



Monte Carlo simulation of free radical polymerization of styrene in a spinning disc reactor



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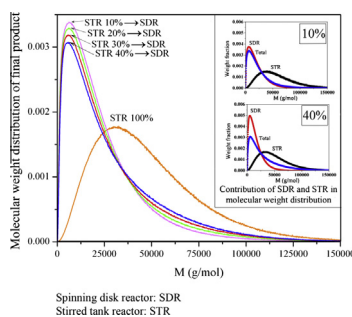
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HIGHLIGHTS

- Monte Carlo-simulated styrene free radical polymerization in STR–SDR arrangement.
- Theoretically tracked microstructural evolutions during STR–SDR polymerization.
- Predicted M_n , M_w , PDI, $[R]$, $[M]$ and $[I]$ in SDR utilizing KMC simulation.
- Monitored STR and SDR contribution in final MWD based on pre-polymer conversion.

GRAPHICAL ABSTRACT



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ABSTRACT

We report on modeling of free-radical polymerization of styrene in a stirred tank reactor–spinning disc reactor (STR–SDR) arrangement using Kinetic Monte Carlo (KMC) simulation algorithm. The prepolymer from batch reactor was transferred to SDR and simulation results were validated comparing conversion and molecular weight of the generated molecules in the batch reactor and SDR with corresponding values from experimental data. The developed model was also applied to simulate SDR under a range of different operating conditions to accurately predict the resulting polymer properties. In this way, different prepolymer conversions were theoretically adapted to probe the evolution in chain microstructure until polymerization terminated on the rotating disc. The developed computer code based on KMC approach enables precise monitoring of molecular-level events in the reactor like variations in molar concentration of macroradicals and molecular weight distribution with time, and provides a greater insight into the STR–SDR cascade polymerization of styrene monomer.

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1. Introduction

Non-ideal mixing in stirred tank reactors (STRs), especially on industrial scale, is one of the major causes of inhomogeneity and poor quality of resulting products. Much effort has been directed towards finding a general solution to the problem of mixing in such

reactors through experimental and mathematical investigations [1–3]. It is well-established that to meet an appropriate mixing degree all processing variables have to be optimized towards the most efficient means of perfecting heat and mass transfer rates. In practice, however, there have always been serious difficulties associated with evaluation of mixing performance of industrial-scale processes.

One of the ways to achieve ideal mixing is to utilize spinning disc reactors (SDRs), where reactions take place in thin, highly mixed films formed on the surface of rotating discs [4,5]. This

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potential springs from a combination of large shear forces and intense surface ripples induced by centrifugal forces generated by disc rotation [6,7]. It is generally believed that this configuration provides the reaction environment with enhanced mass and heat transfer coefficients when compared to classical continuously stirred reactors, static mixer, and even extruder reactors [5,8]. Recent studies aimed at application of SDR reactors have led to homogeneity in the product of organometallic vapor phase epitaxy [9], the prevention of recirculating spots in the chemical vapor deposition [10], the reduction of the time and energy needed to precipitate nanoparticles [11,12] and pharmaceutical products [13], and recently the increment of the efficiency of photocatalytic degradation of pollutants in waste water and solutions [14–17].

In case of polymerization reaction, where the overall bulk viscosity of the system will become increasingly upturned and puts limits on proper transmission of heat and mass to the bulk of polymer at higher conversions, the use of SDRs is deemed to provide an ideal reaction environment. For instance, SDR has been applied to ease the removal of gaseous by-products of polycondensation reactions [18,19], to improve the heat transfer and temperature control of the reactor during highly exothermic cationic polymerization [7], and even to industrialize photopolymerization method [20,21]. Bulk and solution methods of free-radical polymerization which represent a huge portion of industrial polymerization processes suffer from an almost similar problem. In such cases, except at the early stages of polymerization, viscosity upturn of the mixture gradually diminishes the rate of heat and mass transfer leading to hot spots in the reactor. This uncontrolled event will result in some serious disadvantages, mainly inhomogeneity, which reduces the performance of reactor.

