

# **MD Simulation Study of the Influence of Branch Content on Relaxation and Crystallization of Branched Polyethylene Chains with Uniform Branch Distribution**

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## **ABSTRACT**

Linear low-density polyethylene (LLDPE) chains with different levels of branch content (BC), ranging from 10 to 80 branches/1000 C, distributed uniformly along the chain are simulated in vacuum at a temperature of 350K. The influence of BC on the relaxation and crystallization of LLDPE chains is studied. The collapse of the branched chains is found to occur via a local followed by a global collapse mechanism with branches acting as nucleation points for the collapse of the molecule leading to faster collapse of chains with higher BC. Branches are observed to self-assemble away from the backbone at high BC. Radius of gyration correlates to  $M_w$  by a power-law relationship:  $R_g = K_s M_w^\alpha$  with  $\alpha=0.35$ . The trans population is found to be dominant at all branch contents; however, it decreases with increasing BC. Increasing BC is found to decrease order and to strongly influence chain conformation. Chain conformation undergoes a transition from lamellar to a more random coil-like structure near a critical BC of 50 branches/1000 C. Branches are observed to be excluded from the lamella and to self assemble at high BC. This work also provides insight into the conformation adopted during the coil-globule transition experienced by a single chain in an infinitely dilute solution much below the  $\theta$  temperature.

**Key words:** MD simulation, Polyethylene, branch content, chain conformation, radius of gyration

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## INTRODUCTION

Polyethylene is available in three main different types: high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), and low-density polyethylene (LDPE). HDPE is made of mainly linear chains, while LDPE is usually made by free radical polymerization and short and long chain branches characterize the product. On the other hand, Ziegler-Natta and metallocene catalysis are currently used to produce LLDPE. Ziegler-Natta LLDPE (ZN-LLDPE) and metallocene LLDPE (m-LLDPE) are produced by copolymerization of a small percentage (0.1-8%) of 1-butene, 1-hexene or 1-octene with ethylene resulting in short chain branches containing two to six methylene units. The ZN-LLDPE chains are usually highly heterogeneous in chain structure, size and branch distribution. However, m-LLDPE is characterized by higher interchain homogeneity.

Numerous experimental investigations of the crystal structure of polyethylene copolymers have been conducted [1-16]. The crystal structure of PE copolymers depends on the molecular weight of the polymer, branch content, and branch distribution along the chain. In order to carry out a systematic investigation of crystallinity; chains with homogeneous structures are needed. Both commercial ZN and metallocene PE copolymer chains are heterogeneous in structure. However, ethylene copolymers with precisely controlled methyl branching have been recently synthesized using acrylic diene metasyntesis [17,18]. Watson and Wagener synthesized polyethylene copolymer chains with methyl branches that are regularly spaced [18]. Model PE copolymers with well controlled structures have been synthesized and used by many research groups to investigate the influence of certain aspect of molecular structure on properties and miscibility of polyethylenes. For example, hydrogenated polybutadiene copolymers prepared by anionic copolymerization of ethylene and butene have been used as model compounds to study the miscibility of blends of linear and branched polyethylene [19].

Polymer models with well-controlled structures can be studied using molecular simulation. The influence of Molecular parameters, for example, molecular weight, branch distribution, branch size and temperature can be easily investigated using molecular dynamics simulation. Crystal structure is found to depend on many factors, for example, molecular weight of the chain, crystallization medium, branch content and branch distribution. Kavassalis investigated the influence of the torsion potential on the chain folding process of a fully extended linear polyethylene chains with 1000 CH<sub>2</sub> units [20,21]. In presence of torsion potential, the chain was found to collapse globally, while in absence of torsion potential or at higher temperatures, the collapse mechanism was local and small collapsed subdomains formed along the chain. Subsequently, the subdomains coalesced to form the extended crystal. Liao and Jin studied the influence of chain length and type of torsion potential on the collapse mechanism [22]. It was found that the collapse process is independent of the torsion potential used in the force field. It was also shown that for chains composed of more than 1200 CH<sub>2</sub> units, the relaxation proceeds via local collapse. The influence of starting configuration on the crystallization mechanism was studied using Langevin dynamics for chains composed of 700 and 2000 CH<sub>2</sub> units [23,24]. Also, the collapse mechanism of the 700 CH<sub>2</sub> chain was observed to be more global in nature while for the 2000 CH<sub>2</sub> chain, it was more local. This result indicates that the starting configuration does not influence the crystallization mechanism.

