Molecular dynamics study of the conformation and dynamics of precisely branched polyethylene

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ABSTRACT

The conformation and dynamics of precisely branched polyethylene, i.e., polyethylene molecules containing regularly spaced, short chain branches along its linear backbone, were studied using molecular dynamics simulation. Models with branch content varying from 0 to 47.6 branches per 1000 backbone carbons were studied over a temperature range of 273—550 K and under a constant pressure of 1 bar. Two types of models were built, one of which contained ethyl branches while the other contained hexyl branches. The results indicated that at a given temperature, the global orientation order parameter decreased almost linearly with increasing branch content up to a value of approximately 38.5 and increased considerably and unexpectedly at a branch content of 47.6. The order parameter was insensitive to the branch length except at high branch contents. The computed packing lengths and activation energy for diffusion are consistent with the above observations.

1. Introduction

Polyethylene, a commodity thermoplastic, is used in a variety of consumer products and its global demand is expected to exceed 200 billion pounds by 2017 [1]. Polyethylene can attain a wide range of physical properties suitable for an assortment of applications, as a result of its potential for differing branch characteristics. In effect, polyethylene is one of the few commercial polymers deliberately produced with differing branch configurations, including number of branches (i.e., branch content), branch length (short versus long branches) as well as intra- and intermolecular branch distributions. All of which can significantly influence the processing and performance characteristics of polyethylene. For example, linear low-density polyethylene (LLDPE) synthesized using single site catalyst will exhibit significantly different dart impact and tear resistance than that synthesized using a Ziegler—Natta (ZN) catalyst, even though these two materials may contain the equivalent number and type of short branches [2]. This results from their differing intra- and intermolecular branch distributions. For instance, the single site catalyst incorporates the co-monomer (i.e., branches) at the same frequency regardless of chain length whilst the ZN catalyst incorporates co-monomers

heterogeneously (higher frequency in shorter chains and lower frequency in longer chains) [3].

Most recently, Wagener et al. used acyclic diene metathesis (ADMET), a step growth polymerization technique, to synthesize polyethylene with regularly spaced, short chain branches along its linear backbone, which they termed a precision polyethylene [4,5]. In comparison, the use of a single site or ZN catalyst produces LLDPE molecules with short chain branches distributed randomly along the backbone. Unfortunately, only small quantities of this precision polyethylene have been prepared, making the study of its mechanical properties (e.g., dart impact) unfeasible. However, according to the limited experimental data available from Wagener et al., it can be determined that at lower branch content (e.g., < ~26 branches per 1000 backbone carbon atoms) the melting temperatures of these materials are insensitive to the short chain branch length (short branches with 2 or more carbons). Interestingly, this is not factual for LLDPE with randomly spaced branches. In fact, it is known that ZN LLDPE with ethyl branches (butene co-monomer) exhibits higher melting temperatures than that with hexyl branches (octene co-monomer) at the same branch frequency if other resin variables are the same. The corresponding mechanical properties differ as well. The melting temperatures observed by Wagener et al. suggest that precisely branched LLDPE with low branch content, but differing branch lengths, may exhibit comparable mechanical properties. Additionally, for materials with high branch content (e.g. one branch on every 20 backbone carbon

atoms), the melting temperature of butene-based precision polyethylene (24 °C) is about 12 °C higher than that found for octene-based material (12 °C) [5]. Such melting temperature difference differs from that observed in the butene- and octene-based ZN LLDPEs. The reasoning behind the ZN observation is because some of the ethyl branches are being incorporated into the crystal lattice and hence the ability to disrupt the crystallization is lower than that of the hexyl branches that lead to observed difference in the melting temperatures.

The aforementioned branch length effect suggests that there exists a critical branch content where branch length begins to play a significant role in determining polymer conformation. It is the main interest of the present work to identify such a critical value. Molecular dynamics simulations were used to study effects of branch content and branch length on the conformation and dynamics of a series of model polyethylenes with regularly spaced short chain branches.

2. Molecular models and simulation

Molecular dynamics (MD) simulations were performed using GROMACS 4.6.3 [6–10], with the ffG53a5 force field [11], on the precisely branched polyethylene models. An isobaric-isothermal (i.e., NPT) ensemble was used, and, the Nose-Hoover thermostat [12] with a time constant of 0.1 ps and Parrinello-Rahman barostat [13] with a time constant of 2.0 ps was utilized to control the temperature and pressure, respectively. Studies were performed at a pressure of 1 bar over a temperature range of 273–550 K. MD trajectories were generated for each simulation by integrating the Newtonian equations of motion using a leap-frog algorithm [14] with a time step of 1 fs and a simulation time of 100 ns. Unless stated otherwise, all reported static properties (e.g., radius of gyration) are averages of the last 10 ns of the respective trajectories, where the cut-off distance of the non-bonded interactions (dispersion forces only) were set at 1 nm.

