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Polymer 43 (2002) 6333–6340

polymer

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MD simulation of the influence of branch content on collapse and conformation of LLDPE chains crystallizing from highly dilute solutions

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Received 28 March 2002; received in revised form 25 July 2002; accepted 27 July 2002

Abstract

The influence of branch content (BC) on conformation of Ziegler–Natta linear-low density polyethylene (ZN-LLDPE) in dilute solutions was studied by molecular dynamics simulation. Octene LLDPE with different levels of BC distributed *randomly* along the chain mimicking ZN-LLDPE were simulated in vacuum at 400 and 500 K. Increasing BC was found to decrease chain folding and change chain conformation. Chain conformation undergoes transition from lamellar to a more random coil-like structure near a BC of 40 branches/1000 backbone carbons. Results are in agreement with recent experimental results of Zhang et al. [Polymer 42 (2001) 3067]. Extended chains with higher BC collapse faster and form more kinks than chains with lower BC with branches acting as nucleation points for the chain collapse. At high BC, branches are observed to self-assemble away from the backbone. © 2002 Published by Elsevier Science Ltd.

Keywords: Polyethylene; Conformation; Coil size

Commercial polyethylene is available in different grades and types. High-density polyethylene is mainly composed of linear chains. However, Ziegler–Natta linear-low density polyethylene (ZN-LLDPE) are usually produced by co-polymerization of a small percentage (0.1–8%) of 1-butene, 1-hexene or 1-octene with ethylene resulting in short branches containing two to six methylene units. These branches are not uniformly distributed along the chain [1,2].

The subject of chain conformation and size of polyethylene chains is of technological importance because of their direct influence on solution properties and characterization of the polymer. For example, gel permeation chromatography (GPC) characterization is based on hydrodynamic volume of chains in dilute solutions, which is directly related to chain conformation and coil size. Also, temperature rising elution fractionation (TREF) is based on crystallization from dilute solutions and is strongly influenced by short-chain branching (SCB) and its distribution as shown in recent studies of Zhang et al. [2].

Many molecular dynamics (MD) simulations have been performed on the relaxation of fully extended chains of linear PE (LPE). Many of these simulations were carried out in vacuum [3–8]. Crystallization of LLDPE has been the subject of extensive experimental investigation by many research groups [2,9–17]. Crystal structure was found to depend on many factors, for example, molecular weight of the chain, crystallization medium, branch content (BC) and SCB distribution. Crystallization of PE chains results in lamellar morphology. Several models were suggested to describe the molecular arrangement of chains in the lamella. Flory [18–21] suggested that nonadjacent reentry into lamella during folding is predominant. Experimental work of Sadler and Harris [22] on crystallization from the melt showed that up to 60% of the folds are nonadjacent. The work of Hoffman [23] favors predominant adjacent reentry.

Unlike many experimental investigations, MD simulation can be easily used to study the chain conformation and crystallization process of single chains under well-controlled conditions of molecular structure. The evolution of crystals from highly dilute solutions can be investigated by simulating single chains in vacuum, in which case intermolecular interactions are absent. The objective of this investigation is to study the influence of SCB on the collapse mechanism; lamellar conformation, order and size of single chains of LLDPE crystallizing from highly dilute solutions.

Numerous MD simulation studies by several groups have been conducted on polyethylene [24–28]. Roe and coworkers used MD simulation to study the structure and conformation of LPE below, at and above the glass

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0032-3861/02/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0032-3861(02)00537-2

transition temperature. Zuniga et al. [29] studied the transitions between rotational isomers in LPE chains. De Pablo et al. [30] used Monte Carlo simulation to study PE chains near the melting point. Noid et al. [31,32] studied the conformational changes associated with the melting process of linear PE. Kavassalis and Sundararajan [3], Choi et al. [33] and Liao and Jin [34] investigated collapse, crystallization and chain conformation of fully extended LPE chains at different temperatures. Studies have also been conducted on the effect of chain length and initial structure on the mechanism of crystallization and final chain conformation [35,36]. Boyd's group [37] conducted numerous MD simulation studies on linear polyethylenes using anisotropic united atom approach. Most of the PE simulation studies mentioned were conducted on LPE chains. One of the few studies that addressed branched PE is that of Choi [38] which examined the miscibility of branched polyethylene blends using MD simulation. Recent studies by Zhang et al. [2,39,40] reported the role of uniformly distributed branching resulting from copolymerization of ethylene with butene and propene on crystal structure of branched polyethylene. Systematic investigations of the influence of random branching on chain folding, conformation and order in PE chains have not been reported.

Hence, in this paper the influence of branching on the collapse mechanism, chain shape, conformation, size (quantified by the radius of gyration) and order (measured by the order parameter) of single chains of polyethylene is considered for randomly distributed SCB. Conformation of the chain is monitored by following and evaluating changes in dihedral angle distribution. Also, the influence of BC on chain folding, evolution of the lattice and energetics of the chain are investigated.