In this paper, the influence of uniform branching on the chain collapse and crystal properties of polyethylene-chains with regularly spaced hexyls branches is investigated. The influence of chain length and branch content on crystal structure, shape and level of order is studied. Also, the influence of branching on evolution of the lattice and energetics of the chain are investigated. Conformation and local order of the chain are monitored by following and evaluating changes in dihedral angle distribution. Also, the influence of branch density and branch interaction on the internal structure of the crystal is examined. PE chains with branch content ranging from 10 to 80

branches/1000 are constructed and MD simulation is used to study the influence of varying branch content and temperature on structure and order in single chain crystals

## MODEL AND SIMULATION METHOD

Single chains of PE composed of a 1000 backbone CH<sub>2</sub> units with 10, 20, 30, 40, 60, 70 and 80 branches per 1000 main chain carbons were constructed in the fully extended conformation. Longer chains composed of 1250 backbone carbons and shorter chains containing 500 and 750 backbone carbons were also simulated to study the influence of molecular weight on chain collapse and characteristics. The branches are evenly spaced along the chain. The chains are initially constructed in the fully extended all trans conformation. The branches are composed of five methylene units and an end methyl. Each methylene and methyl unit is treated as a spherical united atom as discussed earlier. United atom approach has been widely used in studying the crystallization of PE chains [20-24]. The simulations were carried out using Cerius2 (version 4.2, Accelrys Inc.) molecular modeling code. The time evolution of conformation of the chain was simulated for 2 ns for low BC and for up to 3 ns for high BC. Simulations were carried out 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 [27]. The Simulation was conducted at a temperature of 350 K. This temperature was high enough to accelerate equilibration but low enough to be below the melting temperature. An integration time step of 0.001 ps was used. A relaxation constant of 0.1 for the relaxation heat bath variable was applied throughout the simulations. The Dreiding II force field potential was employed [28]. The geometric and energetic parameters were as described by Mayo et al [28]. Nonbonded interactions were modeled using a Lennard-Jones potential with a cutoff distance of  $10\overset{\circ}{\text{Å}}$ . Standard tail corrections were applied.

## RESULTS AND DISCUSSION

### Folding of the Chains

Figure 1 shows the progression of the collapse of branched PE chains with 1000 backbone carbons and 10 and 60 branches at 350K. The fluctuation in temperature of the system did not exceed  $\pm 10$  °C. It can be observed that for both BCs, the collapse of the chain occurs via a local followed by a global collapse mechanism similar to previous findings on long linear PE and linear PE at high temperatures [20,21]. It can also be observed that the number of initial kinks that lead to folding increases with BC leading to faster collapse of chains with higher BC, which suggests that backbone segments connected to branches act as nucleation sites for the collapse of the molecule. The time taken for total collapse is shorter than that reported for linear PE chains [20,21]. It is clear that presence of branches facilitates and accelerates the folding process. The mechanism of collapse of the chain with 750 backbone carbons and 30 branches is similar to that of the longer chain.

The driving potential for folding as shown by a plot of the total, torsion and van der Waals (vdW) energies vs time (Figure 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, compared to the extended chain, which is more than accounted for by the gain in vdW energy. Presence of branches which have more translational freedom (due to their free ends compared to backbone groups) accelerates the folding process as branch segments seek to minimize their vdW energy by assuming positions in the vicinity of other main chain or branch segments, thus disturbing the extended structure of the chain to allow more inter-segmental interactions. The influence of increased number of branches on accelerating the folding process is illustrated in Figure 3a, which shows that the rate of initial drop in vdW energy is sharper for the higher BCs indicating that chains with lower BC initially fold at a slower rate. This observation is in line with the earlier observation of more kinks and folding sites in the more densely branched chain shown in Figure 1. It is also observed that the vdW energy decreases with increasing BC. The lower vdW

energy is a consequence of the greater total number of segments per chain in the more branched chains. The vdW energy per segment is plotted in Figure 3b and is observed to increase with branch content as a result of the larger number of free end groups present in the systems with higher branch content.

### **Torsion Angle Distribution**

The population density of torsion angles along the backbone of the chains at 350K is shown in Figure 4 for different BCs. It can be observed that the predominant distribution of angles is trans with small population of nonstaggered conformations ( $\pm 30^\circ$  from  $180^\circ$ ). The trans population decreases as BC increases, however, trans conformation remains dominant even at the high BC of 80. The dominant trans conformation results in chains folding into the lamellar structures shown in Figure 5 for the chains with 10, 20, 40 and 60 branches/1000C. Order in the lamellar structures can be visually distinguished up to a BC of 40 branches/1000 C. The chains assume a more coil like structure beyond that BC as shown in Figure 5 for the chain with 60 branches/1000 C. In order to qualitatively monitor order in the structure of the folded chain, the trans population at  $180^\circ$  is plotted as a function of BC in Figure 6. A low slope decrease in trans population at  $180^\circ$  is observed for BCs up to a branch content of 50 branches/1000C followed by a sharper decline for the 60, 70 and 80 BCs. The two lines intersect at approximately a branch content of 50. This trend differs from that observed for PE chains containing randomly distributed branches for which the transition from the lamellar to the less ordered structure is observed at a BC of 40 branches/1000 C [27]. The random distribution of branches participates in lowering the transition BC because the randomly distributed branches interrupt the lamellar structure at irregular intervals causing the observed randomization [27]. Another interesting observation is that the  $180^\circ$  branch population of the 40 branches/1000 C chain deviates positively from the near straight-line relationship observed for the chains with 10, 20 and 30 branches/1000C. In order to understand the higher order observed in the chain with 40 branches/1000C, we take a closer look at the structure of the folded chain shown in Figure 7. At a BC of 40, the backbone chain contains 25 carbons between branches. This number of

