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Dynamic Monte Carlo Simulation of Graft Copolymers Made with ATRP and Metallocene Catalysts

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The synthesis of polyolefin graft copolymers made with coordination polymerization was studied by dynamic Monte Carlo simulation. Narrow molecular weight distribution macromonomers, containing terminal vinyl groups made with atom-transfer radical polymerization (ATRP), were incorporated randomly into the polyolefin backbone. In addition to average molecular weights and polydispersity index, the model predicts the complete molecular weight distribution (MWD) and branching density of the graft copolymer. The effect of the concentration of macromonomers on the grafting efficiency was also studied.

Keywords: Atom-transfer radical polymerization (ATRP); coordination polymerization; graft copolymer; Monte Carlo simulation; polyolefins

Introduction

Polyolefins are the largest volume commodity polymers produced in the world and many researchers in industry and academia are actively studying the production of new polyolefins for specialty applications. For instance, some researchers are seeking coordination catalysts that can efficiently copolymerize olefins and polar comonomers; others are trying to copolymerize olefins with macromonomers (polymer chains containing a terminal vinyl group) made by coordination and other polymerization mechanisms to make block or graft copolymers.

Controlled polymerization is an excellent method to produce macromonomers with well-defined, uniform molecular architectures. Indeed, living (or controlled) free-radical polymerization (LFRP) is a vibrant area of polymer reaction engineering. The three most common types of LFRP are reversible addition-fragmentation chain transfer (RAFT),[1,2] nitroxide-mediated polymerization (NMP)[3–5] and atom-transfer radical polymerization (ATRP).[6,7]

We can combine two different polymerization mechanisms, such as coordination and living polymerization, to produce polymers with unique graft microstructures. In this approach, one polymer is made with one type of polymerization mechanism in a first step, and the other type of polymerization mechanism is used to prepare the final polymer. Two main techniques have been tried: *graft-to* and *grafting-from* approaches.

In the graft-to approach (Figure 1), macromonomers with narrow MWD (B) are prepared using a suitable living polymerization technique. These macromonomers are then modified chemically to introduce vinyl groups at their chain ends. Finally, a metallocene catalyst is used to copolymerize the macromonomers and the olefin monomer (A).

In the *graft-from* approach (Figure 2), a metallocene catalyst is used to produce polyolefin copolymers (A+B) having reactive comonomer units (B) that can be modified to become controlled free radical initiators. The resulting polymeric initiators can be used to initiate living polymerization reactions from the backbone of the previously formed polymer.

Graft copolymers with well defined side chains have been produced by combining

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Figure 1.
Grafting-to approach.

anionic and coordination polymerizations.[8–11] Anionic polymerization was used to produce macromonomers with narrow MWD, while metallocene polymerization was used to produce the grafted chains (graft-to approach). Similarly, nitroxide-mediated polymerization was used to synthesize macromonomers that were grafted to a polymer backbone using metallocene catalysts [12,13].

The graft-to method was also used to produce poly(propene-*g*-styrene) copolymers. Polystyrene macromonomer with different molecular weights were synthesized by ATRP and metallocenes were used to copolymerize them with propene.[14]

Matyjazewski et al. used the graft-from method to incorporate n-butyl acrylate (BA) and methyl methacrylate (MMA) into linear polyethylene. Ethylene and 10-undecen-1-ol were copolymerized using a metallocene catalyst and the resulting copolymer chains were modified to become ATRP macroinitiators. The resultant multifunctional macroinitiator was used to initiate the BA and MMA polymerization.[15]

Even though these interesting polymers have been studied experimentally by several researchers, little has been done to describe their microstructures with a detailed mathematical model. Zhu published an interesting paper showing some analytical solutions to describe random grafting.[16] Monte Carlo simulation is a powerful technique to predict the microstructure of polymers produced with any polymerization mechanism. In addition, because there is no need to solve systems of differential equations, Monte Carlo models are generally easier to develop and implement than models using population balances, albeit at a higher computational time. Monte Carlo simulation has been widely used to study coordination polymerization,[17–19] free radical polymerization,[20,21] and living polymerization.[22–27]