1. Model and simulation method

The PE model used in these simulations is a single chain composed of a thousand backbone CH_2 units with 10, 20, 30, 40, 50, 60 and 80 short branches per 1000 main chain carbons. The branches are randomly distributed along the chain. The chain is initially constructed in the fully extended all *trans* conformation. The branches are composed of five methylene units and an end methyl unit simulating the copolymerization of ethylene with 1-octene. A fairly long branch is used to highlight the influence of branching. Each methylene and methyl unit is treated as a spherical united atom. Many investigators adequately used this simplification to represent essential characteristics of PE. The united atom representation may introduce some errors especially in modeling the torsional potential. The branches are randomly distributed along the chain to mimic the structure of ZN-LLDPE (In fact, ZN-LLDPE is made of a 'soup' of molecular structures and a random distribution of branches is the first step towards mimicking the actual structure). The simulations were carried out using Cerius2 (version 4.2, Accelerys Inc.) molecular modeling code. The time evolution of conformation of the chain was simulated up to 2 ns in vacuum using the Nose–Hoover method. In absence of density constraints, segments composing the chain have more chances to reorient and assume their optimal configurations in a shorter time [34]. Simulation temperatures of 400 and 500 K were employed and an integration time step of 0.003 ps was used. A temperature of 400 K was used because this is the temperature near which most GPC, TREF and crystallization studies from solution are conducted. A relaxation constant of 0.1 for the relaxation heat variable bath was applied throughout the simulations. The Dreiding II force field potential was employed [4]. The geometric and energetic parameters were as described by Mayo et al. [41]. Nonbonded interactions were modeled using a Lennard-Jones potential with a cutoff distance of 10 Å. Extending the cutoff distance beyond 10 Å did not have significant influence on structure and energy of the systems investigated. Standard tail corrections were implemented.

2. Results and discussion

2.1. Folding of the chains

Fig. 1 shows the progression of the collapse of branched PE chains with 10, 40 and 80 branches at 500 K. The fluctuation in temperature of the system did not exceed ± 10 °C. It can be observed that for all BCs and at the high temperature of 500 K, the collapse of the chain occurs via a local followed by a global collapse mechanism similar to previous findings on LPE. It can be observed that the number of initiation sites for folding increases with BC leading to faster collapse of chains with higher BC, which suggests that branches act as nucleation points for the collapse of the molecule. For example, six folding sites (kinks) are formed in a chain with 80 branches only after 60 ps of simulation (Fig. 1(c)). The number of globules decreases afterwards as small kinks combine to form large globules. Four globules form after 90 ps. The chain undergoes total collapse to a single globule after only 100 ps. On the other hand, only two folding sites are formed in a chain with 10 branches after 60 ps. The globules grow in size with time forming the two large globules shown in Fig. 1(a) after 120 ps. The chain collapses to a single globule after 130 ps (Fig. 1(a)). Intermediate BCs yield intermediate numbers of initial kinks and times taken to totally collapse to a single globule. With 40 branches, six kinks form after 60 ps and total collapse takes place after 110 ps as shown in Fig. 1(b). The time taken for total collapse is shorter than that reported for LPE chains [3]. It is clear that the presence of branches facilitates the formation of kinks in the chains and accelerates the chain collapse process with short branches acting as nucleation points. In addition, the kinks formed during collapse for the chains