backbone carbons agrees with the number of carbons in a straight segment of PE chains observed by x-ray scattering [28,29]. The chain folds once every 25-backbone carbon segments allowing the branches to assemble at the folding site without disrupting the lamella. This behavior is clearly displayed in Figure 7, which shows the equilibrium structure of the 40-branch chain. The branches, shown in gray assemble at the folding sites causing minimum disruption to the lamellar structure. It is also observed that branches tend to self assemble away from the backbone. This self-assembly is more evident at higher BCs as shown in Figure 8 for the 80-branches/1000C molecule. The branches tend to be excluded from the lamella as shown in Figures 7 and 8. Furthermore, the branches assume an extended conformation perpendicular to the backbone and do not align with the lamella.

The arrangement of branches along the backbone influences the conformation of the chain. Figure 9 shows a comparison of the torsion angle distribution for chains containing uniformly distributed branches and chains containing randomly distributed branches along the backbone. It is observed that the trans population is higher for the chain with uniformly distributed branches at a branch content of 40. However, at the higher branch content of 80, the trans population is nearly the same for both types of branch arrangements. This result supports our earlier visual observations that at high branch content, the chain is less ordered and has a more coil like structure. The type of arrangement of the branches does not influence the coil conformation. At the low branch content of 40, the uniform spacing of branches allows better alignment of the chain and results in a more lamellar structure. In addition, the molecular weight of the chain has an influence on the conformation of the chain measured by torsion angle distribution. Figure 10 shows that lowering the molecular weight of the 30 branch/1000 C chain reduces the trans population of the chain leading to a less ordered structure. Similar molecular weight effects were obtained on linear PE from NMR results of Folland and Charlesby [30]. Presence of a larger number of branches acts to stabilize the lamellar structure of the chain by supplying enough number of segments to form more folds in the lamella.

## Radius of Gyration

Change in radius of gyration ( $R_g$ ) as function of simulation time for different BCs at 350K is shown in Figure 11.  $R_g$  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 100ps for the high BCs and after 150ps for the 10 branch/1000 C. 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. In order to study the influence of  $M_w$  on the  $R_g$ , the equilibrium  $R_g$  is plotted as a function of  $M_w$  for the 30 branch/1000 C chain in Figure 12. The relationship follows a power-law of the form.

$$R_g = K_s M_w^\alpha \quad (1)$$

where  $K_s$  is a constant,  $M_w$  is the weight-average molecular weight of the chain and  $\alpha$  is a scaling exponent. The scaling exponent obtained at 350K is found to be 0.35, which is very close to the 1/3 value observed for polymer chains in poor solvents. Simulating a polymer chain in vacuum simulates poor solvent conditions [33]. The strong attractive interactions between chain segments and absence of equivalent interactions with a solvent cause the environment of the chain to be more poor solvent like. The polymer segments tend to associate and the polymer chain collapses to a dense globule.

## CONCLUSION

This study investigates the influence of uniform short chain branching on conformation, order, mechanism of crystallization and structure of LLDPE. For uniformly distributed branches, this study shows that the conformation of LLDPE is a strong function of BC. Increasing the content of branches results in an increase in the chain size. In addition, increased BC reduces order in the lamella. Molecular conformations are observed to undergo a transition from an ordered lamellar

structure to a more random coil-like structure at a BC of 50 branches /1000 C. Branches tend to self-assemble at higher BC contributing to the disruption of the lamellar structure of the chain. This study also provides an insight into the crystallization mechanism of branched m-LLDPE especially from highly dilute solutions and how it is influenced by BC. Long-range vdW interactions drive the folding process and a balance of vdW and torsional energies dictates the final structure. The suggested influence of branching on  $R_g$  raises questions about the characterization of branched PE that is based on elution volume (like molecular-weight characterization by GPC) where LDPEs are usually used as standards.

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## Figure Captions

- Figure 1 Collapse of chains containing a) 10 and b) 60 branches/1000 backbone C at different simulation times.
- Figure 2 Total, torsion, and vdW energies for BC of 10 branches/1000 C at 350K.
- Figure 3a vdW Energy for different BCs at 350K.
- Figure 3b vdW Energy per segment as a function of BC at 350K
- Figure 4 Dihedral distribution as function of BC at 350K.
- Figure 5 Equilibrium conformations of PE chains with 10,20,40 and 60 branches/1000C at 350K.
- Figure 6 Trans population at  $180^\circ$  as function of BC at 350K.
- Figure 7 Equilibrium conformations of the PE chain with 40 branches/1000C at 350K.
- Figure 8 Equilibrium conformations of the PE chain with 80 branches/1000C at 350K.
- Figure 9 Influence of Branch Distribution on Dihedral Distribution of octene-LLDPE with 40 and 80 branches/1000 C at 350K.
- Figure 10 Influence of  $M_w$  on torsion angle distribution of 30 branches/1000 C at 350K
- Figure 11  $R_g$  for different BCs at 350K.
- Figure 12  $R_g$  as function of  $M_w$  for m-LLDPE with 30 branches/1000C at 350K.

