in modeling of RDRP techniques (ATRP, NMP, and RAFT polymerization) that were carried out for designing and controlling the polymerization processes or resulting polymer structures using the method of moments. Compared with the other two commonly used methods (Monte Carlo simulation and Predici software), the method of moments is a relatively simple, convenient, and low-cost approach for simulating the monomer conversion and the average properties of resulting polymers. Although it cannot predict the full chain length distribution of resulting polymer, it should be noted that the reconstruction of the chain length distribution from the moments (i.e., inversion method) can overcome this problem. The key aspect is off course the identification of a good inversion method, which is not straightforward.

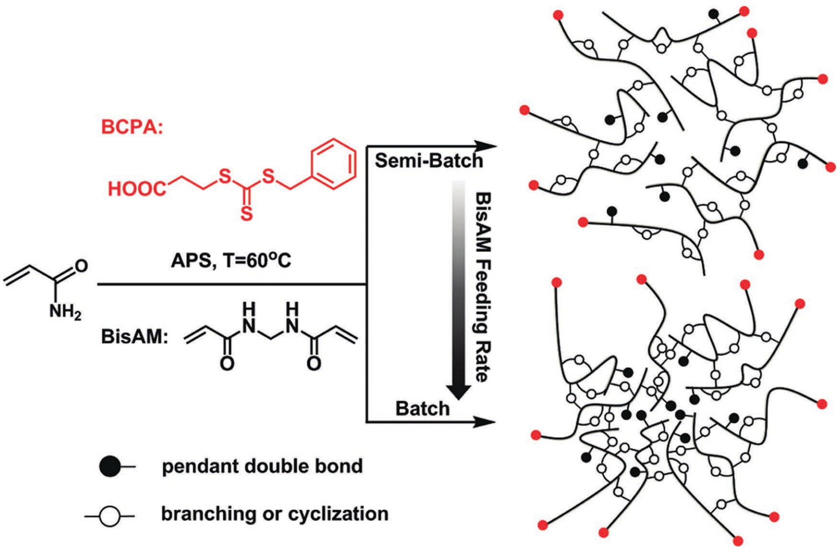

Figure 14. Synthesis of b-PAM through batch or semibatch RAFT copolymerization of AM with BisAM using 3-benzyltrithiocarbonyl propionic acid (BCPA) as chain transfer agent. (Reprinted with permission.[180] 2012, American Chemical Society.)

Albeit significant progress in modeling of RDRP has been made in recent years, one can find that most of the works focus on the kinetics of RDRP systems. The effect of diffusional limitation on radical termination was proven to be important in all RDRP systems. From the reactor engineering view point, a majority of present kinetic modeling works were carried out in batch or semibatch reactor, while much less study was given to coupling kinetics with continuous processes (continuous tank reactors and tubular reactors), which is commonly used in polymer industry as they offer more consistent product quality and higher reactor productivity. Semibatch operation is considered to be a facile strategy for controlling the copolymer composition distribution and copolymer sequence distribution. As a whole, the above well-constructed mathematical models for RDRP systems, including kinetic model and reactor model, have been used in kinetic simulation, technology optimization, microstructure control, and mechanistic investigation. We believe that these advanced results can help researchers promote the lab-scale research to industrial applications of RDRP.

It should be pointed out that current simulation works were mostly carried out under ideal conditions, such as homogeneous reaction system (especially for ATRP) and isothermal condition. Therefore, further studies under non-ideal conditions are indispensable. Significant challenges with regard to implementation of RDRP in industrial scale still remain, which require synergy between chemists and engineers to make more efforts in the future. From the aspect of chemistry, further investigations should be done on detailed and valid elemental reactions, which help in constructing accurate models. From the perspective of engineering, the effect of flow field and temperature field on RDRP product properties and the importance of residence time distribution and reactor backmixing on RDRP should be considered in the future research work. Especially, relevant work can also be carried out on fixed bed reactor in ATRP system, which needs transition metal catalyst for proceeding. We believe that well-validated models will be beneficial for the industrialization of RDRP techniques.

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