In this study, we developed a Monte Carlo model to describe the synthesis of

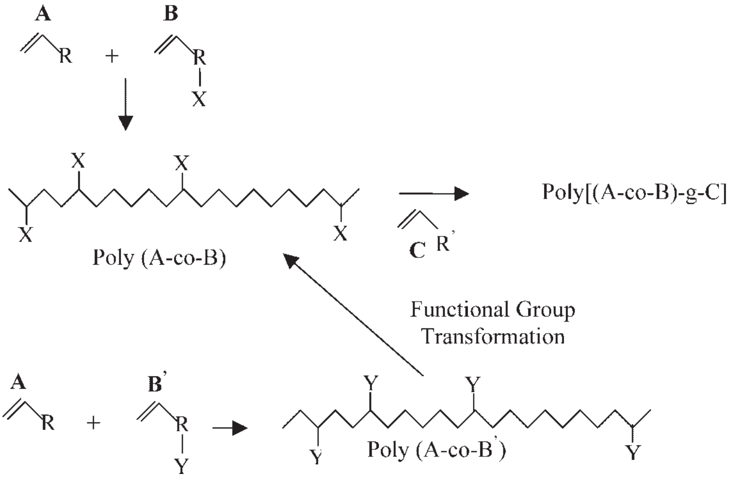

Figure 2.
Graft-from approach.

polyolefin graft copolymers made with ATRP and coordination polymerization with the graft-to approach. The simulation considers two types of macromonomers: *ex-situ* macromonomers produced by ATRP, and *in-situ* macromonomers produced during coordination polymerization. The first type of macromonomer is called ex-situ because they are produced in a separate reactor using ATRP, before being copolymerized with an olefin by coordination polymerization; the second type is called in-situ because macromonomers are produced in the same reactor during the polymerization of the olefin with a coordination catalyst.

ATRP Mechanism

The elementary reactions that constitute the polymerization mechanism of ATRP are: *Equilibrium*

$$D_r + C \xrightarrow{k_a} R_r \bullet + CX \tag{1}$$

$$R_r \bullet + CX \xrightarrow{k_d} D_r + C \tag{2}$$

Propagation

$$R_r \bullet + M \xrightarrow{k_p} R_{r+1} \bullet \tag{3}$$

Transfer to monomer

$$R_r \bullet + M \xrightarrow{k_{tr}} P_r + R_1 \bullet \tag{4}$$

Termination by combination

$$R_r \bullet + R_m \bullet \xrightarrow{k_{tc}} P_{r+m} \tag{5}$$

Termination by disproportionation

$$R_r \bullet + R_m \bullet \xrightarrow{k_{td}} P_r + P_m \tag{6}$$

In Equations (1) to (6), C and CX is the catalyst in its low and high valence states, M is the monomer, $R_r\bullet$ is a polymer radical, P_r is a dead polymer chain, D_r is a dormant polymer chain, k_p is the propagation rate constant, k_{tc} is the rate constant of termination by combination, k_{td} is the rate constant of termination by disproportionation, k_a is the activation rate constant, k_d is the deactivation rate constant, k_{tr} is the transfer rate constant, and the subscripts r and m indicates the number of monomer molecules in the chain.