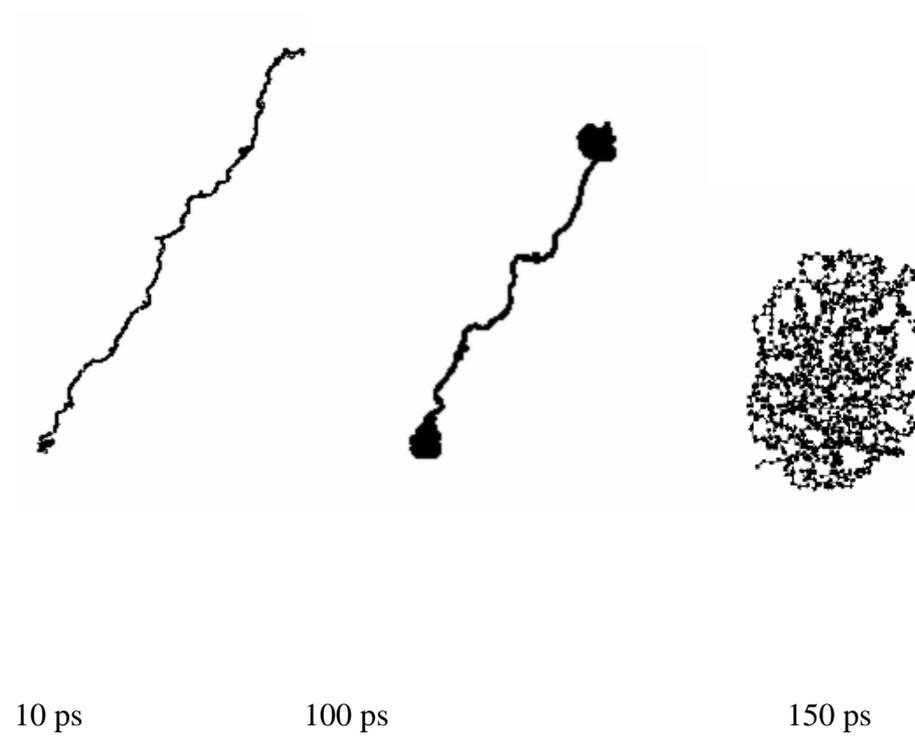


Figure 1a.

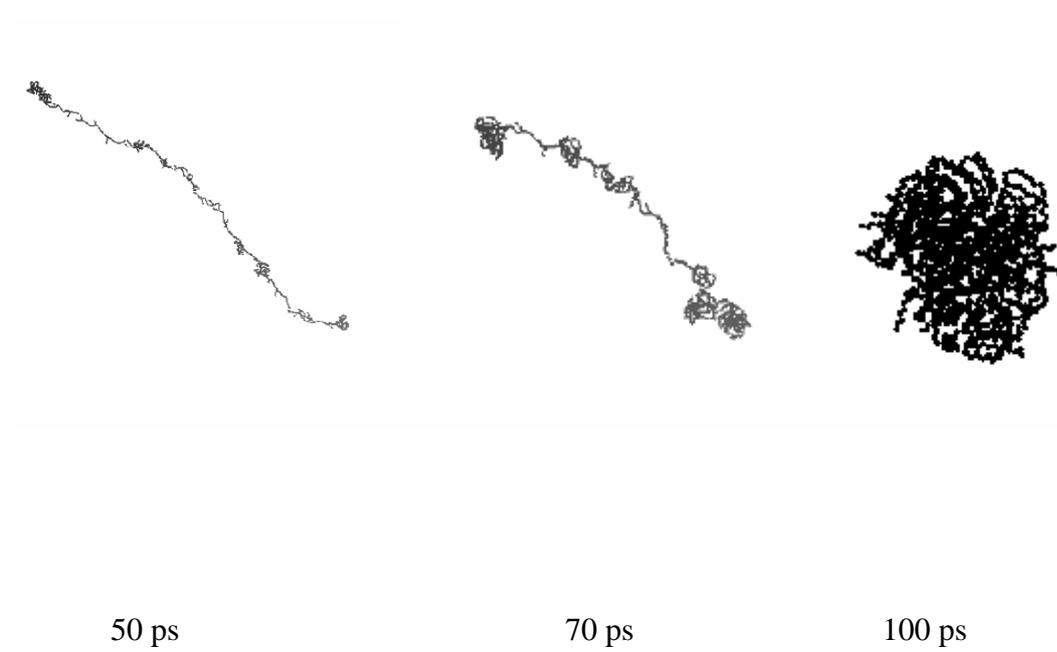


Figure 1 b.

