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Integrated Kinetic Monte Carlo–Structure–Rheology Model for Solution Copolymerization of Ethylene and \( \alpha \)-Olefins

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Supporting Information

ABSTRACT: An integrated Kinetic Monte Carlo–structure–rheology model is developed for polyolefins produced using solution copolymerization of ethylene and \( \alpha \)-olefins. The proposed algorithm is completely first-principle and can be used to simulate any homogeneous single-site polymerization process resulting in full topological and chemical composition details of the product formed. The model maintains simple hierarchical data structures to track the structure and composition of polymer chains and efficiently generates a full ensemble of polymeric molecules under varying process conditions. The model has a control-volume description with no implicit assumptions regarding the dynamic state of the process, and hence the methodology can be used for any reactor configuration. We benchmark the model by simulating two semibatch pilot plant runs and use the benchmarked model to simulate production of three industrial grade polyolefins which differ significantly in their molecular weight distributions, long-chain branching fractions, and chemical composition. For modeling the continuous state production process with the control volume description, we propose a simple inflow/outflow step in the algorithm to model continuous stirred-tank reactors (CSTR) which eliminates use of idealized flow and steady-state approximations. The simulated molecular topology and bivariate long-chain branching (LCB) molecular weight distributions are used to select a representative ensemble of molecules that is used to calculate linear rheology using the branch-on-branch model of Das et al. The resulting product distributions for the semibatch trials reproduce the measured molecular weight distributions. For the polyolefins simulated with the continuous process the virtual products have closely matching molecular weight distributions and branching fractions compared to measured values of the industrial polyolefins. The simulated rheology also agrees quite closely with the experimental values without use of any fitting parameters in the full integrated approach. In addition, microstructural characteristics as measured by the crystallization elution fractionation technique also match closely with the simulated crystallization elution fractionation distributions calculated using the longest ethylene sequence distributions obtained for the three products.

INTRODUCTION AND BACKGROUND

Designing new industrial grade polymers involves running multiple laboratory scale synthesis experiments or pilot plant trials and carrying out rigorous rheological and mechanical characterization to achieve the target properties. Recent breakthroughs in polyolefin catalysis have provided polymer chemists and engineers opportunities to precisely control polymer structure and properties using novel catalyst families. This level of control over polymer structure with the new generations of metallocene and postmetallocene technologies enables a molecular architecture approach to product design which enables faster need-based product development. Progress in modeling methods for polymerization processes tracking topological and chemical composition details of the molecules formed and concurrent progress in predictive theoretical models for calculating rheological and mechanical

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properties from polymer structures hold the potential to significantly lower the required number of experimental synthesis and characterization trial runs. These computational design tools will help accelerate process and product design in polymer industry by minimizing the experiments to a much smaller process design space. Multiple simulation methodologies exist for simulating different kind of polymerization chemistry (free radical, single-site homogeneous, condensation reactions) and for predicting rheology of polymer molecules from their architectural details. In this study we focus on polyolefins formed by solution copolymerization of ethylene and \( \alpha \)-olefins such as butene, hexene, and octene, with densities in the elastomer domain. These molecules are typically synthesized using metalloocene or single-site constrained geometry catalysts which selectively polymerize ethylene and comonomer sequences. Increasing the comonomer content disrupts the crystallinity and increases the elasticity of the product. In addition, the molecular weight of the polymer and their long-chain branching (LCB) would determine their processing characteristics and end-use properties (e.g., enhanced toughness for higher molecular weight resins).

To construct a predictive methodology, we need a detailed polymerization model that tracks the architecture of these molecules in sufficient details for calculating properties of interest directly from the generated molecular structures. For this, the model needs to keep account of both long-chain and short-chain branches in addition to the chain lengths of polymer molecules as both types of branching have a significant impact on various mechanical, rheological and thermal properties. Most polymerization processes can be mathematically formulated in the form of multivariate population balance equations (PBEs) where time evolution dynamic equations of various polymeric species are formulated and solved by reducing the number of equations to a finite order system with various assumptions. These methods are broadly classified into kinetic lumping methods, polynomial expansion methods, global orthogonal collocation, method of moments, discrete weighted Galerkin, and orthogonal collocation on finite elements and sectional grid methods (fixed-pivot technique). The accuracy and efficacy of predictions from these methods are highly delimited by the accuracy of discretization scheme, kinetic assumptions such as steady-state approximation of live polymers, and the absence of gel effects and associated numerical complexities in developing the solution algorithm. Additionally, for developing an integrated property-predicting model such as for calculating rheology of the simulated molecules, one of the limitations is that while these methods predict distributions of molecular weight and various branching distributions, no explicit information about distribution of branches within the polymer molecule is available. Hoefsloot and Iedema attempted to solve this issue using a conditional Monte Carlo scheme, where the bivariate distributions are calculated using a Galerkin method and the distributions are then used in a graph theory based Monte Carlo algorithm to produce polymer shapes. However, the assumptions made about the sequence of chemical steps in these algorithms delimit their predictive capabilities.

Metallocene-catalyzed polymerization of ethylene is a well-studied problem, and multiple deterministic and stochastic modeling techniques exist for determining the molecular weight and branching distributions as well as for constructing ensemble of molecules generated with this technology. Soares and Hamielec developed a population balance method to obtain bivariate distribution of molecular weight and branching number in a continuous stirred-tank reactor (CSTR). Later, a Monte Carlo simulation scheme was developed by the same authors to verify their analytical solution for the joint distribution. This approach was further extended by Beigzadeh et al. to classify the long-chain branches formed as comb or dendritic. Costeux et al. improved the stochastic model further by allowing distributions of molecular topologies to be sampled and representing their structure in rheologically relevant details. They presented a ternary diagram approach to represent the topology of long-chain branched polyethylenes by accounting for different chain segments as linear chains, free arms, and inner segments. Simon and Soares extended the Monte Carlo approach to model polymerization with two single-site catalysts, where one catalyst makes only linear chains while the other makes linear as well as long-chain branched chains. They also classified the polyolefins chains made with this dual catalyst into distinct families with distinct branch topologies for families with more than three long chain branches. Another popular class of method used to model microstructures of polymers under different polymerization conditions is the method of instantaneous distributions popularized by Soares et al. The working principle for these methods is to represent the various distributions (molecular weight, chemical composition, and LCB) using an instantaneous distribution which represents the microstructure of the polymer at an infinitesimal time interval and reactor volume, which can then be integrated over time and space to obtain the macroscopic distributions at desired reactor conditions.