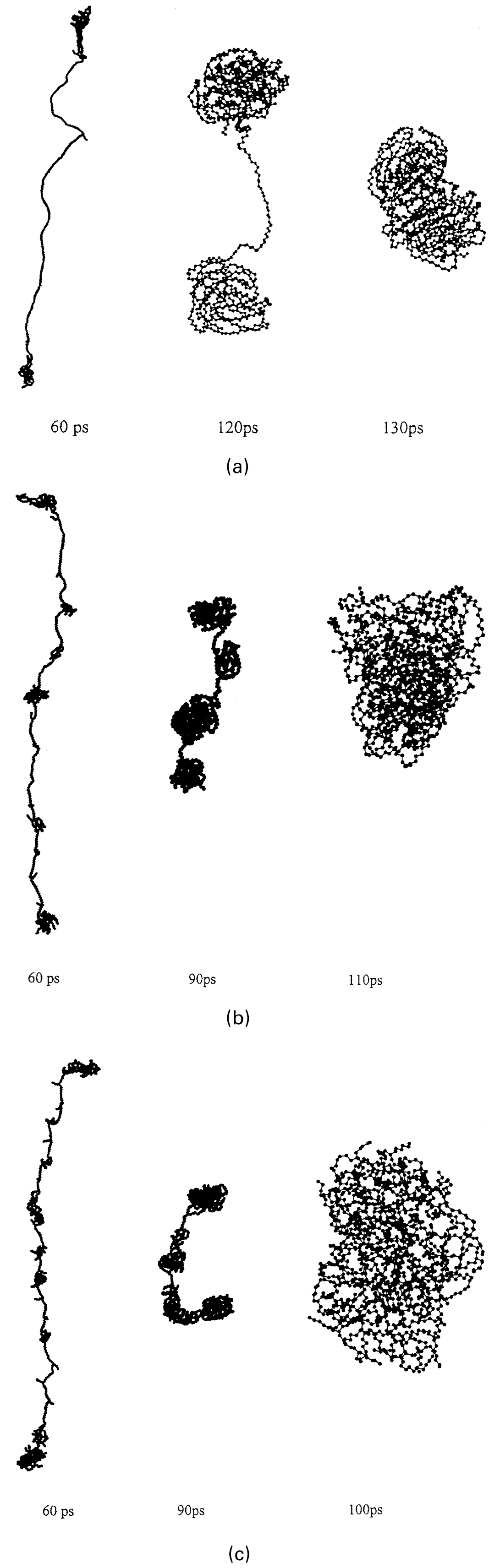


Fig. 1. Collapse of chains containing (a) 10, (b) 40 and (c) 80 branches/1000 backbone C at different simulation times.

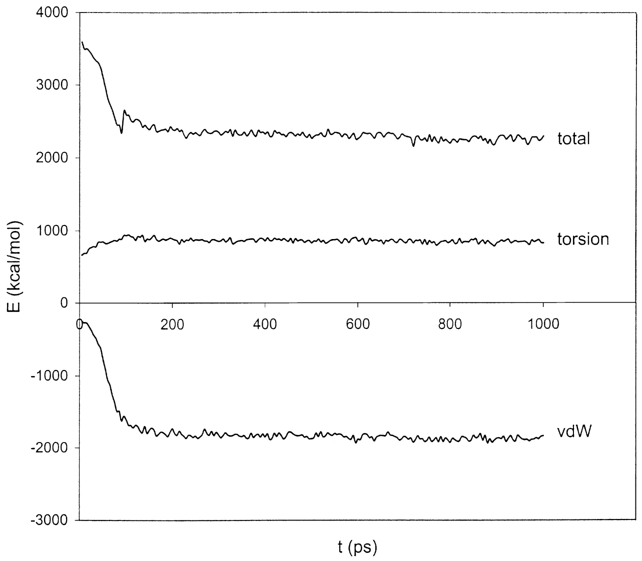


Fig. 2. Total, torsion and vdW energies as function of time for 50 branches/1000 C at 500 K.

with 10, 20 and 30 branches/1000 C have a locally lamellar structure. The locally lamellar structure of globules at low BC supports the proposal of Muthukumar [35,36] that the crystallization of polyethylene is a lamellar thickening process. The driving force for folding as shown by a plot of the total, torsion and van der Waals (vdW) energies vs time (Fig. 2) is long-range vdW forces. Long-range attractive interactions force the molecule to assume the folded structure despite the slight increase in torsional energy, which is more than accounted for by the gain in vdW energy. The presence of branches, which have more translational freedom (due to their loose ends) compared to backbone groups, accelerates the folding process as these branches try to place themselves next to other groups, thus disturbing the extended structure of the chain and allowing more intermolecular interactions between backbone segments. The influence of branches on accelerating the folding process is illustrated by plotting the vdW energy vs time as a function of BC in Fig. 3(a). It can be observed that the rate of initial drop in vdW energy is sharper for higher BC indicating that the chain is folding faster. At high BC, it is observed that the lowering in vdW energy is higher with higher BC. The lower vdW energy is a result of the larger number of segments in the highly branched molecules. A similar trend is observed at the lower temperature of 400 K (Fig. 3(b)). The increased rate of folding is also reflected in the total energy of the chain, which reaches a steady level faster for higher BC (Fig. 4). The increased freedom of movement of the chain induced by increased number of loose branch ends is reflected in the increased fluctuation in both bond and angle energies shown in Figs. 5 and 6. The total, bond and angle energies increase with BC as a consequence of the increased total number of segments in a chain with BC. However, when corrected for number of segments, the energies per segment slightly increase with