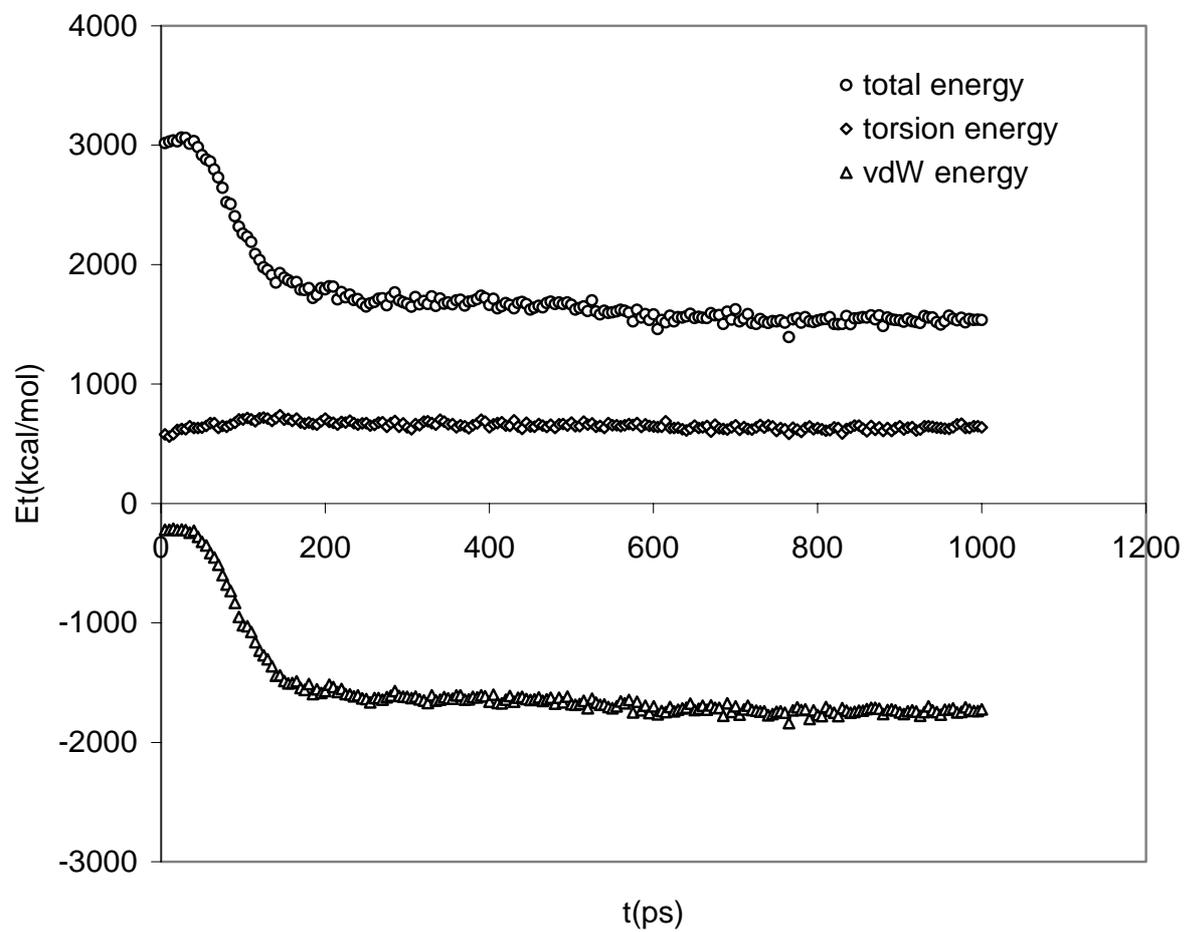


Figure 2.