Modeling copolymerization processes of ethylene and \( \alpha \)-olefins in full microstructural detail has been a challenging problem in polymer reaction engineering. Many advances have been made in both deterministic and stochastic modeling of copolymerization processes and in correlating the microstructure with crystallization behavior, mechanical and processing properties. The earliest analytical model for determining comonomer content in copolymers has been proposed by Mayo and Lewis which correlated the comonomer content of polymers to the feed and reactivity ratios based on terminal (or Morkov) polymerization model. Tebita used the theory of Markovian processes to develop a matrix calculation procedure for determining the bivariate chain length and composition distributions in free-radical polymerization for a generalized case of \( N \) types of monomers. For metallocene-catalyzed polyolefins, Soares and Hamielec derived an analytical solution for distribution of molecular weight, LCB, and chemical composition which agreed well with their Monte Carlo calculations. Kim et al. used this mathematical model with experimental results to predict polymerization conditions and metallocene combinations that produce polymers with desired molecular weight and chemical composition distributions. Costeux et al. further derived analytical solutions verified with pseudo-Monte Carlo simulations for the bivariate distribution and the longest ethylene sequence distribution which correlates with crystallization analysis fractionation (CRYSTAF) and temperature-rising elution fractionation (TREF). A more detailed Monte Carlo model for copolymerization of ethylene and \( \alpha \)-olefins was designed by Al-Saleh and Simon which predicts molecular weight and detailed chemical composition distributions in the
form of monomer sequence distributions. Kiparissides et al. used two-dimensional fixed pivot techniques and an efficient implementation of a Monte Carlo algorithm to calculate the bivariate molecular weight–copolymer composition distributions in batch free-radical copolymerization reactions. In another recent study a fully deterministic general and powerful numerical toolbox for modeling linear copolymerization of two monomers has been formulated. This scheme allows a rigorous computation of the complete bivariate chain distributions and sequence length distribution by numerical integration of the two-dimensional population balance equations using a linear combination of the Gaussian basis function approach. Similarly, Steenberge et al. introduced composite binary trees for improving kinetic Monte Carlo calculation of chemical composition and molecular weight distributions by improving the computational speed and ensuring accurate calculations even for high chain lengths.

In addition to the microstructure describing distributions, explicit information about polymer chain topology is crucial for predictive structure–property modeling. Recently, Meimargoglou and Kiparissides proposed a novel stochastic method for accurate prediction of molecular topology of highly branched polymer chains without using any simplifying assumptions regarding the distributional form of live or dead chains. They further used the molecular information obtained from the kinetic topology Monte Carlo algorithm to predict the rheological behavior of low-density polyethylene (LDPE) melts in a high-pressure ethylene polymerization tubular reactor. The first attempt to connect molecular structures generated from metallocene-based polymerization to their rheological properties was made by Read and Soares. Many improvements were made over the years with progress in tube theory based models. However, most of these models simulate homopolymerization of ethylene and use simplifying assumptions to obtain branching and propagation probabilities which are used in the Monte Carlo scheme to generate the ensemble of molecules for rheology predictions. This approach limits the predictive capabilities and is not extendable to simulate different industrial processes.

In this study, we propose a novel scheme for simulating copolymerization process of ethylene and α-olefins in full molecular detail. In our approach, we use a control-volume description where the polymer microstructure evolves with reaction time, and the reactor residence time distribution can be reproduced for different reactor types. For continuous stirred tank reactors, we incorporated a simple inflow/outflow step to reproduce the experimental reactor conditions. We have also formulated a new hierarchical bookkeeping algorithm which requires the branching information to be updated only at certain steps when a macromonomer addition reaction takes place and is efficient in memory management and computational performance. It results in the generation of huge molecular ensembles in addition to precise average properties, which can then be integrated with molecular modeling and other empirical/theoretical tools to predict product properties. We use these molecular ensembles as input to a tube theory based rheology calculation model which results in prediction of linear rheological properties of the model molecules. We first benchmark our reaction modeling scheme by simulating two semibatch pilot plant runs for copolymerization of ethylene and octene and compare the molecular weight distribution profiles with experimental data. We then demonstrate the predictive capability of the integrated reaction and tube theory scheme by simulating three Dow industrial polyolefins starting with just the process parameters as inputs and comparing their rheological behavior and crystallization behavior with experimental measurements.

**Methodology**

An integrated approach with detailed topology bookkeeping implementation of the kinetic Monte Carlo algorithm (for simulating copolymerization reactions) followed by tube theory calculations is used to predict rheology of polyolefins directly from the reactor process conditions. The kinetic Monte Carlo model generates a time-varying ensemble of polyolefin molecules which represent a finite volume of the reactor. This model can in principle be used with any detailed reactor model with spatial and time varying details such as temperature and pressure profiles and concentrations of monomers, catalyst, and initiator species. In our implementation for modeling the semibatch pilot plant runs we used a time-varying inflow of one of the monomers along with varying reactor temperatures which are obtained by monitoring them during the pilot plant trials (ideally, they can also be calculated using a detailed reactor model with heat and thermodynamic pressure calculations). For modeling the three polyolefins produced in continuous industrial process, we modeled the desired residence time distribution of a CSTR using a simple inflow/outflow mechanism. This approach allows us to work without using any simplifying assumptions such as the quasi-steady-state approximation or the ideal flow distribution in the reactor, allowing the model to capture formation of molecules with extremely rare architectures such as high number of branch points and molecular weight. Another important application of this form of a dynamic model for a CSTR is that it allows us to study average properties as well as architectural distribution of polymer molecules formed during start-up phase of the reactor. This would give substantial insights into how the polymer mass evolves during the transient start-up phase of the reactor. Discussions in the Results section illustrate how polydispersity and average branching frequency change during the transient phase for one of the polyolefin runs. These insights might be crucial for troubleshooting processes where gelation or any form of uncontrolled growth is possible. The polymer molecules that exit the reactor at any time instant are chosen randomly, and all species (unreacted monomers, catalyst, and live and dead polymer chains) exit in proportion to their existing mass/molar fraction in the reactor. The whole inflow/outflow balance is designed to satisfy the mass balance of the whole reactor with the total out-flowing mass being the same as the total inflowing mass of the unreacted species. The details of the implementation of this simplistic reactor model will be described after the details of the topology-describing kinetic Monte Carlo algorithm below.

The kinetic Monte Carlo method is completely firstly incorporates and simulates all catalyst initiation, propagation, macromonomer addition, chain transfer, chain termination, and catalyst deactivation reactions explicitly for the molecular catalyst family with known kinetic parameters. The kinetics of different reactions are determined by the terminal functional group attached to the active catalyst site with the macromonomer terminated chains having similar rate constants as octene. The reaction rate constants used in this study are approximate numbers proportional to detailed reaction kinetics data obtained from extensive pilot plant trials conducted.
internally within The Dow Chemical Company. The scheme simulates the copolymerization of ethylene and 1-octene with a constrained geometry catalyst. The reaction scheme used to simulate the copolymerization process of ethylene and octene along with long-chain branch (LCB) formation is as follows.

Catalyst initiation and propagation reactions:

\[ C^* + E \xrightarrow{k_{\text{int}}} L^E \]  

\[ C^* + O \xrightarrow{k_{\text{int}}} L^O \]  

\[ L^E_{c,\alpha,b} + E \xrightarrow{k_{\text{prop}}^{E}} L^E_{c+1,\alpha,b} \]  

\[ L^O_{c,\alpha,b} + O \xrightarrow{k_{\text{prop}}^{O}} L^O_{c+1,\alpha,b} \]  

\[ L^E_{c,\alpha,b} + E \xrightarrow{k_{\text{prop}}^{E}} L^E_{c+1,\alpha,b} \]  

\[ L^O_{c,\alpha,b} + O \xrightarrow{k_{\text{prop}}^{O}} L^O_{c+1,\alpha,b} \]  

\[ L_{c,\alpha,b} \xrightarrow{k_{\text{prop}}^{\text{MME}}} L^E \]  

\[ L_{c,\alpha,b} \xrightarrow{k_{\text{prop}}^{\text{MMA}}} L^O \]  

\[ k_{\text{int}}^E = k_{\text{prop}}^{E} = k_{\text{prop}}^{\text{MME}} = 102000 \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1} \]  

\[ k_{\text{prop}}^{O} = 19000 \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1} \]  

\[ k_{\text{int}}^O = k_{\text{prop}}^{O} = k_{\text{prop}}^{\text{MMA}} = 500 \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1} \]  