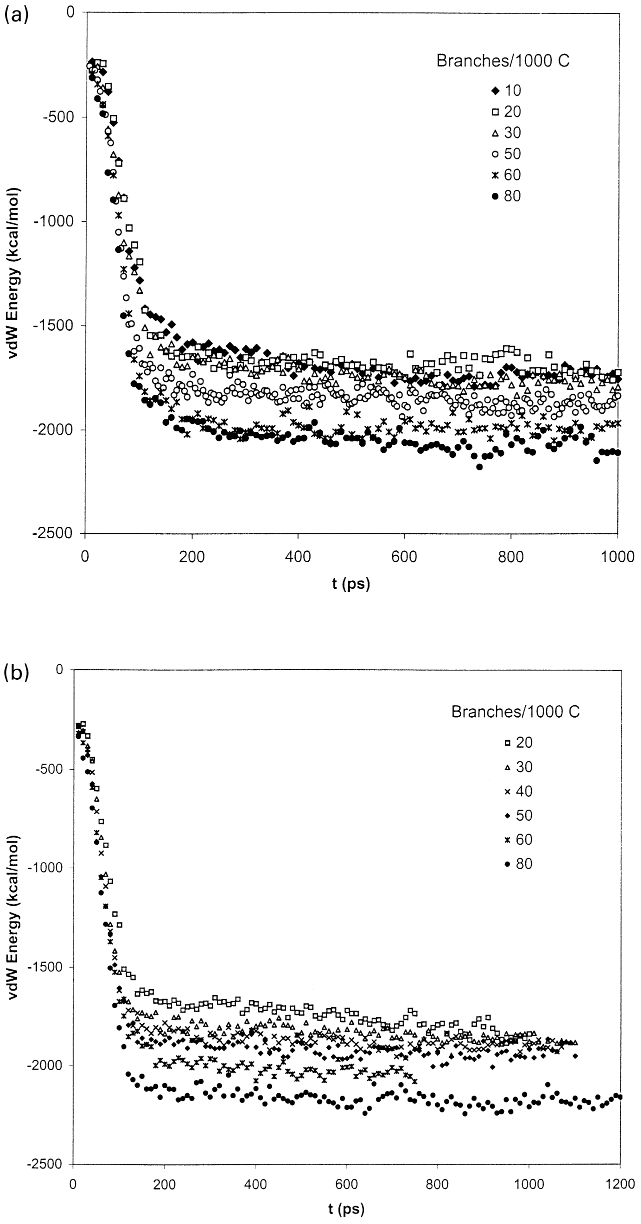


Fig. 3. (a) Influence of branching on accelerating the folding process at 500 K. (b) vdW energy vs time for different BCs at 400 K.

increasing BC and reach a constant level at higher BC (Fig. 7). The increased energy per segment results from the higher freedom of the branches.

2.2. Torsion angle distribution

The population density of torsion angles along the backbone of the chain at 400 and 500 K are shown in Fig. 8(a) and (b) for different BCs. The torsional angle barrier used in the Dreiding force field is 2 kcal/mol. It can be observed that the predominant distribution of angles is *trans* with small population of nonstaggered conformations (±30° from 180°). The *gauche* population is small and deviates significantly from perfect staggering as a consequence of treating CH_2 groups as spherical united atoms [3]. The *trans* population decreases as BC increases, however, *trans* conformation remains dominant even at the high BC of 80. Increasing the temperature decreases the *trans* population and broadens the distribution of torsion angles as shown in Fig. 9 for the 10 and 80 branch/1000 C molecules. The decrease in *trans* population and broadening of distribution is not as significant for the higher BC, as is the case for the low BC case. This is a consequence of the already disordered structure of the highly branched polymer. The conformation becomes less sensitive to temperature with increasing BC. The dominant *trans* conformation results in the chain folding into the lamellar structures shown in Fig. 10 for the chains with 10, 20, 30, 40 and 80 branches. It can be observed that order in the lamellar structure is maintained up to a BC of 30 branches/1000

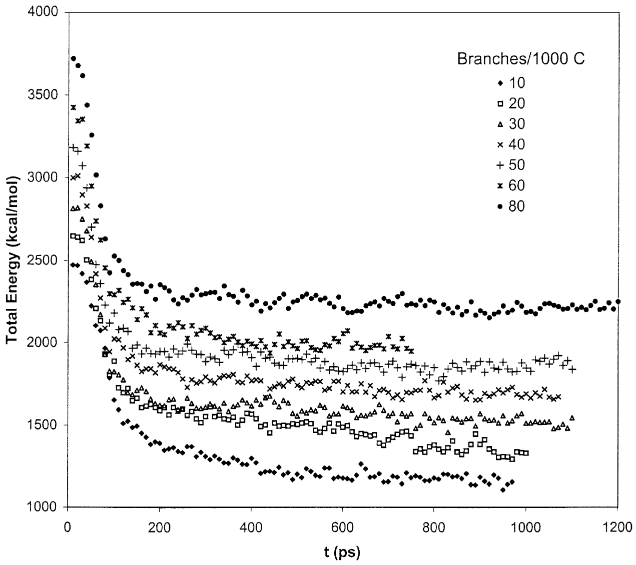


Fig. 4. Total energy vs time for various BCs at 400 K.