Coordination Polymerization Mechanism

The main elementary reactions involved in the copolymerization of olefins and ex-situ macromonomers with coordination catalysts are: Initiation:

$$C^* + M \xrightarrow{k_i} P_1 \tag{7}$$

Propagation:

$$P_{r,i} + M \xrightarrow{k_p} P_{r+1,i} \tag{8}$$

In-situ macromonomer insertion:

$$P_{r,i,j} + D^{=}_{q,n,m} \xrightarrow{k_{LCB}} P_{r+q,i+n+1,j+m} \tag{9}$$

Ex-situ macromonomer insertion:

$$P_{r,i,j} + S^{=}_{z} \xrightarrow{k_S} P_{r+z,i,j+1} \tag{10}$$

β-Hydride elimination and in-situ macromonomer formation:

$$P_{r,i,j} \xrightarrow{k_\beta} P_{0,0,0} + D^{=}_{r,i,j} \tag{11}$$

Transfer to monomer and in-situ macromonomer formation:

$$P_{r,i,j} + M \xrightarrow{k_{tm}} P_{1,0,0} + D^{=}_{r,i,j} \tag{12}$$

In Equations (7) to (12), $P_{r,i,j}$ is a living polymer chain of chain length r having i in-situ macromonomer branches and j ex-situ macromonomer branches, C^* is the catalyst, $D^{=}_{r,i,j}$ is a dead polymer chain with a terminal vinyl group (in-situ macromonomer) of chain length r and i and j in-situ and ex-situ macromonomers, respectively, $S^{=}_{z}$ is an ex-situ macromonomer, M is an olefin monomer.

Principles of Monte Carlo Simulation

The Monte Carlo model we developed is based on the procedure suggested by Gillespie.[28] Two random numbers r_1 and r_2 are generated (using the statistic package built in Visual Basic) to select reaction type and time increment, according to the following equations:

$$\sum_{\upsilon=1}^{\mu-1} P_{\upsilon} < r_1 < \sum_{\upsilon=1}^{\mu} P_{\upsilon} \tag{13}$$

$$\tau = \frac{1}{\sum_{\upsilon=1}^{\mu} R_{\upsilon}} \ln\left(\frac{1}{r_2}\right) \tag{14}$$

where μ is the number of the selected reaction type, P_{ν} is the probability of reaction ν, τ is the time interval between two successive reactions, and R_{ν} is the reaction rate of the ν^{th} reaction. The probability of a generic reaction (P_{ν}) taking place at a given time can be calculated with the equation,

$$P_{\upsilon} = \frac{R_{\upsilon}}{\sum_{\upsilon=1}^{N} R_{\upsilon}} \tag{15}$$

In order to calculate the stochastic rates, all the rate constants must be transformed from macroscopic ($k^{\exp}$) constants to microscopic (k^{MC}) constants according to the following equations:

$$k^{MC} = k^{\exp} \quad \text{for first order reactions} \tag{16}$$

$$k^{MC} = \frac{k^{\exp}}{VN_A} \quad \text{for bimolecular reactions between different species} \tag{17}$$

$$k^{MC} = \frac{2k^{\exp}}{VN_A} \quad \text{for bimolecular reactions between similar species} \tag{18}$$

where V is the size of the control volume and N_A is Avogadro's number. Moreover, the molar concentration of the species in the reactor should be transformed into the number of molecules inside the control volume.

A flowsheet summarizing the Monte Carlo simulation procedure used in this investigation is shown in Figure 3.

A microcomputer (Intel® Pentium® 4 with 2.8 GHz processor and 504 MB of RAM) was used in the simulations. The program was written in Visual Basic version 6.

Modeling Macromonomer Formation

Practically, there are two ways to produce macromonomers with ATRP: 1) modify the terminal functional group (halide atom) to a terminal double bond through a post-polymerization reaction, or 2) use initiators that have two functionalities (a halide atom and a terminal double bond) such as allyl bromides or allyl chlorides (Figure 4).

ATRP can produce polymers with controlled molecular weights and narrow molecular weight distributions. The molecular weight can be controlled either by changing the molar ratio of monomer to initiator or by varying polymerization time. Al-Harthi et al. used Monte Carlo simulation to study the polymerization kinetics of ATRP with monofunctional[26] and bifunctional initiators.[27] As expected in living polymerization processes, the chain length increases almost linearly with monomer conversion and the polydispersity index approaches one, as shown in Figure 5. Figure 6 shows the time evolution of chain length distribution in ATRP. The MWD peaks are narrow and shift to higher averages with increasing monomer conversion.