Chain transfer to monomers:

\[ L^E_{c,\alpha,b} + E \xrightarrow{k_{\text{trans}}^{E}} D^E_{c,\alpha,b} + L^E_{1,0,0} \]  

\[ L^O_{c,\alpha,b} + O \xrightarrow{k_{\text{trans}}^{O}} D^O_{c,\alpha,b} + L^O_{1,0,0} \]  

\[ L^O_{c,\alpha,b} + E \xrightarrow{k_{\text{trans}}^{O}} D^O_{c,\alpha,b} + L^E_{1,0,0} \]  

\[ L^O_{c,\alpha,b} + O \xrightarrow{k_{\text{trans}}^{O}} D^O_{c,\alpha,b} + L^O_{1,0,0} \]  

\[ L_{c,\alpha,b} \xrightarrow{k_{\text{trans}}^{\text{MME}}} D^E_{c,\alpha,b} + L^E_{1,0,0} \]  

\[ L_{c,\alpha,b} \xrightarrow{k_{\text{trans}}^{\text{MMA}}} D^O_{c,\alpha,b} + L^O_{1,0,0} \]  

\[ k_{\text{trans}}^{E} = 16 \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1} \]  

\[ k_{\text{trans}}^{O} = 48 \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1} \]  

\[ k_{\text{trans}}^{\text{MME}} = k_{\text{trans}}^{\text{MMA}} = 0 \]  

\[ k_{\text{trans}}^{O} = k_{\text{trans}}^{\text{MMA}} = 19 \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1} \]  

Chain transfer to hydrogen:

\[ L^E_{c,\alpha,b} + H_2 \xrightarrow{k_{\text{trans}}^{H_2}} D^E_{c,\alpha,b} + C^* \]  

\[ L^O_{c,\alpha,b} + H_2 \xrightarrow{k_{\text{trans}}^{H_2}} D^O_{c,\alpha,b} + C^* \]  

\[ L_{c,\alpha,b} \xrightarrow{k_{\text{trans}}^{\text{MM}}} D^H_{c,\alpha,b} + C^* \]  

\[ L_{c,\alpha,b} \xrightarrow{k_{\text{trans}}^{\text{MM}}} D^H_{c,\alpha,b} + C^* \]  

Thermal termination by \( \beta \)-hydride elimination:

\[ L^E_{c,\alpha,b} \xrightarrow{k_{\text{th}}^E} L^E_{c,\alpha,b} + C^* \]  

\[ L^O_{c,\alpha,b} \xrightarrow{k_{\text{th}}^O} L^O_{c,\alpha,b} + C^* \]  

\[ L_{c,\alpha,b} \xrightarrow{k_{\text{th}}^{\text{MM}}} L_{c,\alpha,b} + C^* \]  

Macromonomer addition leading to LCB formation:

\[ L_{c,\alpha,b} + D_{c+1,\alpha,b} \xrightarrow{k_{\text{th}}^{\text{MM}}} 
\]  

\[ L_{c,\alpha,b} + D_{c+1,\alpha,b} \xrightarrow{k_{\text{th}}^{\text{MMA}}} \]  

Deactivation reactions:

\[ L^E_{c,\alpha,b} \xrightarrow{k_{\text{deact}}^{E}} D^E_{c,\alpha,b} + C \]  

\[ L^O_{c,\alpha,b} \xrightarrow{k_{\text{deact}}^{O}} D^O_{c,\alpha,b} + C \]  

\[ L_{c,\alpha,b} \xrightarrow{k_{\text{deact}}^{\text{MME}}} D^E_{c,\alpha,b} + C \]  

\[ L_{c,\alpha,b} \xrightarrow{k_{\text{deact}}^{\text{MMA}}} D^O_{c,\alpha,b} + C \]  

\[ k_{\text{deact}}^E = 0.0036 \text{ s}^{-1} \]  

\[ k_{\text{deact}}^{E/O/MM} = \text{a live polymer with the superscript denoting whether the terminal monomer attached to the active catalyst site is ethylene (E), octene (O), or macromonomer (MM). Subscripts } c, \alpha, \text{ and } b \text{ denote the number of ethylene and octene monomers and number of branches in the chain, respectively. Similarly } D_{c,\alpha,b} \text{ is a dead polymer with subscripts } c, \alpha, \text{ and } b \text{ denoting the number of ethylene and octene monomers and number of branches in the chain. Macromonomers } D_{c,\alpha,b} \text{ are formed in chain transfer to monomer reactions or thermal } \beta \text{-hydride elimination reactions. The active catalyst sites are denoted by } C^*, \text{ and every live polymer is implicitly connected to an active catalyst site; the deactivated catalyst sites are denoted by } C. \text{ The indicative kinetic rate constants listed below each reaction type are approximate constants calculated for the reaction temperature at hand.} \]
and the reaction time is updated by using a stochastic updating rule with each reaction step leading to time being incremented by

$$dt = -\ln(a_0)/\sum_i r(i, t)$$

(26)

where $a_0$ is a random number from 0 to 1 and $r(i, t)$ is the rate of reaction of type $i$ at time $t$. The reaction rates are calculated for each of the listed reaction types using various zeroth-order moments of the live and dead polymers, number of monomers, comonomers, hydrogen molecules, and vacant catalyst sites. The rates are then used to calculate the reaction probabilities according to Gillespie’s algorithm. The live or dead polymer which reacts is then chosen randomly from the entire set of that particular subtype of live chains. The numbers of monomers, hydrogens, and vacant catalyst sites are updated according to the reaction type. The corresponding chain describing and branching information arrays are updated for the selected chain for simulating the selected reaction, and the index arrays that track the indices of chains of different types are updated in case the reaction changes the terminal bonding of a live polymer or a macromonomer generation/addition reaction occurs.

In Figure 1 (top frame) we illustrate the bookkeeping structure for the live and dead chains. The primary chain information is stored in a chain describing array with one entry for each reaction step leading to time being incremented by

$$dt = -\ln(a_0)/\sum_i r(i, t)$$

(26)
information such as the position of the branch on the backbone chain, its length, and details about number of sub-branches on that particular branch, and in the case of sub-branches it also stores the addresses in the branch description array for each of them. One important detail here is that the backbone branching array only stores the address for branches directly attached to the backbone of the growing (or last growing) polymer chain. The sub-branches attached to any of these branches are directly referenced to in the branch description array. In this scheme, each branch description array element stores the number of sub-branches on it and the array indices for each such sub-branch. This hierarchical data structure allows the full topology of the branched molecules to be stored and involves minimal changes in most of the reactions involved in the copolymerization scheme illustrated above. For any branching change only the reference address for this branch (sub-branch) needs to be updated in the growing chain data structures. This data structure maintains all required information for LCB topology and comonomer content required for detailed rheology calculations and crystallization behavior. To speed up the bookkeeping process, we also maintain different index arrays (depicted rightmost in Figure 1, top and Figure 2) which keep track of all the live polymers indices in the chain description arrays with different kinds of end-groups attached to active sites and also maintain an index array for macromonomers. These arrays accelerate the stochastic selection of the desired live or dead (macromonomer) chains which react at any time instant during the simulation.

