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Review

Effect of short-chain branching on the tie chains and dynamics of bimodal polyethylene: Molecular dynamics simulation

Yanling Hu, Yunqi Shao, Zhen Liu, Xuelian He*, Boping Liu

Shanghai Key Laboratory of Multiphase Material Chemical Engineering, East China University of Science and Technology, Meilong Road 130, Shanghai 200237, China

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A B S T R A C T

Molecular dynamics simulations were performed on bimodal polyethylene (BPE) in order to shed light on the molecular mechanism of short-chain branching on BPE nucleation process, crystallization process and especially the formation process of tie chains. The study contemplates two kinds of BPE model chains with the same branch content (BC), branch length (BL) but with different short-chain branching distribution (SCBD): short chain branches incorporated in either the long chain or the short chain. For the nucleation process, nucleation time of all models increased with the increase of BC. Short branches distributed on the long chain provoke a delay of the nucleation as compared to the case of short branches distributed on the short chain. Additionally the nucleation process is further delayed as the BL increases. Crystallization rate and crystallinity decrease as BC increases. The crystallinity of the BPE mode chains with branches placed on the long chain were lower than the case of branches placed on the short chain above a critical BC (5/1000C), and this critical BC was independent with BL. When branches distribute on the long chain, short chain is more likely to locate inside the long chain, while for the case of branches distribute on the short chain, the results are opposite. The concentration of tie chains increased with the increase of BC. For BPE model chains with branches placed on the long chains are more likely to form tie chains when compared with the case of branches placed on the short chain. The concentration of tie chains is insensitive to BL. A modified tie chains formation process mechanism is proposed to explain the SCBD effect on tie chains.

1. Introduction

Polyethylene (PE), a commercial thermoplastic, is widely used in a great number of different applications due to its semicrystalline nature. Over 80 million tons of polyethylene are produced every year in the world polymer market. Polyethylene properties are mainly affected by chain microstructure, including molecular weight distribution (MWD), branch content (BC), branch length (BL), as well as short-chain branching distribution (SCBD). Understanding and controlling these molecular architectures are of great importance to elucidate structure-property relationship and to develop high-performance polyethylene. For example, Bimodal Polyethylene (BPE), a typical high density polyethylene (HDPE) product, is very widely used in many high performance applications, such as high grade pipes and high-strength films, because of its outstanding slow crack growth (SCG) resistance, very good stiffness, and easy processability [1–3]. It is well-known that the excellent properties of BPE originate from the well-defined MWD and SCBD [4–7]. Molecular dynamics (MD) simulation is a powerful and advantageous tool to bring to light the chain microstructure effects at molecular level.

Polymer crystallization process can be described by a two-stage process of homogeneous nucleation and crystal growth. Many research efforts have been down in the second stage, crystal growth process, while research work about branch effects on nucleation process of PE is still in lack [8–17]. Lan et al. [18] proposed that primary nucleation process of PE in 1,2,4-trichlorobenzene solution may be characterized by three stages: stem-aggregation for embryo formation, extension of the embryonic bundle, and the “solidification” of the extended bundle. Hikosaka et al. [19] related primary nucleation rate of PE crystals under fixed supercooling to number-average molecular mass and inferred that the nucleation process is kinetically controlled by the axial diffusion of PE chains within the embryos. Anwar et al. observed that crystal nucleation in a PE (C500) melt is initiated by the alignment of the chain segments which participate in the formation of critical nucleus, similar to the mechanism reported for shorter polymer chains [20–22]. Rutledge et al. [23,24] calculated the nucleation rate of n-pentacontahectane (C150) and a linear polyethylene (C1000), and identified the critical nuclei by using a mean first-passage time analysis. In our

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* Corresponding author.
E-mail addresses: yunqi_shao@mail.ecust.edu.cn (Y. Shao), liuzhen@ecust.edu.cn (Z. Liu), hexl@ecust.edu.cn (X. He), boping@ecust.edu.cn (B. Liu).

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previous study, three crystallization states were observed in the crystallization processes of a single PE chain with chain length from C1000 to C10,000: (i) nucleation controlled state, (ii) competitive state of crystal growth process and new nuclei formation and (iii) crystal growth controlled state [25]. Recently, Sanmartín et al. [26] performed MD simulations of a series of ultralong n-alkanes to study the branch effect on the early stage of nucleation and crystal formation process. They discovered that the short branch provokes a delay of the nucleation as compared to the linear chain. Additionally, as the branch length increases, the nucleation process is further delayed. There isn’t any experimental and theoretic study about the branch effects on industrial BPE nucleation process, so that is one of the key issues to be addressed in this work.