Modeling Graft Copolymer Formation

Some coordination polymerization catalysts can copolymerize olefins with chains containing terminal vinyl groups (macromonomers). Constrained geometry catalysts (CGC) are among the best coordination catalysts having high reactivity towards macromonomer incorporation. These macromonomers can be of two types: 1) in-situ macromonomers, generated via β-hydride

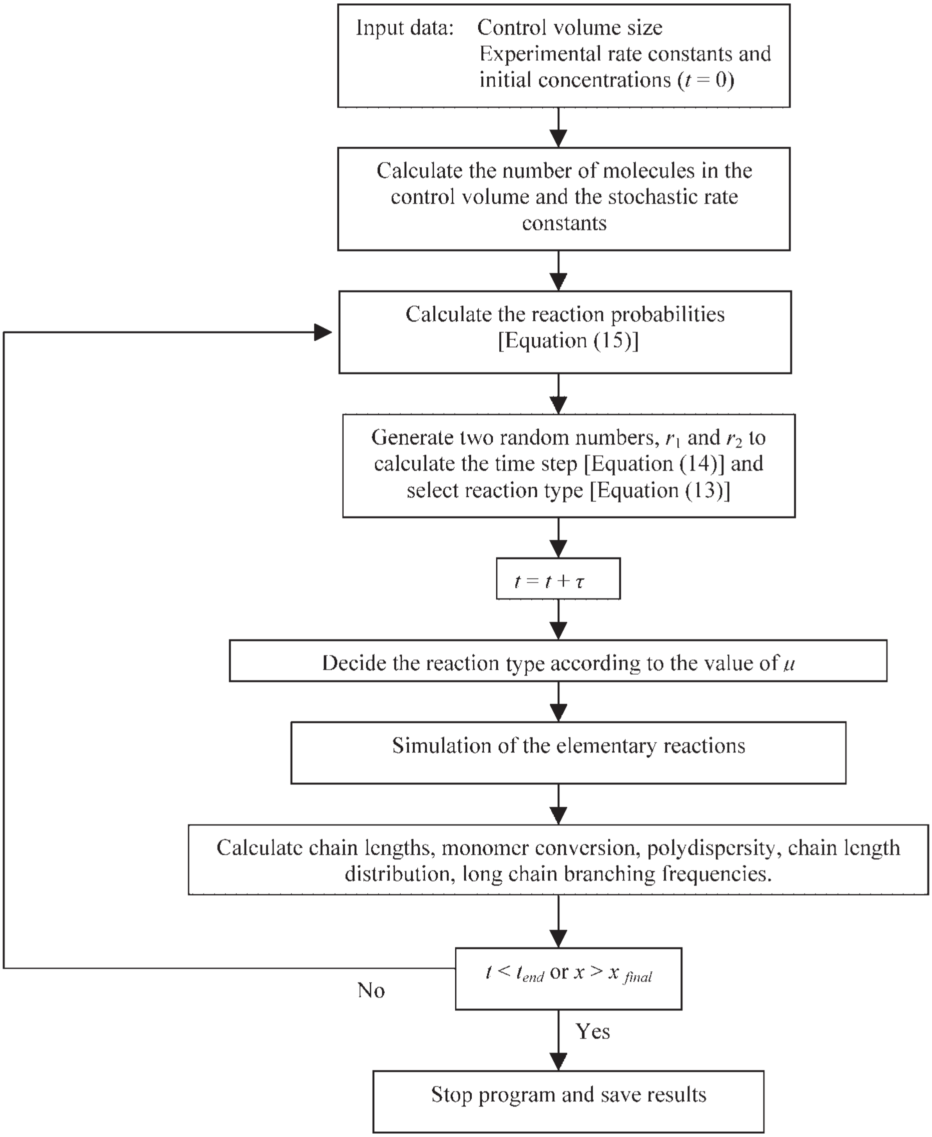

Figure 3.
Algorithm for Monte Carlo simulation.

elimination and chain transfer to ethylene directly in the reactor, and 2) ex-situ macromonomers, synthesized in a separate reactor and added at the beginning of the polymerization. In our case, we will assume that the ex-situ macromonomer was made with ATRP and can be considered monodisperse.

$$H_2C = CHCH_2Br \qquad H_2C = CHCH_2Cl$$

Figure 4.
Allyl bromide (left) and allyl chloride (right).