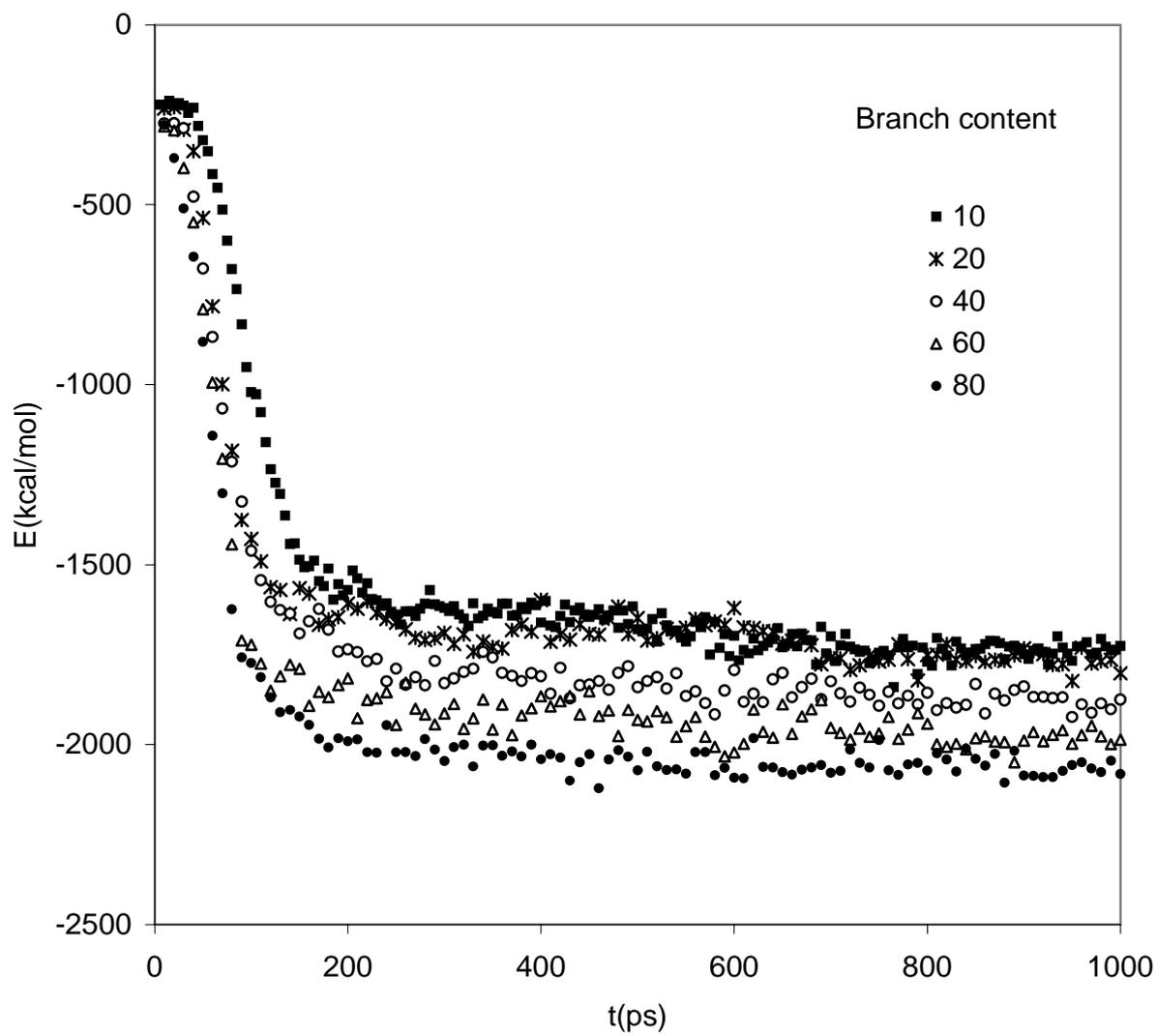


Figure 3 a

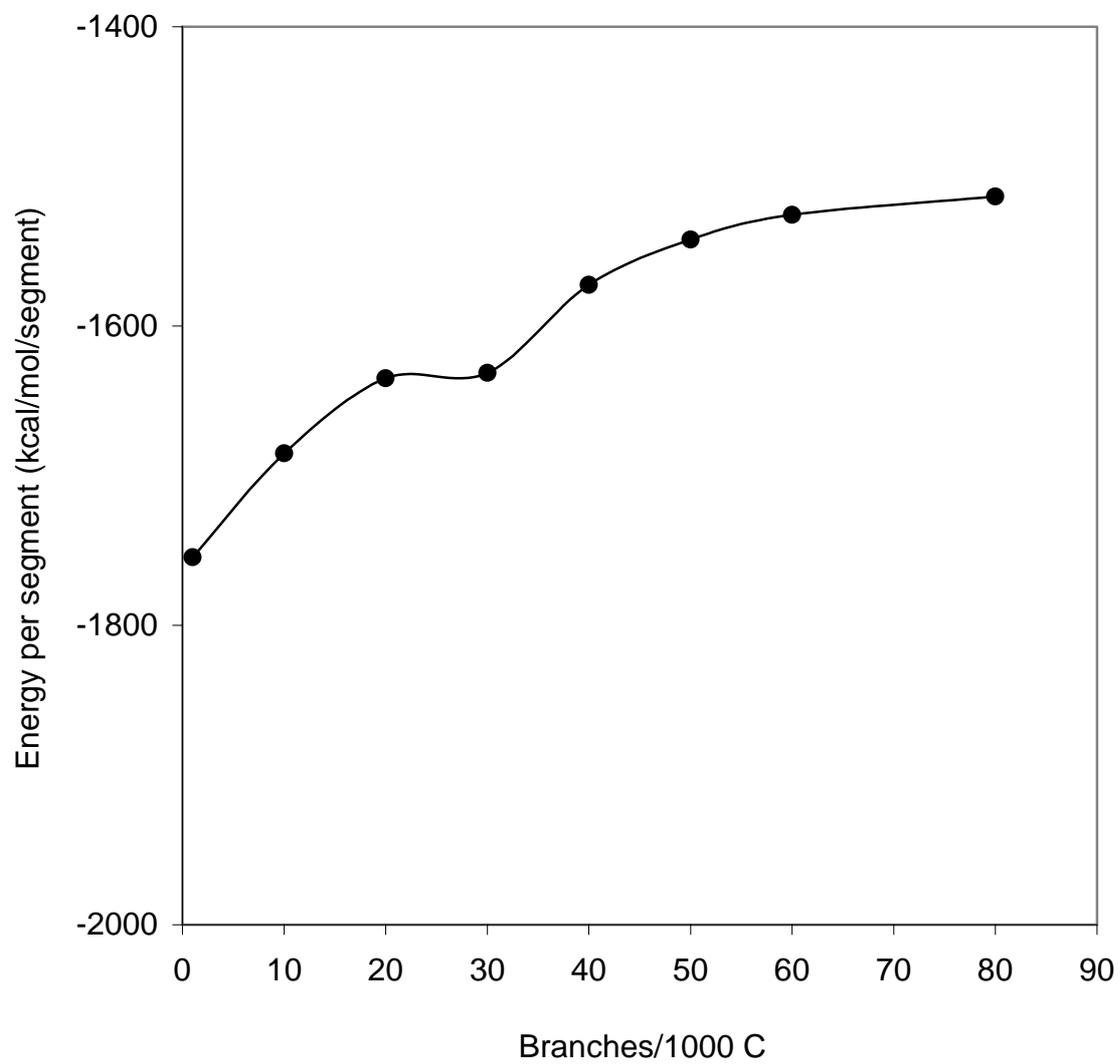


Figure 3b.

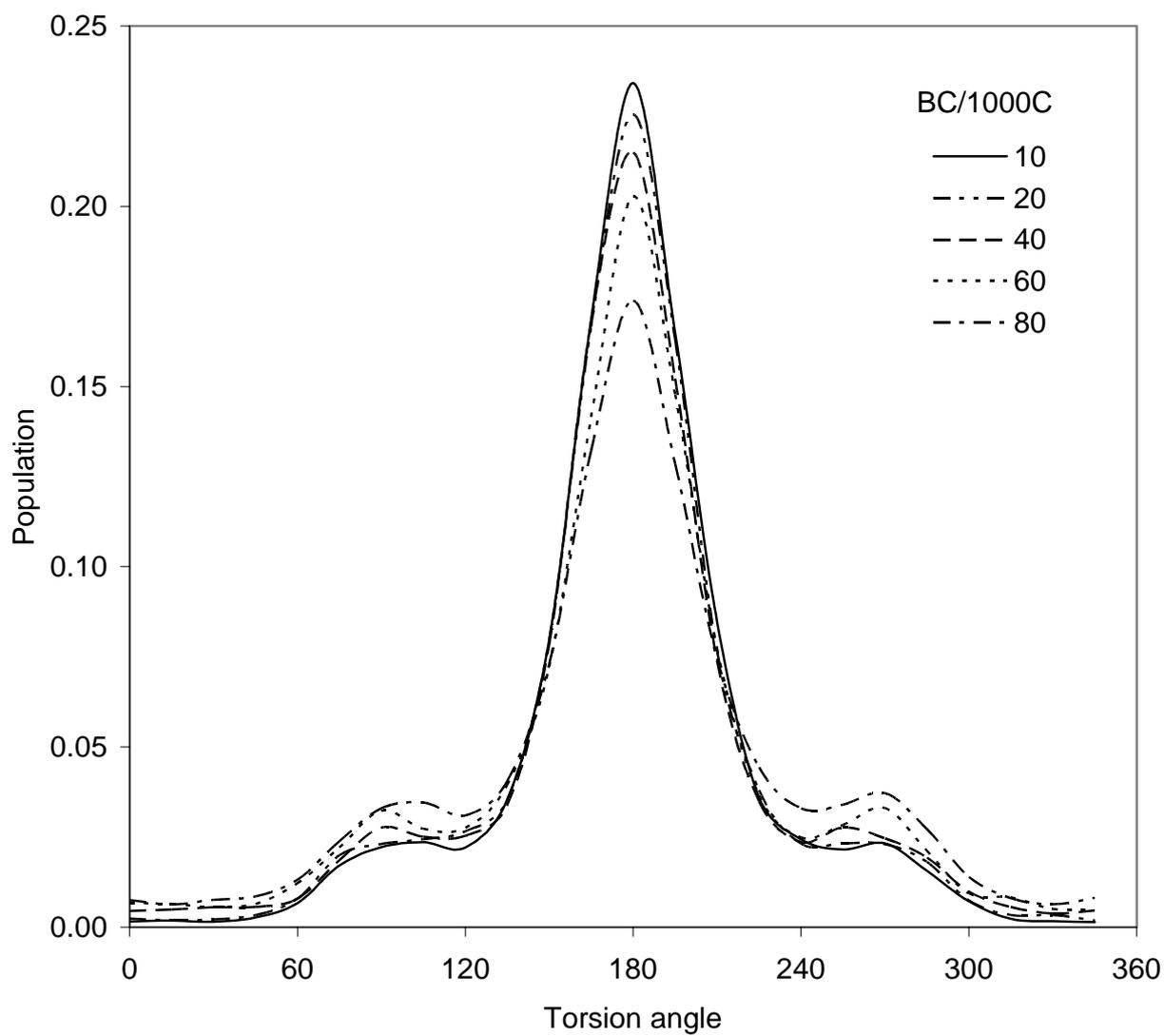


Figure 4.



10 branches/1000C



20 branches/ 1000C



30 branches/1000C



40 branches/1000C



60 branches/1000C



80 branches/1000C

Figure 5.