An illustration of how these data structures store the topology of a long chain with multiple branches is provided in the bottom frame of Figure 1. The living chain L(1050) has 610 monomer units (10 of which are octene) and has 3 branches on its backbone with current ethylene sequence length of 4 and longest ethylene sequence length of 20. Its current molecular weight is 17952.4, and the index location of the backbone branching array which stores its backbone branches information is 55. In the 55th element of the backbone branching array we get the respective locations of array elements which stores their branch description (131st, 132nd, and 133rd). From these locations we can read the total monomer contents of branch 1, 2, and 3 being 126, 95, and 78, respectively, and their positions being 87th, 146th, and 250th on the main chain. On the basis of these numbers the backbone length of the growing chain is calculated as 311, and the branch point positions are known. Now only for branch 1 there is a sub-branch which is stored in the 23rd element in branch description array. By reading that, we know its position as 29th on the branch 1 backbone and its length as 37. The length of branch 1 backbone is hence calculated as 89, and the entire structure could be visualized and input in rheology calculations as depicted in the bottom frame of Figure 1.

To further describe the working of this bookkeeping method during simulation of various reactions in the copolymerization process, we illustrate the initial and final states of the live chain and macromonomer (dead) chain description arrays and backbone branching and branch description arrays during a macromonomer addition reaction in Figure 2. In this scheme the 25th element of the live chains undergoes a macromonomer addition reaction with the macromonomer stored as the sixth element. We see entries storing the number of ethylenes at the first position, octenes at the second position, and molecular weight at the sixth position are updated by addition of corresponding entries for live chain and the macromonomer. The number of branches stored at the third position is updated by summing the number of branches in both molecules and incrementing the sum by one. The current ethylene sequence length stored at the fourth position is updated to zero while the longest ethylene sequence stored at the fifth position is based on the maximum between the live chain and macromonomer entries. A new entry is created in the backbone branching array as the 55th element to store information about the branch attached to the growing backbone chain. This array stores the number of branches on the chain (1) and stores the location of array element storing the branch description (49). A new entry is also created in the branch description arrays (49th element) which stores the location of the branch on the main chain as the 46th position, the total monomer content of the chain (73), and information about the number of sub-branches attached to this
branch (1) with the location of branch description array storing the sub-branch information (23rd element). We can observe that sub-branch array elements remain unchanged in the branch description array (23rd element), and the pointing index is updated to indicate it is now a sub-branch on the branch stored as 49th element. For all other reactions, even simpler bookkeeping operations are required. For initiation and propagation creating a new entry in the chain description array or updating two entries of chain description arrays is required. Chain transfer reactions or thermal termination reactions would involve no changes to the architecture describing arrays but just a change in index arrays with the chain index being moved from live chain index array to dead chain (macromonomer) array. Chain transfer to hydrogen reactions require only a deletion of the index from live chain index array and storing the molecule (in a chain description array) as a dead chain. Similarly, deactivation of catalyst reactions would involve similar deletion of chain entry from the live chain index arrays. Illustrations of bookkeeping data structures for a propagation and chain-transfer reaction are included in section S2 of the Supporting Information.

Additional examples of how bookkeeping arrays change during propagation and chain transfer to monomer reactions are also illustrated in the Supporting Information.

For the semibatch process the inflow of the ethylene monomer is simulated every 0.1 s of reaction time, and their flow rate and reactor temperature values are updated at respective time intervals as they are measured during the experimental runs. Ideally, the flow and temperature profile of the polymerization process could also be calculated by using a full scale reactor model accounting for the enthalpies of reactions, partial pressure and solubility of ethylene, and heat transfer rates. For our modeling scheme we use the experimentally measured values. This is useful in benchmarking the kinetic reaction model.

For simulating the continuous process, the outflow of the reactor mixture and the inflow of the reacting species are simulated after every 0.2 s of reaction time (due to a residence time of around 400 s this number translates to 0.05% of reacting mass being removed and added in each outflow/inflow step). A comparison of how different time increments to perform the inflow/outflow step impact the resulting product characteristics and compute time is illustrated in section S4 of the Supporting Information. The mass flow out is calculated by assuming a homogeneous mixture of reacting species and products formed. A calculated number of reacting species, catalyst sites, and live and dead chains exit from the reactor such that the total mass inside the reactor remains constant at each time step. This is done by calculating a fraction of the total mass inside the reactor that needs to be removed to accommodate the fresh feed-in (which is calculated using the mass flow rates of the monomers, hydrogen and catalyst sites, and the time elapsed since the last mass flow event). The numbers of monomers, hydrogen molecules, and catalyst sites (including those with attached polymeric live chain) are calculated on a weighted number basis. A flowout factor is calculated (eq 27) by using the mass of monomers and catalyst sites flowing into the reactor in the differential time the reactor has been operating since the last mass flow event and the total mass in the reactor.

\[
\text{flow-out factor} = \frac{\text{mass flowing in} + \text{total mass in reactor} - \text{total mass in reactor at } t=0}{\text{total mass in reactor at } t=0}
\]

This flow-out factor is used to calculate the number of monomers, catalyst sites, and live polymer chains that need to
be removed from the reacting mass on a number basis (with respect to the number of each of these species in the reactor at current time instant). If the number of catalyst sites, monomers, or live polymer chains to be removed turns out to be a fractional number, the number to be removed is the nonfractional part + 1 or 0 (depending on generation of a random number and comparing with the fractional part of the number). The live chains are selected randomly from the index arrays, and these molecules are removed and their corresponding masses are added to calculate the total mass which is removed. The mass of this mixture is then subtracted from the total mass which has to be removed from the reactor to calculate the mass of dead chains to be removed. Next, dead chains (including macromonomeric species) are randomly selected until the required mass is removed from the reactor. Once the flow out step is completed, the numbers of monomer molecules, hydrogens, and catalyst sites are updated to account for the inflow of the mass, and reaction simulation is continued for the next 0.2 s. This process is repeated for about 20 times the residence time of the reactor (as illustrated in the schematic flowchart in Figure 3) which ensures formation of an ensemble of molecules needed to represent the steady-state product formed in the process. This ensemble of chain molecules represents the outflow product of the copolymerization process and is used to calculate various distributions and average properties describing the molecular details of the product. These ensembles are also subsequently used to build a representative ensemble of selected molecules which is used to calculate rheology of the products. The transient values of many key parameters such as monomer conversions (as discussed in section S3 of the Supporting Information), average molecular weight, higher moments, and polydispersity index of the polymer chains formed are also monitored during the simulation to ensure convergence.

The process conditions such as the inflow rate of all the reacting species (different monomers (ethylene, octene), hydrogen, and catalyst), the volume of the reactor, the approximate residence time (based on volume flow rate), temperature (same as output temperature), and pressure are inputs to the model. The detailed molecular ensembles with the structural details as discussed above for each dead and live chain are written in different files every 1 × 10⁹ Monte Carlo steps after convergence of the simulation. These files can then be used to extract a representative ensemble of molecules for the tube theory based calculations for rheology and can also be used for determining various multivariate distributions such as molecular weight–comonomer composition (short chain branching) distribution (SCBD), molecular weight–long chain branching distribution (LCBD), and longest ethylene sequence (LES) distribution. Average properties such as total comonomer content are also calculated from these files as needed (e.g., for estimating tube theory parameters). These tube parameters are then used to calculate the rheological properties of the representative ensemble of molecules as discussed in detail in the Results and Discussion section.

We construct the representative ensemble of molecules from the structural files written for the molecular architecture by binning the bivariate molecular weight long chain branching distribution (MW-LCBD) and selecting a few polymer molecules from the files for each such bin with the appropriate weight. These ensembles are then used for rheology calculations with the tube parameters calculated using the comonomer composition as described in the Results and Discussion section.