The ATRP ex-situ macromonomer is fed to the reactor with several concentrations in batch mode. The concentration of the ex-situ macromonomer decreases with the polymerization time, as they are incorporated into the polymer chains. The in-situ macromonomers are produced

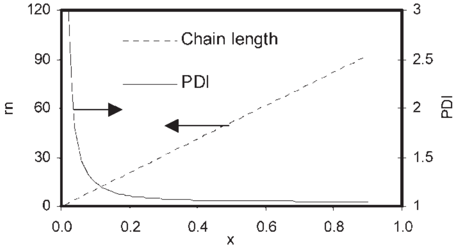

Figure 5.
Monte Carlo simulation of number average chain length and polydispersity index in ATRP of styrene as a function of monomer conversion.[26]

Table 1.
Summary of polymerization kinetic parameters.

Kinetic parameter	Value
k_i	373.22 $L/(mol.s)$
k_p	373.22 $L/(mol.s)$
$k_\beta + k_{tm}$	0.0824 s^{-1}
k_{LCB}/k_p	0.0248
k_S/k_p	0.0248

throughout the polymerization and their concentration increases with time. Naturally, the incorporation of both macromonomer types produces a polymer having long chain branches of ex-situ and in-situ types.

The values of the polymerization kinetic parameters used in this study are summarized in Table 1. These values were estimated from experimental results published in a previous study in our laboratory.[29] The rate constant for the incorporation of ex-situ and in-situ macromonomers is assumed to be the same, for simplicity, in the following simulations. The monomer concentration was kept constant at 1.0 mol/L because we assumed semi-batch monomer feed in our simulations.

As the polymerization starts, the ex-situ macromonomer chains start copolymerizing with ethylene and incorporating into the living chains. This incorporation decreases with time, since the concentration of ex-situ macromonomers is decreasing and, therefore, the number of incorporated ex-situ macromonomer branches per chain also decreases, as shown in Figure 7.

On the other hand, the concentration of in-situ macromonomers increases with time because of the chain transfer reactions that take place in coordination polymerization. As a result, their branching frequency also increases with the time, as depicted in Figure 8.

One of the most important information that Monte Carlo simulation can predict is the complete chain length distribution (CLD). As the concentration of in-situ macromonomer increases, its probability to be incorporated into the living chains increases. Therefore, the grafting density increases and this affects the CLD. Flory's most probable distribution, used to describe the CLD of linear polymers made with single-site coordination catalysts, is no longer applicable to graft copolymers.

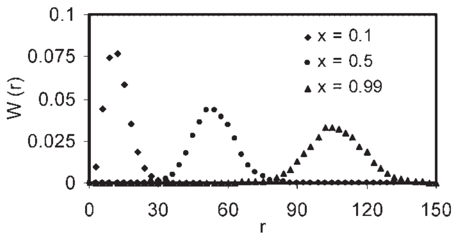

Figure 6.
Monte Carlo simulation of chain length distribution as a function of monomer conversion for ATRP of polymerization of styrene.[26]

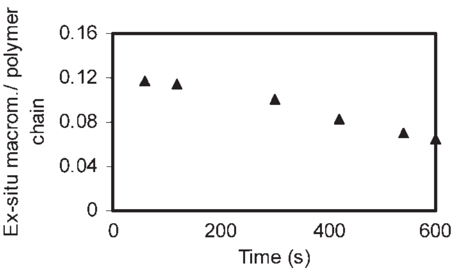

Figure 7.
Average number of ex-situ macromonomer branches per polymer chain as a function of time.