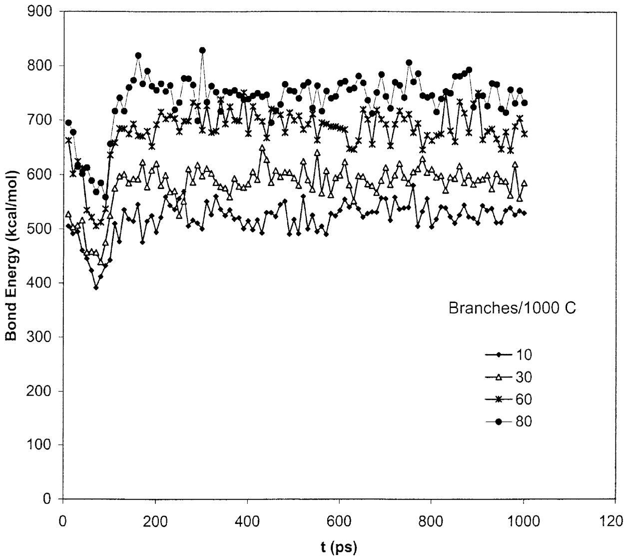


Fig. 5. Bond energy vs time at 500 K.

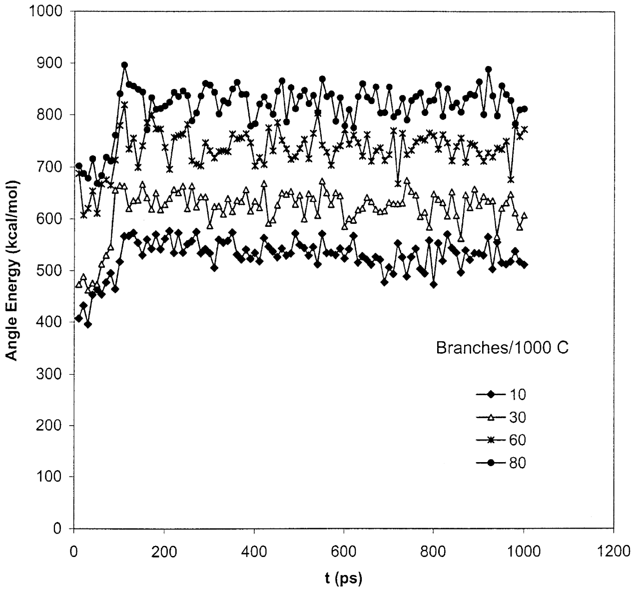


Fig. 6. Angle energy vs time at 500 K.

C. However, order in the folded structure drops significantly beyond that BC and the chain assumes a random coil-like structure at the high BCs of 40–80 at 500 K. This result is in agreement with experimental results of Zhang et al. [2] who calculated SCB as function of lamellar thickness (Fig. 6 of Ref. [2]) for ZN-LLDPE from DSC and TREF measurements. They observed an increase in lamellar thickness with increasing SCB at low BC and little increase in lamellar thickness at high BC. Although Zhang et al. have reported that the critical BC (CBC) is more than 15 SCB/1000 C; a closer look at their results (see Fig. 6 of Ref. [2]) shows that the CBC is ~30 SCB/1000 C. In addition, lamellar dimensions observed in the simulation are smaller than those measured by experiment. This is a consequence of the use of a single molecule in the simulation in addition to the large value of the torsional potential used in the Dreiding force field, which has been reported to have a significant effect on the sizes of the lamella [4,39].

In order to qualitatively monitor the ordering of the structure of the folded chain, the *trans* population at 180° is plotted as a function of BC in Fig. 11. At 400 and 500 K, a sharp decrease is initially observed in the *trans* population with increasing BC up to 30 branches/1000 C. A more gradual drop is then observed in the *trans* population density for BCs of 40 and higher. The observed change in slope indicates a conformational transition near BC of 40. This

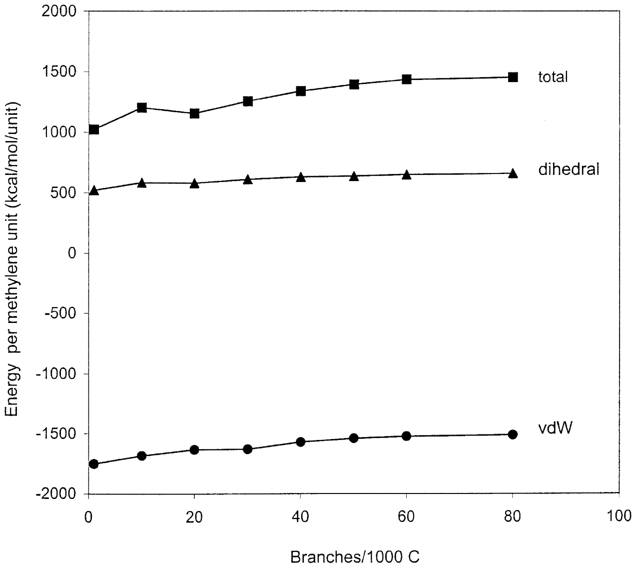


Fig. 7. Total, torsion and vdW energies divided by number of methyl and methylene units per chain at 400 K.