We focus on the calculation of linear viscoelastic properties from molecular structure. For polymer melts, a foundational concept for a physics-based structure–property connection has been the tube concept. A long polymer test chain in an entangled system is envisioned as being surrounded by a tube formed by the surrounding polymer chains (Figure 4a). The tube constrains the motion of the test chain. The main stress relaxation mechanism of the test chain is snake-like back and forth diffusive motion along the tube contour, called reptation (Figure 4b), which leads to a power-law relation between linear chain molecular weight and longest relaxation time. Later refinements of these mesoscopic models for linear chains have included mathematical representations of physical phenomena related to additional dynamics, such as contour length fluctuations (related to the flexibility of the chain) and constraint release (related to the motion of the chains forming the constraining tube).

The polymer ensembles resulting from the kinetics described here are mixtures of linear and long-chain branched chains. A certain fraction of the branched molecules of each ensemble can architecturally be described as three-arm stars, whereas a smaller but often significant fraction has a more complex topology, which in general terms can be termed “branch-on-branch”. Long-chain branching changes the physical picture. Reptation cannot occur, which is most easily explained when considering a star system. When long enough, each arm of a star test chain is entangled and thus in a tube. The branch point severely restricts the relaxing motion of the chain. Relaxation dominantly occurs by retraction of each arm toward the branch point (Figure 4c), which depends exponentially on arm molecular weight and thus can be long for metallocene-type systems of high molecular weight. Combined treatment of this test chain retraction mechanism with additional dynamics resulting from the simultaneous motion of the entire set of molecules is described by Ball and McLeish. The concept of dynamic dilution was introduced to account for solvent-like effects of fast relaxing segments. It has become a central element in subsequent modeling of generalized branched systems.

Any topologically more complex molecule can be envisioned to basically relax stress by a combination of arm retraction and reptation. An example is shown in Figure 4d, where first the segments with a free end will relax by arm retraction (contour...
length fluctuation) and where inner segments relax only at time scales where the outer segments are likely to have relaxed completely. The outer segments create additional friction at long times but are no longer entangled. This hierarchical relaxation ends with reptation-like (branch point hopping) of the deepest remaining effective linear segment. Larson et al.\textsuperscript{48,49} have combined these various mechanisms into a framework (hierarchical algorithm) that enables calculation of linear viscoelastic properties for mixtures of linear and branched molecules.

A parallel development is the “BoB (branch-on-branch)” algorithm of Das et al.\textsuperscript{41} There are some differences\textsuperscript{50} between these two models in terms of numerical methodology used for solving the relaxation equations and related to the detailed physics of branched polymer relaxation. Another important difference is in the data structure used for storing and calculating rheology in both these softwares, which does not easily allow branch-on-branch geometries (such as Cayley trees) to be modeled in the hierarchical algorithm. Hence, for modeling industrial polymers with no limiting assumptions in their architectural detail we used the “BoB” model for our calculations. The kinetic simulations results will show that the simulated polymers here indeed contain branch-on-branch calculations. The kinetic simulations results will show that the simulated polymers here indeed contain branch-on-branch calculations. The kinetic simulations results will show that the simulated polymers here indeed contain branch-on-branch calculations. The kinetic simulations results will show that the simulated polymers here indeed contain branch-on-branch calculations.

We also model the crystallization elution fractionation (CEF) profile for all the three resins using the longest ethylene sequence values and compare them against experimentally measured distributions. We first calculate the weight fraction and number-average molecular weight values corresponding to different longest ethylene sequence lengths. We then use these distributions to build a control volume based mathematical model using the methodology proposed by Chokputtanawutti et al. to model the fractionation process and use optimization methods as described in Chokputtanawutti et al.\textsuperscript{51} to determine the kinetic and Gibbs–Thomson parameters for the different polyolefins.

**EXPERIMENTAL METHODS**

**Chromatography for Molecular Weight Distribution.** The polymer molecular weight distribution is characterized by high-temperature triple detector gel permeation chromatography (3D-HTGPC). The chromatographic system consists of a “PolymerChar HT-GPC-IR” high-temperature chromatograph, equipped with a “Precision Detectors” (Amherst, MA) 2-angle light scattering detector, Model 2040, and a 4-capillary differential viscometer detector, from PolymerChar. The 15° angle of the light scattering detector is used for the experiments. Concentration is measured by using the PolymerChar IR4 infrared detector in the PolymerChar HT-GPC-IR. The system is equipped with a (HPLC) pump and online solvent degassing device from PolymerChar/Agilent. The solvent used is 1,2,4-trichlorobenzene. The samples are prepared at a concentration of 1.5 g/L of polymer in ~8 mL of solvent. The solvent used to prepare the samples contains 200 ppm of butylated hydroxytoluene (BHT). The samples are dissolved for 60 min in a carousel compartment operated at 160 °C, and then 200 μL is injected into the columns. The flow rate is 1.0 mL/min. The column set consists of four Agilent PLgel Mixed-A, 20 μm particle columns: length/i.d.: 300 mm × 7.5 mm. Columns are operated at 145 °C.

Calibration of the GPC column set is performed with narrow molecular weight distribution polystyrene standards (Easical GPC/SEC Calibration Standards) purchased from Agilent. The calibration of the detectors is performed in a manner traceable to NBS 1475 using an in-house linear polyethylene homopolymer. The viscometer detector is calibrated based on a molecular weight of 96000 Da. Data reduction and sample calculations are done with GPC-One software obtained from PolymerChar and integrated macros made by Dow.

**Rheology.** Rheological properties (complex viscosity, loss, and storage modulus) are measured via a frequency sweep from 0.1 to 316 rad/s (5 points per decade) at 10% strain, which is well within the linear viscoelastic region of the materials. The measurements are performed at 190 °C in a nitrogen environment to avoid oxidative degradation. An ARES-2 rheometer from TA Instruments equipped with 25 mm diameter parallel plates is used. The gap between the plates is set at ~1.8 mm. Temperature is controlled with a convection oven. The samples are prepared by compression-molding polymer pellets into 2 mm thick plaques and punching out a 25 mm diameter puck. After placing the puck onto the bottom plate of the rheometer,

The crystallization and dissolution kinetics were simulated using Avrami’s equation of the form

\[
X_s(\text{LES}, T_e) = \begin{cases} 
0, & T_e \leq T_0(\text{LES}) \\
1 - \exp \left( -k_e \frac{T_e - T_0(\text{LES})}{HR} \right)^n, & T_e > T_0(\text{LES})
\end{cases}
\]

(30)

where \(X_s\) is the dissolved fraction of polymer with LES segments at elution temperature \(T_e\) and \(k_e\) and \(n_e\) are the kinetic rate constants and Avrami’s exponent, respectively. \(T_0(\text{LES})\) is the equilibrium crystallization temperature of polymer chain with LES segment. \(T_e\) is determined using the modified Gibbs–Thomson equation with eq 31.

\[
T_e(\text{LES}) = A_e - \frac{B_e}{\text{LES}}
\]

(31)

We used the experimental conditions of the CEF experiments described by Hermel-Davidock et al.\textsuperscript{53} to model the fractionation process and use optimization methods as described in Chokputtanawutti et al.\textsuperscript{51} to determine the kinetic and Gibbs–Thomson parameters for the different polyolefins.
the sample is allowed to reach thermal equilibrium. The gap is then closed, and excess sample is removed with a trimming tool. 