Over the last decades, a great number of research works about the chain microstructure effect on PE crystallization have been reported. Mandelkern et al. [27–31] studied branch effects on copolymers crystallization including ethylene-butylene, ethylene-hexene and ethylene-octene copolymers, and found that the melting temperatures, crystallinity and lamellae thickness decreased with the increase of BC, but the BL effect was not obvious. Recently, Wagener et al. [32–40] used acyclic diene metathesis (ADMET) method to synthesize polyethylene with precisely controlled branch identity and frequency, which they termed a precision polyethylene. Melting temperatures and heat of fusion decreased with the increase of BC. And at lower BC (e.g., $< \sim 26$ branches per 1000 backbone carbon atoms) the melting temperatures of these precision polyethylenes are almost the same regardless of the BL (branches equal to or greater in mass than ethyl). However, for materials with high BC (e.g. 50 branches on every 1000 backbone carbon atoms), the melting temperature of ethyl branched precision polyethylene is much higher than that of butyl branched precision polyethylene. As the experiment studies of branch effect on polyethylene crystallization is limited to the macroscopic properties of materials, computer simulation has gradually come to front to show great capability of describing microstructure changes on molecular level. Zhang et al. [41,42] carried out MD simulations to study the effects of BC, BL, and branch distribution on the crystalline structure of the LLDPE of several single chain models. Branch acted as a nucleating seed in nucleation and a defect in the crystal growth process and branch with length above 10 cocrystallized with the main chain. Choi et al. [43,44] simulated the solid state structure of LLDPE and found that the interchain branch distribution and intrachain branch distribution play important role in determining the degree of crystallinity and tie molecule concentration of the materials. Recently, they discovered that BL begins to play a significant role in determining polymer conformation and the order parameter at a critical BC (47.6 branches per 1000 backbone carbons) [45]. In our previous work [46], the critical BC (20 branches per 1000 backbone carbons) to form lamellae crystal was identified. BL has no influence on the crystallization kinetics, but affects the final morphologies. Most of the works were observed to focus on the crystallization process of linear or branched PE, but researches of the branch effect on BPE crystallization behavior is few especially the simulation study as the molecular weight (MW) of PE was always lower than 5000 CH_2. By selectively blending homopolymers (linear PE) with copolymers, Krishnaswamy et al. [47] explored the effects of the placement of short-chain branches (SCB) on crystallization kinetics, morphology and mechanical properties of high-density polyethylene (HDPE). For blends with nearly matched molecular weight distribution and average SCB content shows that preferential placement of SCB on the longer chains exhibits slower crystallization kinetics at high crystallization temperatures compared with the case of branches on the short chains. Blends with SCB on the longer chains have superior ultimate mechanical properties which may due to the enhancement of tie chain formation. They proposed a conceptual model to explain the effects of SCB distribution on crystallization kinetics, lamellar thickness and inferred formation of tie chains. However the conceptual model is just inference, it lacks explanation at molecular level. Moreover, a systematic study of the branch effect on BPE crystallization process and the formation process of tie chain are very essential, and that’s the main interest of the present work.

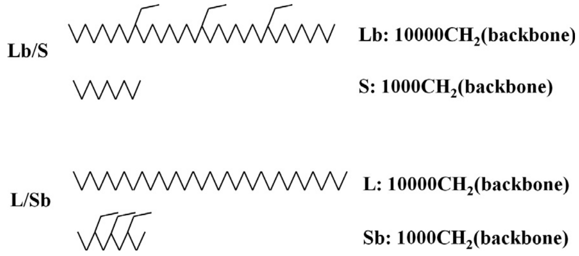

Fig. 1. Chain architectures.

Table 1
Model of branched BPE chain with different branch content and SCBD.[a]

BPE model	Branch	Branch content	Total
HDPE	None	0	11,000CH_2
Lb/S-E-1	Ethyl	1/1000C	11,018CH_2
L/Sb-E-1	Ethyl	1/1000C	11,018CH_2
Lb/S-E-2	Ethyl	2/1000C	11,038CH_2
L/Sb-E-2	Ethyl	2/1000C	11,038CH_2
Lb/S-E-3	Ethyl	3/1000C	11,018CH_2
L/Sb-E-3	Ethyl	3/1000C	11,078CH_2
Lb/S-E-4	Ethyl	4/1000C	11,078CH_2
L/Sb-E-4	Ethyl	4/1000C	11,118CH_2
Lb/S-E-5	Ethyl	5/1000C	11,098CH_2
L/Sb-E-5	Ethyl	5/1000C	11,098CH_2
Lb/S-E-6	Ethyl	6/1000C	11,078CH_2
L/Sb-E-6	Ethyl	6/1000C	11,078CH_2
Lb/S-E-7	Ethyl	7/10,000C	11,078CH_2
L/Sb-E-7	Ethyl	7/1000C	11,118CH_2
Lb/S-E-8	Ethyl	8/1000C	11,078CH_2
L/Sb-E-8	Ethyl	8/1000C	11,118CH_2

[a] The design of branched BPE chain models with butyl and hexyl branches (not show here) are the same as BPE chain models with ethyl branches, and the only differences are the branch length.

This work aims to provide a molecular explanation about molecular mechanism of BC, BL, and especially SCBD on BPE crystallization process. MD simulations were performed for two types of BPE chains: branches all distribute on the long chain or on the short chain but with the same BC and BL. The molecular mechanism of BC, BL and SCBD on the nucleation process, also the crystallization process and especially the formation process of tie chain of BPE chains were systematically investigated.

2. Models and methods

As schematically depicted in Fig. 1, two types of BPE model chains were used in the present work. Each type of chains contained one long chain (backbone: 10,000 CH_2) and one short chain (backbone: 1000 CH_2) but with different SCBD. One type contained branches that distributed equally on the long chain (Lb/S) while the other distributed equally on the short chain (L/Sb). The details of the BPE models are summarized in Table 1. The BPE models covered a branch content range of 0 (i.e., high density polyethylene (HDPE) homopolymer) to 8 branches per 1000 backbone carbons with different SCBD. The naming convention for the BPE models identifies which long chain species and short chain species are blended and the quantity of branch content. For instance, Lb/S-E-1 denotes ethyl branches all distribute on the long chain with branch content of 1 ethyl branches per 1000C in backbone while L/Sb-E-1 denotes ethyl branches all distribute on the short chain with the same branch content of 1 ethyl branches per 1000C in backbone. The branch length effect was also considered in this work. The design of branched BPE chain models with butyl and hexyl branches