

Monte Carlo Simulation of Copolymer Heterogeneity in Atom Transfer Radical Copolymerization of Styrene and N-Butyl Acrylate

Mohammad Najafi, Hossein Roghani-Mamaqani, Mehdi Salami-Kalajahi, Vahid Haddadi-Asl

Abstract—A high-performance Monte Carlo simulation, which simultaneously takes diffusion-controlled and chain-length-dependent bimolecular termination reactions into account, is developed to simulate atom transfer radical copolymerization of styrene and n-butyl acrylate. As expected, increasing initial feed fraction of styrene raises the fraction of styrene-styrene dyads (f_{AA}) and reduces that of n-butyl acrylate dyads (f_{BB}). The trend of variation in randomness parameter (f_{AB}) during the copolymerization also varies significantly. Also, there is a drift in copolymer heterogeneity and the highest drift occurs in the initial feeds containing lower percentages of styrene, i.e. 20% and 5%.

Keywords—Atom Transfer Radical Copolymerization, Monte Carlo Simulation, Copolymer Heterogeneity, Styrene n-Butyl Acrylate

I. INTRODUCTION

IN the recent decades, various attempts have been made to apply control over radical polymerization by using different procedures. Versatile methods, known as controlled radical polymerizations, have been developed to combine the versatility of free radical polymerization with the controlling features of living anionic polymerization. Of the various controlled polymerizations, nitroxide-mediated polymerization, reversible addition-fragmentation chain transfer, and atom transfer radical polymerization are known as the most common techniques. The latter utilizes a transition metal complex for halogen transfer to change a growing radical into a dormant species [1].

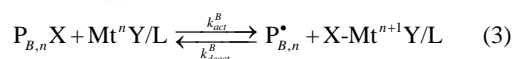
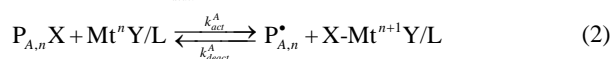
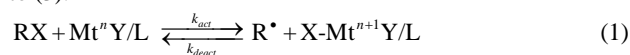
To inspect the behavior of ATRP, several analytical models have been introduced, which are mostly moment equations [2] and kinetic models that can be solved by the PREDICI [3]. Monte Carlo method, owing to the statistical nature of the chain growth and chain terminating reactions, is another

excellent method utilized to simulate polymerization systems. Having proved to be a successful polymerization technique, Atom Transfer Radical Polymerization (ATRP) has been employed in copolymerization systems to obtain specific architectures. In this context, owing to homo- and cross-propagation reactions, the arrangement of statistically distributed monomers in copolymer chains is the cause of structural heterogeneities as already found out in free radical copolymerizations [4]. To evaluate the copolymer heterogeneity, a thorough Monte Carlo simulation of styrene and n-butyl acrylate atom transfer radical copolymerization (ATRCp) has been carried out and the fraction of different dyads has been measured. A high-performance Monte Carlo simulation thoroughly simulates the arrangement of monomers in copolymer chains and calculates the fractions of monomer dyads during ATRCp [5].

II. MODELING

In this contribution, Monte Carlo method is applied to the controlled free radical copolymerization of styrene and n-butyl acrylate by employing a thorough kinetic scheme including chain end degradation reactions and diffusion-controlled chain-length-dependent terminations. The kinetic scheme used in the simulation includes activation, deactivation, thermal initiation of styrene, propagation, termination by combination, transfer to monomer, and chain end degradation reactions. The copolymer composition and fractions of different dyads are calculated and reported as a representative of the copolymer heterogeneity in the simulation.

The ATRP initiation and equilibrium steps for styrene and n-butyl acrylate used in the simulation are listed in Equations (1) to (3).



where, A and B denote styrene and n-butyl acrylate respectively.

The equilibrium rate constants are also given in Table I.

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TABLE I
KINETIC PARAMETERS

Rate constants ($\text{L.mol}^{-1}.\text{s}^{-1}$)	Value
k_{act} [4]	0.45
k_{deact} [4]	1.1×10^7
k_{act}^A	0.45
k_{deact}^A	1.15×10^7
k_{act}^B [5]	0.055
k_{deact}^B [5]	8.0×10^7

III. RESULTS AND DISCUSSION

The plot of f_{AA} , styrene-styrene dyad fraction, and f_{BB} , n-butyl acrylate-n-butyl acrylate dyad fraction, against conversion for various initial feed fractions are presented in Figures 1 and 2. As displayed in Figure 1, as expected, increasing initial feed fraction of styrene raises the fraction of styrene-styrene dyads (f_{AA}). According to Figure 2, the fraction of n-butyl acrylate dyads (f_{BB}) falls as the initial feed fraction of styrene increases. The trend of variation in randomness parameter (f_{AB}) during the copolymerization also varies significantly as a function of conversion and styrene feed fraction (Figure 3).