**Crystallization Elution Fractionation.** The experiments are conducted using the commercial CEF instrument (Polymer Char, Valencia, Spain) with an IR5 detector (Polymer Char, Valencia, Spain). o-Dichlorobenzene with 600 ppm antioxidant butylated hydroxytoluene is used as solvent with the sample prepared at 160 °C for 2 h under shaking at 4 mg/mL. The injection volume in the column is 300 μL, the sample undergoes crystallization cycle conducted at a cooling rate of 3 °C/min from 110 to 30 °C. The sample is then equilibrated at a temperature of 30 °C for 5 min followed by the elution cycle from 3 to 140 °C. The cooling rate used in elution cycle is 3 °C/min. The solvent flow rate during crystallization cycle is 0.052 mL/min while during elution cycle is maintained at 0.05 mL/min. Data points are collected at the rate of one point per second. Further details about column packing and calibration are discussed in Hermel-Davidock et al.53

**RESULTS AND DISCUSSION**

We first benchmark the kinetic Monte Carlo model by simulating ethylene—octene copolymerization for two semi-batch pilot plant runs. The simulated pilot plant runs were performed in a pressurized reactor vessel with ethylene flowing in to maintain a constant pressure in the reactor. A reacting mass of 114 g of ethylene, 217 g of octene, and 310 mL of hydrogen along with 26 μg of catalyst is preloaded at an initial temperature of 130 °C for run 1. Similarly, for run 2, 113 g of ethylene, 214 g of octene, and 286 mL of hydrogen are preloaded with 30 μg of catalyst in the reactor. The temperature and flow rate of ethylene into the reactor are monitored as the two runs progress for the total runtime of 292 and 288 s for runs 1 and 2, respectively. The plots in Figure 5 (top frame) depict the variation of temperature and ethylene flow rate for the two runs. For simulating these pilot plant runs with our kinetic Monte Carlo model a finite elemental volume representing the reactor volume which contains 500 active catalyst sites is constructed. The scaled number of molecules for all reacting species is calculated based on scaling factor for the catalyst sites and the initial feed values for all the species. The data structures maintaining the live and dead chain information and the index arrays storing indices of different chain types for accelerating simulation of different reactions are initialized and maintained. The reaction process along with inflow of ethylene molecules is simulated at the transient temperature values for the total runtime corresponding to the experimental run. The detailed information for live and dead chains are periodically written as data files, and the conversion of reacting species, average molecular weight, and branching frequency of chains formed are also recorded. Figure 5 (bottom frames) show the transient average molecular weight...
distribution process. The close matching of average molecular weight simulated (dotted blue curve) and shows close agreement with the and run 2 (right). The total molecular weight distribution for the three industrial grade polyolefins these pilot plant runs, we perform these calculations only for rheological characterization done for the product formed from theory models. However, since there was no experimental data for calculating the rheology of these virtual products using tubeular weight distributions can be used for selecting molecules branches separately and are plotted in Figure 6 for run 1 (left) and run 2 (right). The molecular weight distribution profile measured experimentally is also included in Figure 6 (dotted blue curve) and shows close agreement with the simulated profiles. The branch number-deconvoluted molecular weight distributions can be used for selecting molecules for calculating the rheology of these virtual products using tube theory models. However, since there was no experimental rheological characterization done for the product formed from these pilot plant runs, we perform these calculations only for the three industrial grade polyolefins produced in continuous process. The close matching of average molecular weight distribution profiles generated via the kinetic model with experimental data for these two unsteady state semibatch runs with minute differences in their feed and process conditions lend credibility to our kinetic Monte Carlo scheme. Hence, we extend our model to simulate continuous copolymerization process and demonstrate the predictability of the integrated kinetic Monte Carlo tube theory approach for predicting rheological properties of three industrial polyolefins.

For simulating the continuous process for the three industrial resins we follow a similar methodology as for the semibatch kinetic Monte Carlo model. A differential elemental volume of reaction mass is constructed with about 100 catalyst sites in the initial reacting feed (which results in about a couple of million polymer chains in the differential element on equilibration). The number of reacting molecules and the size of reaction control volume are determined by using a scaling factor based on the catalyst sites used (100) versus number of catalyst sites in the full scale reactor (calculated based on catalyst flow rate and residence time). Similarly, the flow rates for the reacting species (monomers and hydrogen) and catalyst site are also adjusted with respect to the reaction mass used in the kinetic model (using the same scaling factor). The experimental reactor feed flow rates (scaled to obtain a polymer production rate of 10 kg/h) of ethylene, octene, hydrogen, and catalyst sites, and the reactor residence times used in our models are listed in Table 1. We have scaled the flow rates and have limited the reaction conditions in this study to the minimum required to perform relevant simulations. The kinetic rates (at the desired reaction temperature) along with these scaled experimental data for the two runs match quite well with the measured values obtained by carrying out GPC measurement for products from the two runs. The polydispersity profiles show significant increase in the first 100 s of the reaction and flatten out toward the end of the reaction. This is due to steady increase in branching frequency as the number of available macromonomer molecules keeps increasing in the batch reactor, which is countered by rate of thermal termination and chain transfer to monomer of macromonomer terminated live chains, leading to a flattening of the polydispersity curves toward end point of the reaction runs.

The molecular weight distribution profiles are calculated using the product molecule information stored at end of the kinetic Monte Carlo runs for all the reacting species (monomers and hydrogen) and catalyst sites in the full scale reactor (calculated from the scaled to obtain a polymer production rate of 10 kg/h) of ethylene, octene, and catalyst sites, and the reactor residence times used in our models are listed in Table 1. We have scaled the flow rates and have limited the reaction conditions in this study to the minimum required to perform relevant simulations. The kinetic rates (at the desired reaction temperature) along with these scaled flow rates are sufficient to reproduce the results of this study. The model is run for varying catalyst flow rates and the conversion for ethylene,

![Graph showing molecular weight distribution and long-chain branching distribution](image)

Figure 6. Total molecular weight distribution (blue solid curve) and the long-chain branching distribution in terms of deconvoluted molecular weight distributions for different number of long-chain branches for virtual products from simulated pilot plant run 1 (left) and run 2 (right). The experimentally measured molecular weight distributions are included (as dotted blue curves) in both plots.

| Table 1. Scaled Process Data in Terms of Reactant Flow Rates and Reactor Conditions for PEO1, PEO2, and PEO3 |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| feed | units | reactor feed | reactor exit | reactor feed | reactor exit | reactor feed | reactor exit |
| ethylene | kg/h | 8.9 | 0.89 | 9.5 | 0.95 | 9.6 | 1.4 |
| octene | kg/h | 3.3 | 1.3 | 2.3 | 0.88 | 3.5 | 1.7 |
| polymer | kg/h | 0 | 10 | 0 | 10 | 0 | 10 |
| hydrogen | mmol/h | 840 | 580 | 440 | 310 | 620 | 480 |
| catalyst flow rate | mg/h | 1 | assuming catalyst efficiency of 1 ton PE/g | 1 | assuming catalyst efficiency of 1 ton PE/g | 1 | assuming catalyst efficiency of 1 ton PE/g |
| residence time | min | 6.7 | | 6.1 | | 6.9 | |

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octene, and hydrogen feeds are monitored as a function of reaction time (detailed in section S3 of the Supporting Information). The conversion of various reacting species is defined in terms of amount consumed in the polymerization with respect to the inflow (conversion = (flow in – flow out)/flow in). The optimal catalyst flow rate which matches the conversion (and production rates) observed experimentally is then determined for each polyolefin, and the corresponding runs are used for all further analysis.