Table 1 summarizes the precisely branched LLDPE models used in this work. The LLDPE models covered a branch content range of 0 (i.e., high density polyethylene (HDPE) homopolymer) to approximately 50 branches per 1000 backbone carbons. Whereas, commercial LLDPE produced by either a single site or ZN catalyst contains molecules with a branch content range of 10–25. The use of high branch content, in the precisely branched LLDPE models, will help determine whether a critical branch content exists, where branch length begins to play a role in determining the properties of the polymer, as well as to investigate differences between the melting behavior of butene-based and octene-based precision polyethylene, observed in the work of Wagener et al. [4,5] As indicated in Table 1, nine models were used where each model

Table 1
Characteristics of the precisely branched LLDPE models. Each model contains 5 chains with equal chain length. B and O shown in the model nomenclatures signify the model as a butene-based or octene-based.

Precision LLDPE model	Branch content, number of branches per 1000 carbons	Number of carbons of the precision ethylene sequence	Molecular weight, g/mol
HDPE	0	n/a	4594
1-B	12.2	81	4706
1-O	12.2	81	4936
2-B	25.6	38	4594
2-O	25.6	38	5042
3-B	38.5	25	4716
3-O	38.5	25	5388
4-B	47.6	20	3544
4-O	47.6	20	4160

contained five chains of equal length subjected to three-dimensional periodic conditions, in which the corresponding initial structures were built using the approach of Theodorou and Suter [15]. It is worth mentioning that use of cubic unit cells with five chains (i.e., edge length ~4 nm) correspond to the smallest unit cells that one can use practically with minimal interactions between the parent chains and their images (see Supplementary Material). Energy minimization, using the conjugate gradient method, was performed on the initial structures to remove high-energy overlaps before the high temperature MD simulations. After energy minimization, the final structure of a higher temperature MD simulation was used as the initial structure of a lower temperature MD simulation. The molecular weights were chosen such that the corresponding chain lengths were much higher than the entanglement molecular weight of linear polyethylene, which is approximately 1040 g/mol. [16]

To quantify the amount of order in the models, a global orientation order parameter (f) was calculated for each model, at each temperature, using the last 10 ns of the trajectory. Implicit hydrogen (united atoms) models were used in which each carbon atom and the associated hydrogen atoms were treated as a single interaction site.

$$f = \frac{3\cos^2\theta_{ij} - 1}{2} \tag{1}$$

Here, f ranges from 0 (no order, completely amorphous) to 1 (complete order), and θ_{ij} is the angle between the vector from the $(i-1)$th united atom to the $(i+1)$th united atom and the vector from the $(j-1)$th united atom to the $(j+1)$th united atom. The angular bracket in the above equation signifies the average over all i and j positions.

In addition to the order parameter, the packing lengths of the models were calculated. The packing length (l_p) is defined as follows [17]:

$$l_p = \frac{M}{N_a R_g^2 \rho} \tag{2}$$

where M is the number average molecular weight of the model polyethylene and N_a is Avogadro's number. R_g and ρ are the radius of gyration and density respectively, as computed from the MD simulation. The packing length signifies both the stiffness and thickness of a chain, and is dependent only on the chemical nature, not molecular weight, of the polymer molecule. Stiffness depends on the rotational barriers of the backbone bonds in a chain, where higher rotational barriers lead to increased chain stiffness. The chain thickness depends on the number and type of branches on the backbone. Greater numbers of and/or longer branches lead to thicker chains. Using these concepts, an isotactic polypropylene chain is thicker than a polyethylene chain. Packing length is commonly used in the polyolefin industry to correlate structures of polyolefins with their physical properties.

To determine the mobility of the molecules in each model, the self-diffusion coefficient (D) of the centers of mass of all chains was calculated using the well-known Einstein equation [18]:

$$D = \frac{(r(t) - r(0))^2}{6t} \tag{3}$$

where the numerator signifies the mean square displacement of the centers of mass of the chains in the model and t is the time over which the displacement takes place. Once the self-diffusion coefficients at elevated temperatures (348–550 K) are obtained, the