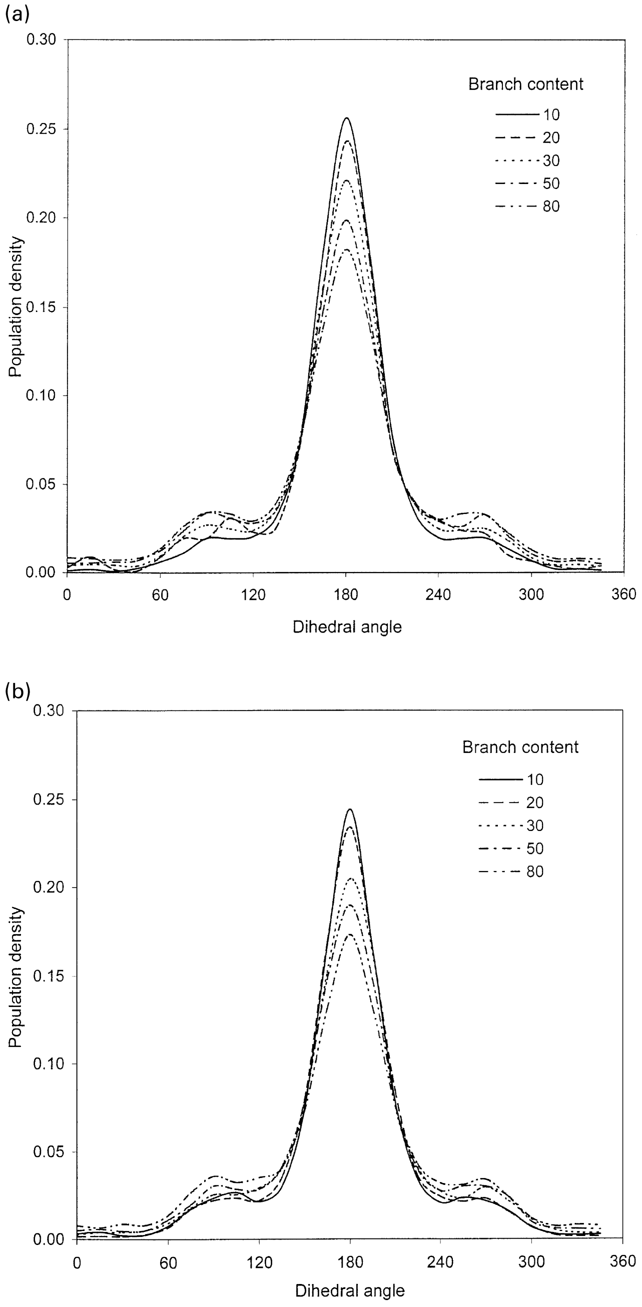


Fig. 8. (a) Dihedral angle distribution as function of BC at 400 K. (b) Dihedral angle distribution as function of BC content at 500 K.

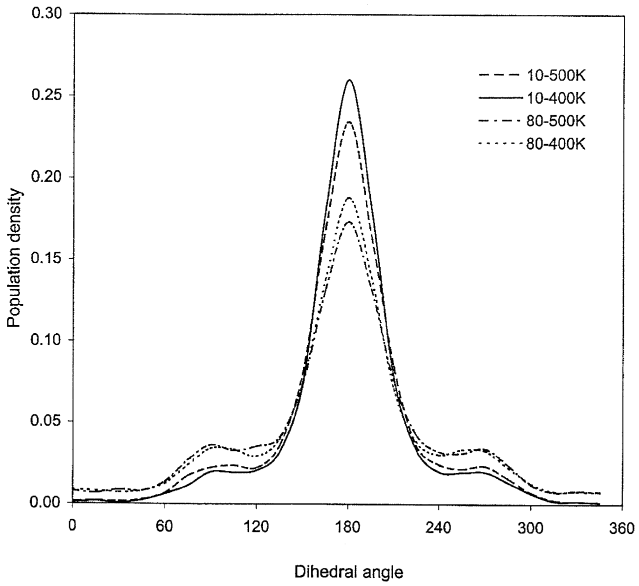


Fig. 9. Influence of temperature on population density of dihedral angles.