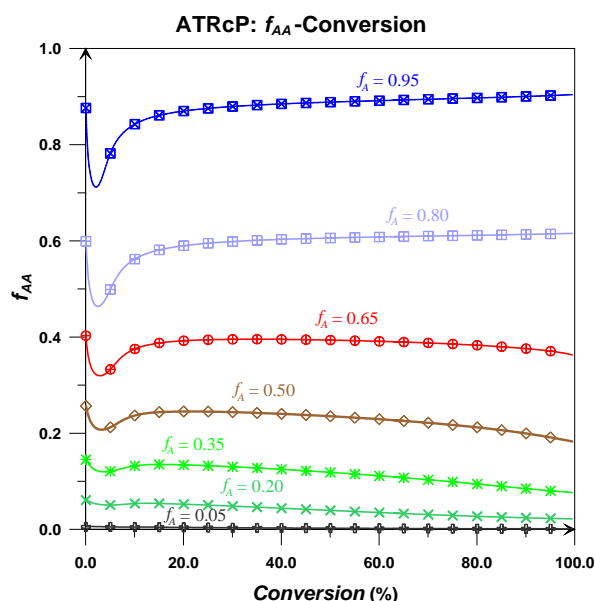


Fig. 1 Effect of feed fraction on styrene-styrene dyad fractions

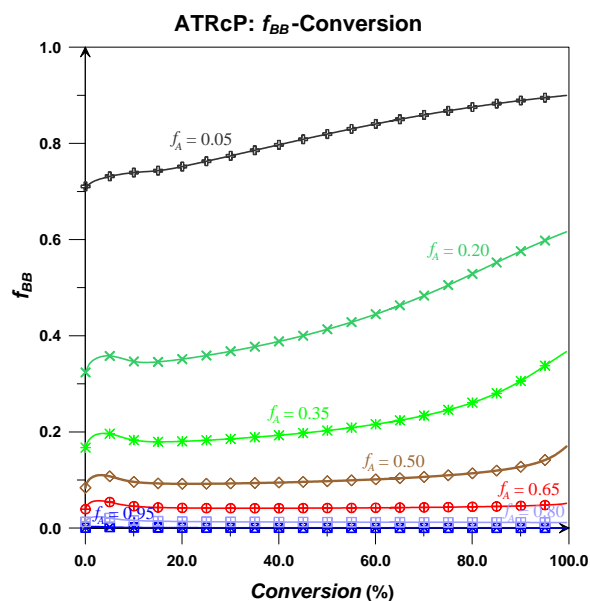


Fig. 2 Effect of feed fraction on n-butyl acrylate- n-butyl acrylate dyad fractions

A feed containing 35% styrene has the highest portion of AB dyads, which means higher alteration. On the other hand, having 95% styrene in initial feed causes the smallest amounts of alteration in copolymer chains. f_{AB} remains nearly intact during the copolymerization when initial feed is rich in styrene. However, the highest drift in the copolymer heterogeneity occurs in the initial feeds containing lower percentages of styrene, i.e. 20% and 5%.

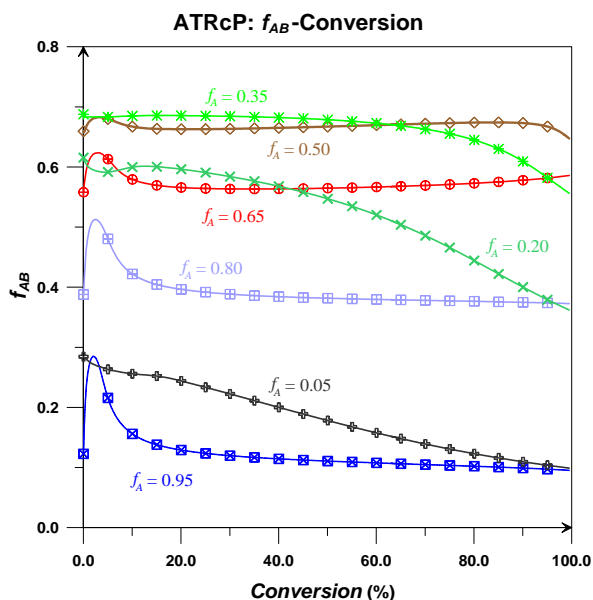


Fig. 3 Effect of feed fraction on styrene- n-butyl acrylate dyad fractions

Moreover, the unexpected variation in the results at the beginning of the reaction is attributed to the lack of a stable

equilibrium between activating and deactivating processes. Since the arrangement of monomers in copolymerization reactions is wholly made by propagation reactions, during this stage due to a larger number of cross propagation of styrene radicals, and therefore instability of the equilibrium reaction, a higher fraction of styrene results in a higher deviation from normal trend.

IV. CONCLUSION

In conclusion, the heterogeneity of copolymer chains in ATRcP is described by measurable parameters known as dyad fractions and investigated and calculated by Monte Carlo simulation. The effect of initial feed fraction of monomers on the dyad fractions is also computed by the simulation and presented as a function of reaction conversion. The drift in copolymer heterogeneity is another response parameter calculated by this Monte Carlo simulation.

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