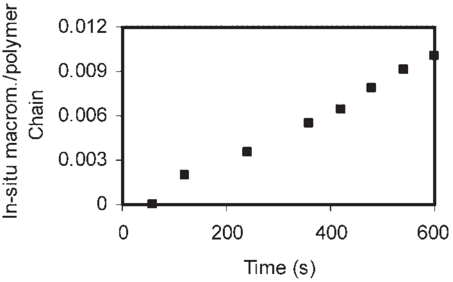

Figure 8.
Average number of in-situ macromonomer branches per polymer chain as a function of time.

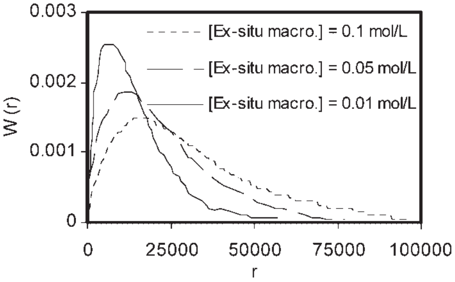

Figure 10.
Effect of ex-situ macromonomer concentration on the CLD for ten minutes of polymerization.

Figure 9 shows how the polydispersity index varies with polymerization time and with the initial concentration of ex-situ macromonomer in the reactor. Notice how, for a given polymerization time, polymers made with a higher ex-situ macromonomer concentration have a higher polydispersity index. In addition, the polydispersity index increases with polymerization time, since the concentration of in-situ macromonomer also increases with polymerization time. This gives us two variables to control the molecular weight and polydispersity index of the final product.

Figure 10 shows how the CLD broadens when the initial concentration of ex-situ macromonomer is increased for a given polymerization time.

Conclusion

Monte Carlo simulation was used to describe the microstructure of polymers made with a combination of coordination polymerization and ATRP. ATRP was used in the first step to produce monodisperse macromonomers that were subsequently copolymerized with ethylene using a coordination catalyst in semi-batch mode. The model is general and can be use to

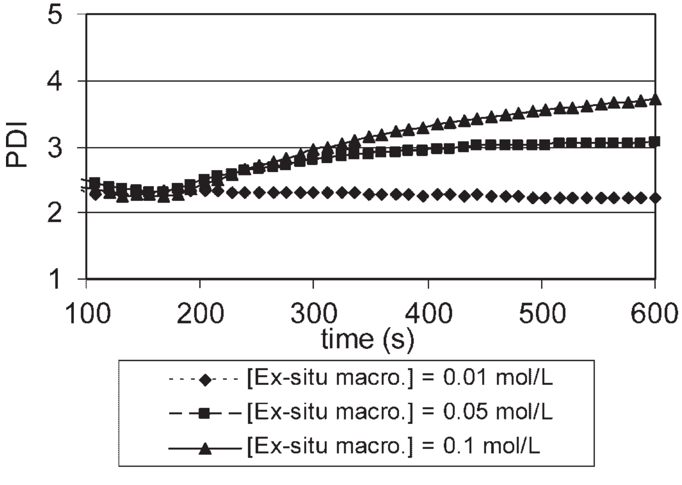

Figure 9.
Effect of ex-situ macromonomer concentration and polymerization time on polydispersity index.

describe any system, provided that the proper rate constants are used.

In this study, we use rate constants of styrene polymerization with ATRP to prepare the ex-situ macromonomers and rate constants of ethylene polymerization with CGC for the grafting polymerization.

The chain length distribution and the grafting density were the most important microstructural details predicted in this study. We showed that the frequency of ex-situ branching decreased with polymerization time, while the frequency of in-situ branched increased linearly with polymerization time. The effects of these grafting reactions on the CLD of the final polymer were also demonstrated.

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