# Modeling free radical polymerization using dissipative particle dynamics

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## ARTICLE INFO

## ABSTRACT

Understanding the details of free radical polymerization (FRP) in multi-component mixtures and solutions is of great importance for the synthesis of polymeric functional materials. Using the framework of dissipative particle dynamics (DPD), we develop a new computational approach to model FRP that couples the reaction kinetics for the polymerization processes to the dynamics of the complex fluid. We specifically consider two mechanisms of chain termination: disproportionation and combination. We analyze the effects of initiation, propagation, and termination on the polymerization kinetics in three-dimensional bulk polymerization by varying the corresponding reaction probabilities. Our model not only allows us to capture the interplay between hydrodynamics and reaction kinetics, but also provides an effective means to model polymerization in the presence of solid inclusions. We demonstrate the latter feature by simulating the formation of polymer-clay nanocomposite gels by FRP in solution in the absence of organic cross-linking agents, where the exfoliated clay particles serve as multi-functional cross-linkers for the polymer network. We observe that increasing the volume fraction of clay particles can lead to an increase in the number of inter-particle cross-linking chains, which could improve the mechanical properties of the material. Our findings provide insight into the polymerization kinetics of the FRP, as well as potential guidelines for tailoring experimental conditions to achieve the desired polymerization products.

## 1. Introduction

Advanced polymeric materials with complex architectures are vital for meeting a range of technological needs. The synthesis of these materials commonly involves *in-situ* polymerization that occurs within complex, multi-component fluids [1–4]. A better understanding of the coupling between the polymerization reactions and the dynamics of the host solution is crucial to achieving precise control of the polymerization, and hence, the properties of the final products. Computer simulations can play a particularly useful role in elucidating such important characteristics of the system as the reactivity of the polymer chains, the evolution of the molecular weight distributions, the structure of polymer matrix, as well as many others features.

Among various polymerization methods, radical polymerization is one of the most versatile and widely applied techniques [5]. It can generally be categorized into two types: free radical polymerization

(FRP) [6,7] and controlled/living radical polymerization [8,9]. In both processes, the active chain end involves a free radical. The major difference between these two polymerization processes is that the termination of a growing polymer chain is negligible in living radical polymerization, while it is an important process and should be taken onto account in standard FRP approaches [6–9]. We recently developed a computational approach based on the dissipative particle dynamics (DPD) method to simulate the living copolymerization of monomer and cross-linker to form a polymer network [10]. In particular, our model captured the characteristic polymerization kinetics of atom transfer radical polymerization (ATRP) [11–14] and reproduced features of gel formation that are consistent with experimental data [10].

Although living radical polymerization produces well-defined (co)polymers with predetermined molecular weight, controllable polydispersity, and preserved chain end functionality [11–14], FRP is still the most commonly used commercial process, especially for preparing high molecular weight polymers [8]. Thus, it is of technological importance to develop an effective computational model for FRP, and thereby, aid in optimizing experimental conditions to

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achieve the desired polymerization products. Moreover, the increasing demand for precisely tailored polymer nanocomposites [15–21], which encompass nanoscale fillers, necessitates models that can capture the interplay between hydrodynamics and chemical reactions in mixtures that include solid inclusions with complex geometries [22,23]. As we show below, the DPD approach offers a powerful framework for addressing these needs [24–26].

Herein, we develop a new DPD model with a reaction scheme to simulate FRP, taking advantage of our previous model for living radical polymerization [10]. Within the framework of this new model, we take into account different mechanisms of chain termination and study the polymerization kinetics and properties of the products. We then apply the model to examining the formation of polymer-clay nanocomposite gels. The simulations allow us to systematically examine the relative effects of the initiation, propagation, and termination reactions, and hence, obtain greater insight into the polymerization process. Consequently, the findings can yield useful guidelines to achieve more effective routes to synthesizing the desired materials.