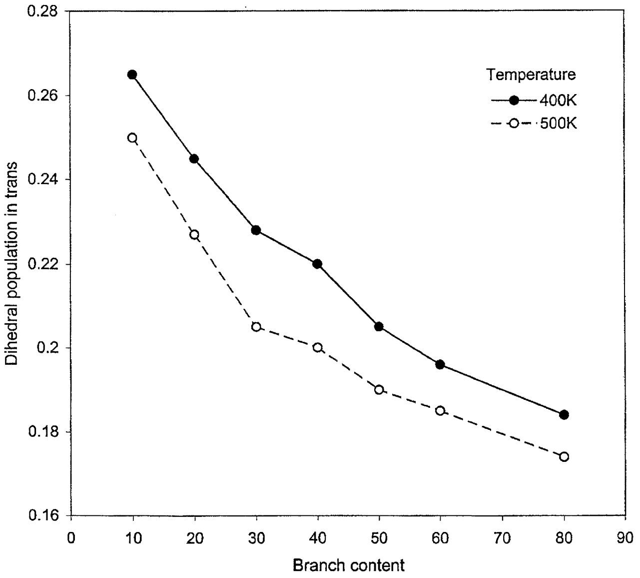
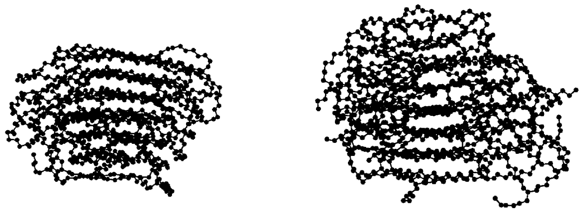


Fig. 11. *Trans* torsion angle population vs BC.

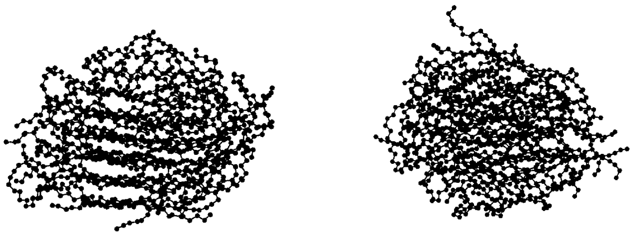
transition corresponds with the loss of order observed visually in Fig. 10 for BCs of 40 and higher. The decrease in *trans* population associated with increased BC results from inability of the fairly bulky branches to fit in the lamellar structure of the chain. In addition, branches that are randomly distributed along the chain try to assume arrangements that minimize their energy, thus influencing the overall arrangement of the chain. Finally, as shown in Fig. 12 for a chain of 80 branches, it is observed that at higher BC, the branches tend to self-assemble and be close to each other. This tendency of branches to self-assemble is another factor that acts to disrupt the lamellar arrangement of the chain. Order in the chains can be quantified by the bond order parameter defined by:

$$S(r) = \frac{1}{2}[3\langle\cos^2\theta(r)\rangle - 1]$$



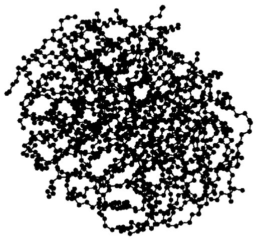
10 branches

20 branches



30 branches

40 branches



80 branches

Fig. 10. Equilibrium conformation of chains with 10, 20, 30, 40 and 80 branches/1000 C.

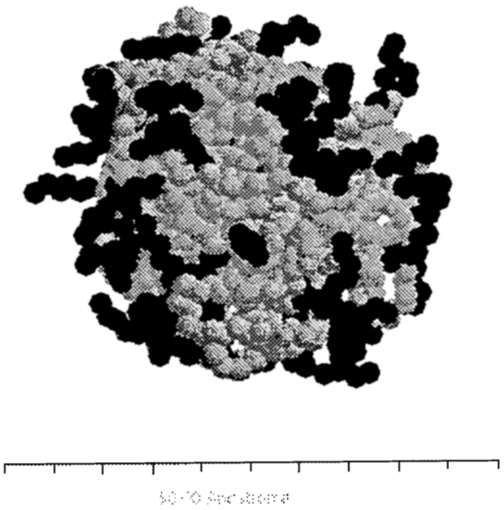


Fig. 12. Equilibrium conformation of PE chain containing 80 branches/1000 C after 1400 ps.

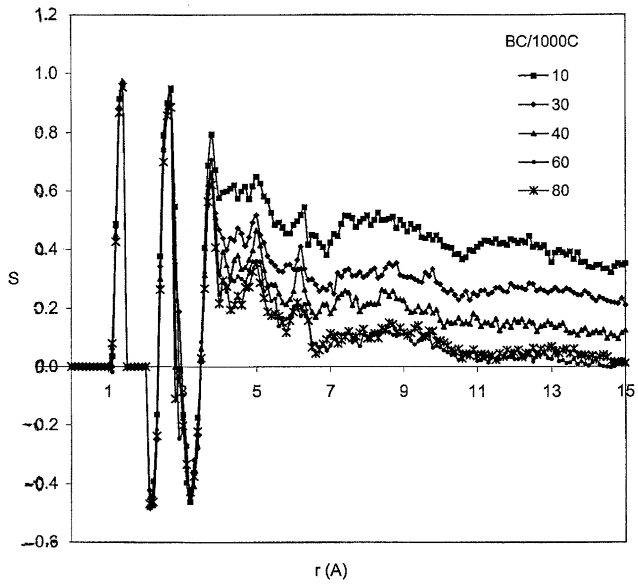


Fig. 13. Bond order correlation function at 400 K.