The kinetic Monte Carlo simulations were run for 20 times the residence time of the process at the optimal catalyst flow rate to ensure the reactor reaches a steady operation state. These simulations can be used to generate full ensembles of molecules, which can be used to calculate the average properties and distributions. The results can be compared with results from other models or product data. In Figure 7 we plot the transient weight-average molecular weight $M_w$ and polydispersity index $(M_w/M_n)$ for all three polyolefin runs.

We observe that weight-averaged molecular weight curves (Figure 7, top frame) start at higher values due to excess monomers in the control volume at beginning of the run (leading to formation of longer molecules) which then decays to the equilibrated values in about 6 residence times. The equilibrated values match closely with the measured values for the respective products (as marked with dotted lines in the plot). The polydispersity curves start at a value of around 2.0 for all three resins (consistent with the polydispersity index expected for unbranched polymer chains) and keep increasing until there are excess monomers in the reactor. Once the desired conversion is reached the polydispersity values start dropping (Figure 7 bottom right frame) and stabilize at the intrinsic value corresponding to the feed ratios and reaction conditions. The measured values for polydispersity indices are marked with a dotted line in the plots, which show reasonable agreement with the equilibrated simulation values. To ensure that converged kinetic Monte Carlo runs correspond to the equilibrated polymer product distribution with molecules representing the tail of the molecular weight curve formed in the correct weight fraction, we check the transient behavior of various moments of molecular weight ($M_n$, $M_w$, $M_z$, and the fourth moment $M_{z+1}$). From the plot in top right frame of Figure 7, we can clearly conclude that all moments of the molecular weight have converged to their respective values after about 6 residence times of run time. The moments also match closely with their respective measured values for the corresponding polyolefin product.

We also calculated the average comonomer content and the LCBf (number of long-chain branches per 10000 C atoms in the polyolefin).
the chain) from the ensemble of molecules produced at steady state. The LCBf were estimated as 0.74, 0.59, and 0.26 per 10000 C for PEO1, PEO2, and PEO3, respectively. These values are consistent with experimentally (SEC-LALLS) derived frequencies for similar polymers by Doerpinghaus and Baird. The comonomer (octene) content in mole fraction is calculated to be 0.061, 0.040, and 0.051 for PEO1, PEO2, and PEO3, respectively. This complete simulation of 20 residence times on a single core machine (Intel Xeon 2.1 GHz processor) takes about 12.5, 3.3, and 13.6 h for PEO1, PEO2,
and PEO3, respectively. However, as observed in Figure 7 all runs equilibrate in about 4–5 residence times; hence, the equilibration can be achieved in about 40–200 min of CPU runtime. To further test the computational performance of our simulation code by varying some of the simulation parameters, we conducted runs with different control volume sizes and different total reaction times. The comparison of performance of our simulation method over different control volume sizes is illustrated in Figure 8, while the variation of compute time with simulated reaction time is discussed in section S4 of the Supporting Information. The control volume in our simulations is set by number of active catalyst sites in the reacting mass at beginning of the run with which all other reacting species and reactor volume are scaled. In our comparative study we vary the number of active sites from 25 to 250 and plot the transient weight-averaged molecular weight profile for PEO2 simulations along with computational run time over a single processor in the inset plot of Figure 8. We observe that while change of control volume size does not change the equilibrated average molecular weight value, there are substantial fluctuations in the simulations run with control volumes with 25 and 50 catalyst sites. The computational run time has a power law dependence with an exponent of 1.75 with the number of catalyst sites (representing the control volume size). Hence, we use a control volume containing 100 catalyst sites in all our simulations as this ensures that the fluctuations in average properties are within acceptable limits, tracking a population of million polymer chains, with reasonable compute resource requirements. In section S4 we show that the compute time scales linearly with simulated reaction time expressed in terms of number of residence time over which the reaction is simulated. We can also reduce the computational run time requirement of our methodology by running our simulations over lower simulated reaction time of around 8–10 residence times as equilibration is typically achieved in 4–5 residence times.

In Figure 9, we plot the LCBD (long-chain branching distribution) of the ensemble in the form of deconvoluted curves of the molecular weight distribution (MWD) each of which include statistics from the molecules with that specific number of long-chain branches on them (collecting statistics from 10 time instants with about a couple of million molecules at each time instant). As can be observed in the curves for all the samples, the majority of the low molecular weight distribution is composed of nonbranched molecules depicted as the green curve. The curves with higher number of branches are positioned at higher molecular weight values and also comprise a lower fraction of the full ensemble. These curves give highly useful information about the product architecture and can be very effectively used to estimate product properties such as to calculate the rheology of these resins. The total molecular weight distribution for all the polymer chains are also plotted (as solid blue curves) for the three polyolefins. We also plot the total MWD curve obtained experimentally from GPC-LALLS for each of these polyolefins (dotted blue curves). We see reasonable match with overall shape and end-points of the curves for all three resins. Another important observation we obtain from the plot showing weight-normalized deconvoluted molecular weight distribution curves for different long chain branches (Figure 8, bottom right) is regarding the polydispersity level of molecules with increasing number of branches. It is clearly evident that the curves with higher number of branches become narrower, indicating their polydispersity level decreases which is consistent with the theoretical result obtained from the method of moments

\[ \text{pd}_i = \frac{1}{1 + 2 \text{pd}_i} \]

where pdi is the polydispersity index of population with branch number i and pdi = 2.0. We also observe that the fluctuations in the curve keep increasing as we move to higher branch number which is due to a lower number of higher branched molecules available in the distribution (we stop at six branched distributions to keep the plots visible). We show all the curves in the un-normalized figures (Figure 8, top and bottom left frames) just to indicate that we include these higher branched molecules even though with a very small weight and less sampling in the rheology input files as even a small fraction of these high molecular weight highly branched chains can impact rheological behavior significantly.

The molecular ensembles generated using the kinetic Monte Carlo model have a huge number of molecules ranging from 500K to 1 million. Rheology simulations based on tube theory for this huge number of molecules are computationally infeasible. Hence, a targeted ensemble is constructed based on the deconvoluted long chain branching–molecular weight distributions. This is done by binning the deconvoluted distributions and representing each bin by a linear molecule or by stochastically selecting a set of five molecules from each bin for branched molecules with appropriate molecular weight and weight fractions. These selected ensembles are then converted into the input format for the “BoB” software using the hierarchical branching information. The tube parameters Me and τe for the rheological ensembles are estimated using empirical correlations eqs 32–34 as detailed in Chen et al.