## 2. Computational method

### 2.1. Dissipative particle dynamics

We use dissipative particle dynamics (DPD) [27–29] to model standard free radical polymerization, taking advantage of our recently developed DPD framework for modeling polymerization [10]. DPD is an effective mesoscale particle-based method to simulate complex fluids and multi-component mixtures. Via this method, a volume of fluid is modeled with individual beads, where each bead represents a cluster of molecules. The motion of each bead is governed by Newton's equation of motion $md\mathbf{v}_i/dt = \mathbf{f}_i$. In particular, each bead $i$ experiences a force $\mathbf{f}_i(t)$ that is the sum of three pairwise additive forces: $\mathbf{f}_i(t) = \sum(\mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R)$. All pairwise forces are truncated at a certain cutoff radius $r_c$. The conservative force is a soft, repulsive force given by $\mathbf{F}_{ij}^C = a_{ij}(1 - r_{ij})\hat{\mathbf{r}}_{ij}$, where $a_{ij}$ is the maximum repulsion between beads $i$ and $j$, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|/r_c$ and $\hat{\mathbf{r}}_{ij} = (\mathbf{r}_i - \mathbf{r}_j)/|\mathbf{r}_i - \mathbf{r}_j|$. This soft-core force permits the use of larger time steps than those typically used in molecular dynamics (MD) simulations, which commonly involve hardcore potentials (e.g., the Lennard-Jones potential). Due to the latter feature, DPD can be used to capture physical phenomena occurring on relatively large time scales (i.e., larger time scales than normally captured by MD).
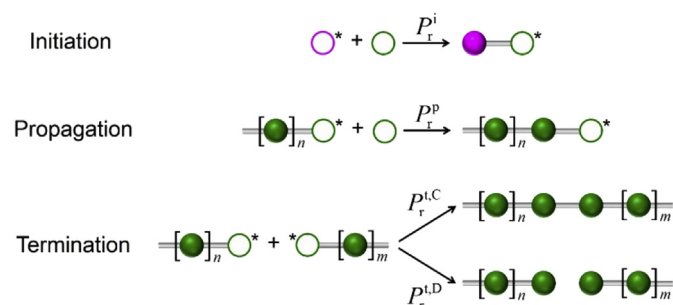
The drag force is $\mathbf{F}_{ij}^D = -\gamma\omega_D(r_{ij})(\hat{\mathbf{r}}_{ij}\cdot\mathbf{v}_{ij})\hat{\mathbf{r}}_{ij}$, where $\gamma$ is a simulation parameter related to viscosity, $\omega_D$ is a weight function that goes to zero at $r_c$, and the relative velocity is $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$. The random force is $\mathbf{F}_{ij}^R = \sigma\omega_R(r_{ij})\xi_{ij}\hat{\mathbf{r}}_{ij}$, where $\xi_{ij}$ is a zero-mean Gaussian random variable of unit variance and $\sigma^2 = 2k_BT\gamma$. Here, $k_B$ is the Boltzmann constant and $T$ is the temperature of the system. The weight functions take the following form: $\omega_D(r_{ij}) = \omega_R(r_{ij})^2 = (1 - r_{ij})^2$ for $r_{ij} < r_c$. With the combination of these three forces, the model reproduces correct hydrodynamic behavior [27–29].

The equation of motion is integrated via the modified velocity-Verlet algorithm [30]. In our simulations, we take $r_c$ and $k_BT$ as the characteristic length and energy scales, respectively. The characteristic time scale is then defined as $\tau = \sqrt{mr_c^2/k_BT_0}$. By setting $\gamma = 4.5$, we obtain a relatively rapid equilibration of the temperature in the system and numerical stability of the simulations with a time step of $\Delta t = 0.02\ \tau$ [29].

### 2.2. Reaction scheme

As in our prior simulations for living radical polymerization [10], we model the standard FRP by a set of elemental reactions. The reaction kinetics are coupled to the dynamics of the system, which are evolved by the DPD simulations. The reactive components in the system are the initiator and monomer, both modeled as coarse-grained DPD beads. The elemental reactions are shown schematically in Fig. 1. The asterisk in the figure represents the free radical and the color of the circle identifies the specific units. The open circles represent unreacted species and filled circles indicate fully reacted species. In the simulation, we use different bead types to represent the "state" of the reactive species. For example, an unreacted monomer is specified as type 1, but this monomer changes to type 2 when it is added to a growing chain and becomes the new active end. Once the monomer has fully reacted, it is labeled as type 3. The result of the specific chemical reaction is modeled by updating the bead types after the reaction has occurred [31–33] (see reaction scheme in Fig. 2).

We previously neglected chain termination reactions due to the nature of living radical polymerization [8,11–14]. Chain termination is, however, prominent in FRP, and thus, the termination reactions between active chain ends are considered in this study. We introduce two mechanisms of chain termination in our current model, namely radical combination and disproportionation [34]. Chain transfer reactions are excluded in the simulation [35].

A list of beads with free radicals (denoted as R-beads), which can be activated by initiators or active chain ends, is constructed at the beginning of every reaction step. In each reaction step, we select an R-bead from the list as the reaction center and search all reactive beads within an interaction radius $r_i = 0.7$ from the given R-bead [10]. If there are reactive beads within this interaction range, one is picked at random and a reacting pair is formed. Based on the types of the R-bead and the selected reactive bead, the elemental reaction is determined.

We use reaction probabilities $P_r^x$ to characterize the reaction kinetics [34,36–38], where the superscript x stands for the type of reaction. A successful reaction changes the type of the reacting beads accordingly. Depending on the reaction, the reacting pair of beads can result in an irreversible bond formation, with the energy of the bond given by $E_{bond} = 1/2K_{bond}(r - r_0)^2$. Here, $K_{bond} = 128$ is the elastic constant and $r_0 = 0.5$ is the equilibrium bond distance [10]. Within every reaction time step, the above steps are conducted for the entire list of R-beads.

Every R-bead within the list is only allowed to go through the reaction procedure once per reaction step regardless of whether



**Fig. 1.** Schematic of the elemental reactions in free radical polymerization. Asterisk indicates active radical. Open beads show unreacted or partially reacted species and filled beads show fully reacted species. Green beads represent monomer and magenta beads represent initiator. $P_r^i$, $P_r^p$, $P_r^{t,C}$, and $P_r^{t,D}$ are probabilities of the respective reactions (initiation, propagation, and termination through combination and disproportionation).