The bond order parameter for chains with different BC is shown in Fig. 13. It is observed that bond order decreases sharply with increasing BC and reaches a constant level at a BC of 60. The level of order extends over a larger distance for low BCs. On the other hand, the extent of order becomes short in range for the two BCs of 60 and 80. This is consistent with our earlier visual observations that show that the lamellar structure nearly disappears above a BC of 30. The influence of temperature on the structure of the collapsed chain is small. This is because simulating a chain in vacuum does not simulate good solvent conditions where segments have more freedom and increasing the temperature strongly influences chain mobility.

2.3. Radius of gyration

The change in the radius of gyration (R_g) as a function of simulation time for different BCs at 400 K is shown in Fig. 14(a). R_g decreases at a fast rate at the beginning of the simulation. The rate of initial decrease is higher for the higher BCs and reaches a plateau after 110–130 ps. The faster rate of decrease in R_g for higher BCs is consistent with the faster rate of decline in total and vdW energies discussed earlier. Subsequent to the initial decline, the R_g fluctuates around a constant value then shows a general slight increase (Fig. 14(b)). The slight increase may be associated with annealing of the chains following the initial collapse to produce the lamellar structure. Rearrangement of the segments causes the chain to elongate along the fold axis and to slightly expand in its search for an optimum arrangement that maximizes vdW interactions and minimizes torsional energy.

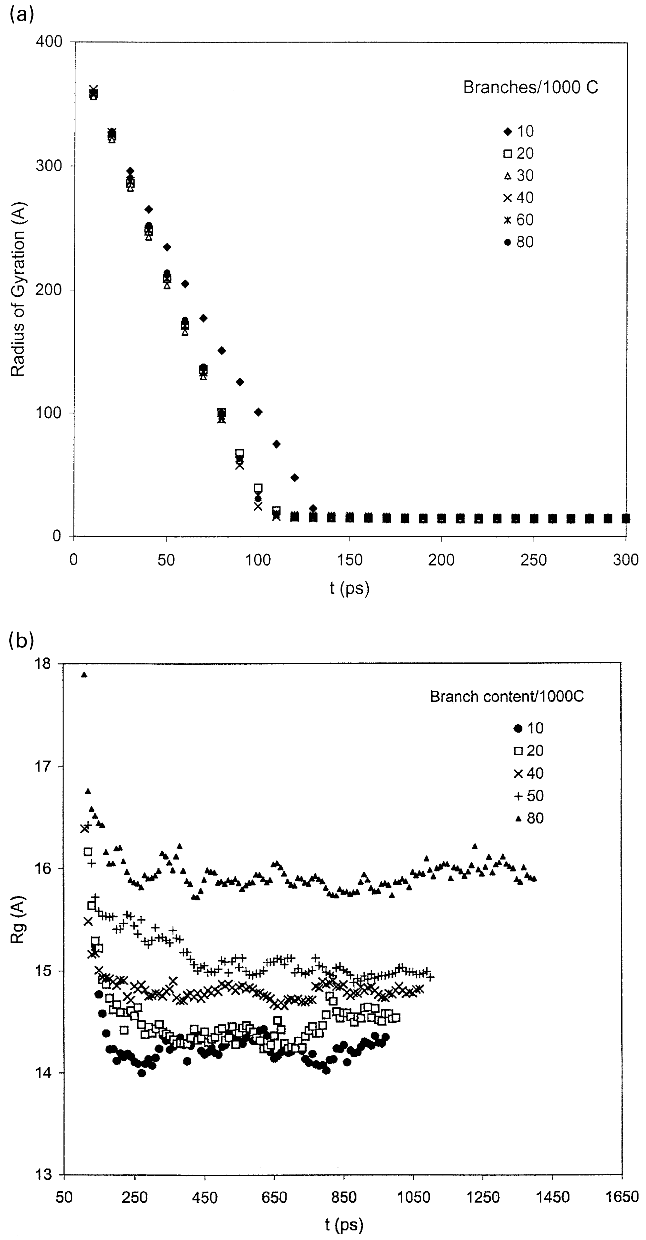


Fig. 14. (a) R_g vs time at 400 K for different BC. (b) R_g vs time at 400 K (long time).

3. Conclusion

This study shows that the conformation of single PE chains crystallizing from highly dilute solutions is a strong function of BC for randomly distributed branches. Increased BC reduces order in the lamellar structure of the chain. Molecular conformations change above a BC of 30 branches/1000 C from an ordered lamellar structure to a more random coil-like structure. This result is found to agree with recent reports of Zhang et al. [2] who obtained SCB as a function of lamellar thickness for ZN-LLDPE from DSC and TREF measurements. Also, branches tend to self-assemble at higher BC contributing to the disruption of the lamellar structure of the chain. Long-range interactions drive the folding process and a balance between vdW and torsional energies dictates the final structure.

Acknowledgements

Authors would like to acknowledge the support of King Fahd University of Petroleum and Minerals.

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