In light of the above discussions, SDR could be considered as a suitable candidate for conducting free-radical polymerization. What we know about this approach is largely based upon recent experimental works that elaborately investigate the polymerization behavior in SDRs [22,23]. The end product is the result of a cascade route through which the polymerization is started in a classical STR and is allowed to continue to a predetermined monomer conversion. Next, the produced prepolymer solution is fed on a heated spinning disc and after a few seconds, e.g. 5–10 s for a 360 mm diameter disc spinning at 0–1500 rpm, the SDR product is thrown off the surface of the disc and collected for analysis [24]. The most obvious finding was that the conversion of product significantly increased after one pass over the disc surface, but number- and weight-average molecular weights have not been notably changed. Furthermore, analyzing the fluid flow on the disc it was found that by increasing the rotational speed more shear was generated whereby higher monomer conversion could be obtained. On the other hand, the higher the disc speed the lower the residence time on the disc would be which lessens the alteration of monomer conversion in the second stage of process [24,25]. Elsewhere, Novakovic et al. attempted to replicate the experimental results of conversion and molecular weight based on SDR arrangement via altering the kinetic constants [22]. The most interesting finding was that either an increased propagation or a decreased termination rate constant in a classical batch reactor ends in products comparable to those obtained in the SDR. Varying the disc temperature, monomer concentration, initiator concentration, disc rotational speed, feed flow rate, and prepolymer conversion, it was elucidated that propagation and initiator decomposition rate constants are higher in a SDR, in opposition to termination rate which is kept almost unchanged when compared to the corresponding termination in a batch reactor [26].

Bearing in mind the essential role of SDRs in achieving polymers possessing more desirable characteristics compared to those delivered utilizing stirred tank reactors; mathematical modeling or simulation of polymerization reaction in such geometries will serve as

a basis in developing our understanding of the structural changes during polymerization reactions for future studies. To the best of our knowledge, there has been no previous work describing STR–SDR cascade free-radical polymerization based on simulation of polymerization reaction on a molecular scale. In continuation to previous experimental investigations, the present work attempts to provide additional evidences based on simulation results in relation to evolution of monomer conversion and initiator consumption during free-radical polymerization of styrene. Utilizing Kinetic Monte Carlo (KMC) algorithm, the reaction is hypothetically started in a batch reactor by addition of styrene molecules and other reactants into the simulation volume, and it is allowed to proceed until the desired prepolymer conversion is achieved. The resulting prepolymer is continuously fed on the surface of an infinite disc assumed so as to provide a deeper sense of microstructure development of growing chains over a prolonged residence time (Fig. 1). This may also help engineers to examine the influence of larger discs on the properties of resultant polymer. Accordingly, the evolutions in the number- and weight-average molecular weight, macroradical concentration, Polydispersity Index (PDI) and molecular weight distribution are simulated in the SDR by feeding prepolymers with different conversions attained in the batch reactor. Eventually, a comprehensive image of growing chains during free-radical polymerization of styrene in the SDR is developed on the principle of KMC algorithm.

2. Simulation studies

2.1. Monte Carlo algorithm

The KMC algorithm was originally introduced by Gillespie in the early 1970s for the purpose of simulating chemical reactions [27] and has frequently been utilized for investigating different polymerization processes in recent years [28,29]. Such simulations have precisely given greater insights into physical and chemical phenomena in polymers such as synthesis and modification.

In the present study, KMC algorithm was used to seed predetermined amounts of reactants including initiator, monomer, and solvent molecules into the simulation volume to produce polystyrene via a combinatorial plan consisting of batch and SDR polymerization processes. In this regard, the simulation volume, V , was typically supposed to be divided homogeneously between initially seeded reactant molecules. Microscopic elementary reactions occurred discretely and stochastically through M reaction channels (each reaction channel representing an event), and an event was selected in a given time interval ($t, t + dt$) from uniformly distributed random numbers in a unit interval, according to the following relationships:

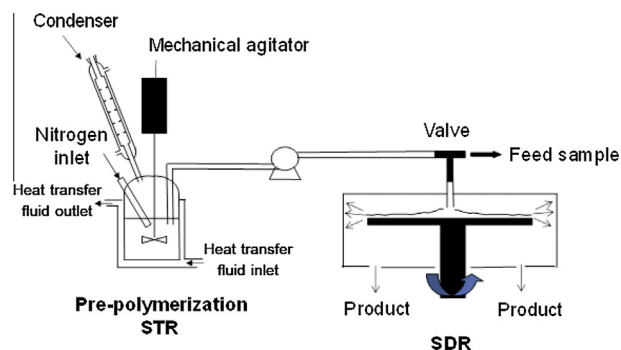


Fig. 1. Schematic of experimental set-up of SDR fed with prepolymer from STR.

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