Following the approach in ref 55, we used PEO1 as the reference sample and obtained the reference equilibration time τe,PEO1 at 190 °C by fitting the rheology curve generated using “BoB” model with the measured rheological data along the frequency axis. We then used the reference equilibration time τe,PEO1 in eq 34 to determine the equilibration times τe at 190 °C for all other polyolefins based on their molecular weight per backbone bond mb. The comonomer content on molar basis nb is calculated from the full molecular ensemble; the density of these polymer melts at 190 °C is typically 762 kg/m3, and the measured rheology temperature of 190 °C is used in eqs 32–34 to obtain the tube parameters for all three polyolefins.

\[ m_b = n_c M_{\text{emono}} + 28(1 - n_c) / 2 \]

\[ M_e = 4 \frac{\rho RT}{S G_n} = 4 \rho RT m_b^{3.49} \]

\[ \tau_e \approx 5.24 \times 10^{-9} \left( \frac{m_b}{16.609} \right)^{16.054} \]

These parameters (Table 2) are set as input in the tube theory calculation as monomer mass Me in g/mol (which is twice of molecular weight per backbone bond mb, calculated using eq 32), the number of monomers in one entangled segment Nc (=}

<table>
<thead>
<tr>
<th>polymer</th>
<th>nb</th>
<th>mb (g/mol)</th>
<th>Me (g/mol)</th>
<th>τe (s)</th>
<th>Nc</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO1</td>
<td>0.061</td>
<td>16.6</td>
<td>1720</td>
<td>5.24 × 10^{-4}</td>
<td>51.7</td>
</tr>
<tr>
<td>PEO2</td>
<td>0.040</td>
<td>15.7</td>
<td>1410</td>
<td>2.11 × 10^{-4}</td>
<td>44.9</td>
</tr>
<tr>
<td>PEO3</td>
<td>0.050</td>
<td>16.1</td>
<td>1550</td>
<td>3.31 × 10^{-4}</td>
<td>48.1</td>
</tr>
</tbody>
</table>
Figure 10. Measured (symbols) and simulated (lines) linear rheology at 190 °C; complex viscosity magnitude $\eta^*$ (left frames) and storage $G'$ and loss moduli $G''$ (right frames for PEO1 (top), PEO2 (middle), and PEO3 (bottom)).

Figure 11. Bivariate short chain branching—molecular weight distribution (left) for PEO3 product and longest ethylene sequence (LES) distributions for all three polyolefins (right).
$M_e/M_w$ where $M_e$ is calculated using eq 33), and the equilibration time $\tau_e$ (calculated using eq 34) of an entanglement strand.

The predictions obtained through this integrated approach are compared with experimental linear rheology values in Figure 10. Key rheological characteristics are matched well. An example is the magnitude of complex viscosity $\eta^*$ and its curvature, related to shear thinning. Also, the frequency-dependent storage and loss modulus profiles are predicted well. Some shifts can be explained from a slight mismatch of predicted and measured $M_w$. The close match highlights the predictive capability of our proposed scheme as we can predict key features of the rheological behavior starting with the industrial process conditions.

Similarly, we can also use the full molecular ensemble to extract other property-determining architectural distributions such as the bivariate short chain branching–molecular weight distribution and the longest ethylene sequence curves (Figure 11). These bivariate distributions can then be used to determine crystallization behavior and other mechanical properties of polyolefins based on theoretical calculations or experimental correlations.7,12,30 The comonomer composition distribution is typically obtained indirectly by measuring either the temperature rising elution fraction (TREF), crystallization fractionation (CRYSTAF), or crystallization elution fractionation (CEF) technique. As described in the Methodology section (eqs 28–31), we calculate the CEF profiles for all the three polyolefins using a finite volume model by combining models for CEF by Chokputtanawuttilerd et al.51 and TREF by Siriwongsard et al.52 In Figure 12 we plot the crystallization elution fractionation curves as well as the weight-averaged molecular weight of the fraction eluted at corresponding elution temperature for all the three resins.

We see significant agreement between the CEF profiles for all the three products. The curve is shifted to lower elution temperatures for higher comonomer content; hence, the PEO1 curve peaks at lowest elution temperature followed by PEO3 and PEO2. The weight-averaged molecular weight profile show close agreement for PEO1 and PEO2. For PEO3 the calculated values are lower than the measured value for 40–60 °C; however, the curves match around the peak in the CEF profile. We also observe that the molecular weight profile in our simulations monotonically increases toward the end of elution cycle unlike the experimental profile which shows a peak. This difference could be attributed to the fact that elution temperature in our CEF simulation is a function of longest ethylene sequence length (which would monotonically increase with eluting volume average molecular weight). The mismatch with experiments could be caused by complex cocrystallization phenomenon or an experimental artifact not captured by the Avrami’s crystallization and elution kinetics model.

**CONCLUSIONS AND RECOMMENDATIONS**

We developed an integrated approach for simulating solution copolymerization with single-site catalysts and predicting the rheological and crystallization behavior of the resulting polymers. The kinetic model can be used to model any reactor configuration and has been used in this study to model dynamic ensemble of molecules in semibatch configuration (for simulating two pilot plant runs) and simulate continuous stirred tank reactor as an idealization of the continuous production process for modeling three industrial polyolefins.

Figure 12. Crystallization elution fractionation curves obtained using finite volume model and longest ethylene sequence distribution of virtual product (solid blue curves) against the experimentally measured curves (dotted blue curves) obtained using PolyChar apparatus53 for PEO1 (top), PEO2 (middle), and PEO3 (bottom). Respective weight-averaged molecular weight of the eluted product at different elution temperature calculated from simulations (solid red curves) and measurements (dotted red curves) are also included.

An efficient hierarchical data structure to store and update the architectural and chemical details of the polymer chains for simulating different reactions with the kinetic Monte Carlo scheme is implemented. The molecular weight distributions, average properties such as long chain branching frequency, and comonomer contents compare well with experimentally measured values. The architecturally detailed molecular ensembles are used to compute linear rheology of these polymers which require no fitting parameters once the reference tube parameter in eq 34 is fixed, and the simulated rheological curves match very well with the experimental measurements (Figure 10). The microstructure of the
polyolefin molecules produced is quantified using the bivariate short chain–molecular weight distributions and longest ethylene sequence distributions. The crystallization elution behavior of these simulated polyolefins is then simulated using a control-volume based approach and shows close agreement with the experimentally measured profiles (Figure 12). The modeling approach is also quite useful in furthering our understanding of how different reactor configurations such as continuous flow reactor versus semibatch reactor would impact the polymer growth dynamics. This could potentially be useful in remediating reactor start-up problems typically encountered in industry. Differences evident in the transient behavior of weight-average molecular weight and polydispersity index for the semibatch reactor (Figure 5) and continuous reactor (Figure 7) are useful in this regard. Most notably, the model successfully predicted rheology of these polymers starting right from their process conditions (with no fitting parameters) which lends the approach to be quite useful in inverse design of new polymer products.

The first-principles implementation of all the reactions in the copolymerization process makes it readily expandable for additional kinetic reactions such as addition of nonconjugated dienes for increasing the branching frequency or to change the specificity of the reactions such as to include regio-/stereoselectivity using post-metallocene catalyst technology. Another possible expansion of the model would be to study formation of block copolymer olefins by introducing reactions with chain-shuttling kinetic mechanisms in the model as they have unique properties due to their blocky structure which need to be fully represented by topologically detailed models for any predictive property determination. Another important work element for predictive kinetic modeling is existence of trustworthy reaction kinetics data which need to be generated for new catalyst families by rigorous experimentation along with microkinetic modeling analysis or by using rigorous ab initio modeling. In this study, we were able to develop an integrated rheology prediction methodology which uses the advanced tube theory calculations for polymer melts. The integration of the results from the topology detailed kinetic Monte Carlo simulations with additional property-determining tools would result in a very effective strategy for process/product design in the polymer industry. This strategy once benchmarked for a certain catalyst system may result in significant reduction of mini-plant/characterization lab time and in accelerated new product design and development.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b02000.

Additional information for tube theory calculations, bookkeeping data structures, and other methodology details (PDF)

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**Notes**

The authors declare no competing financial interest.

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