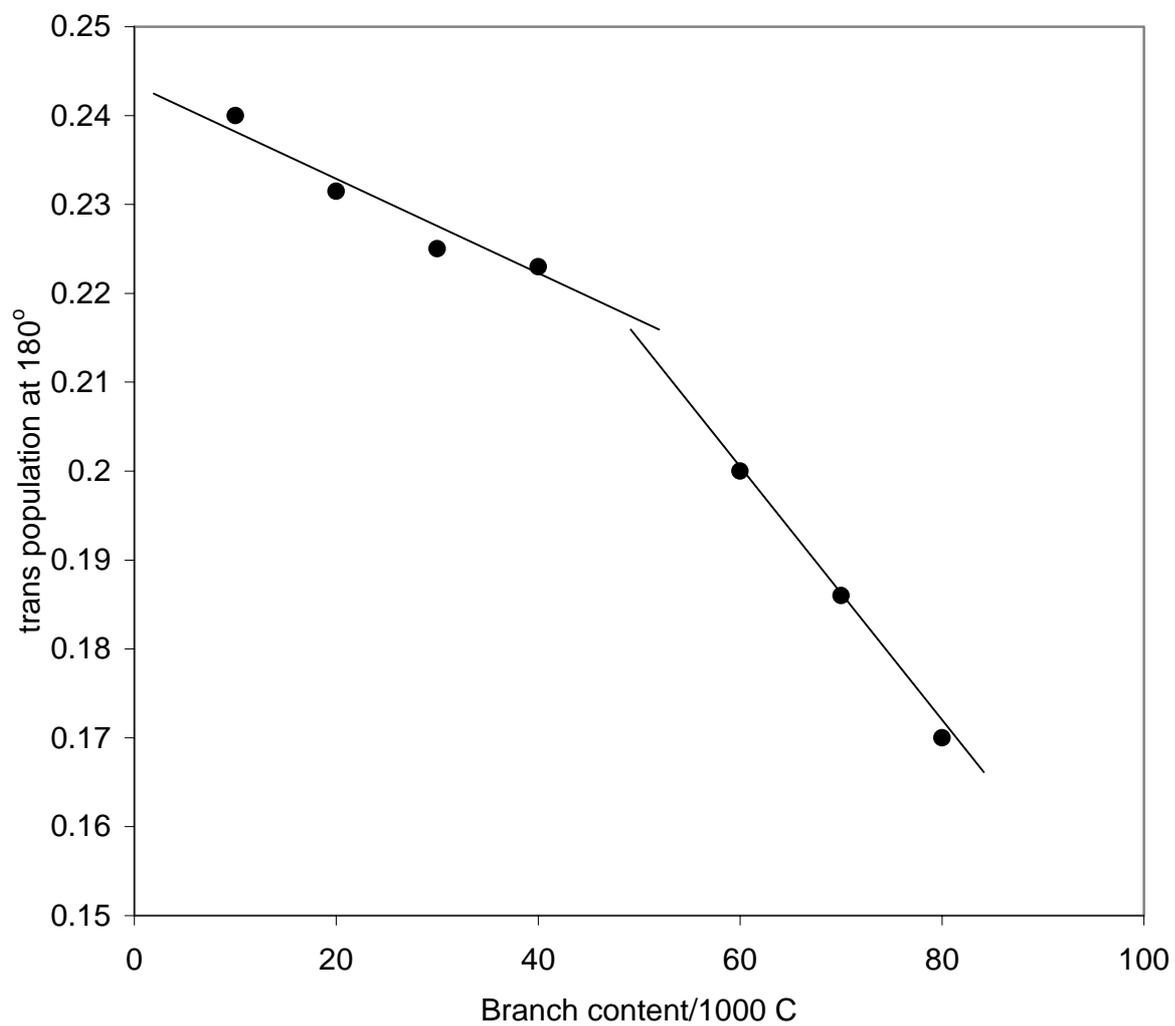


Figure 6.

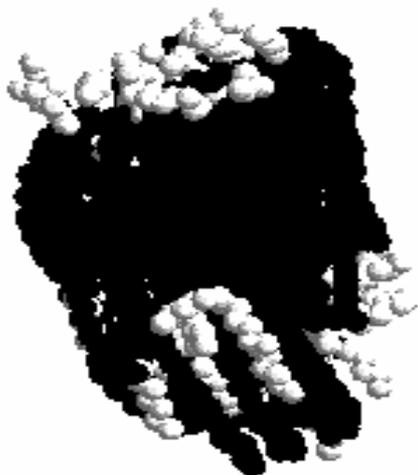


Figure 7.

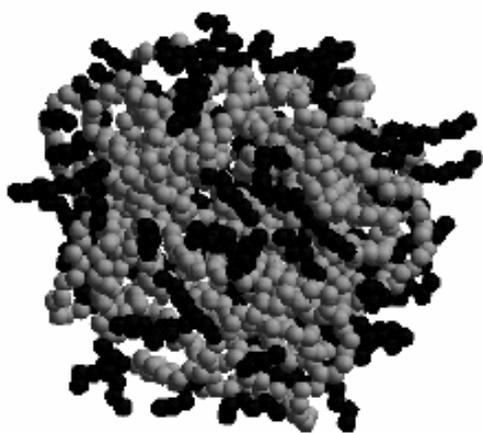


Figure 8.

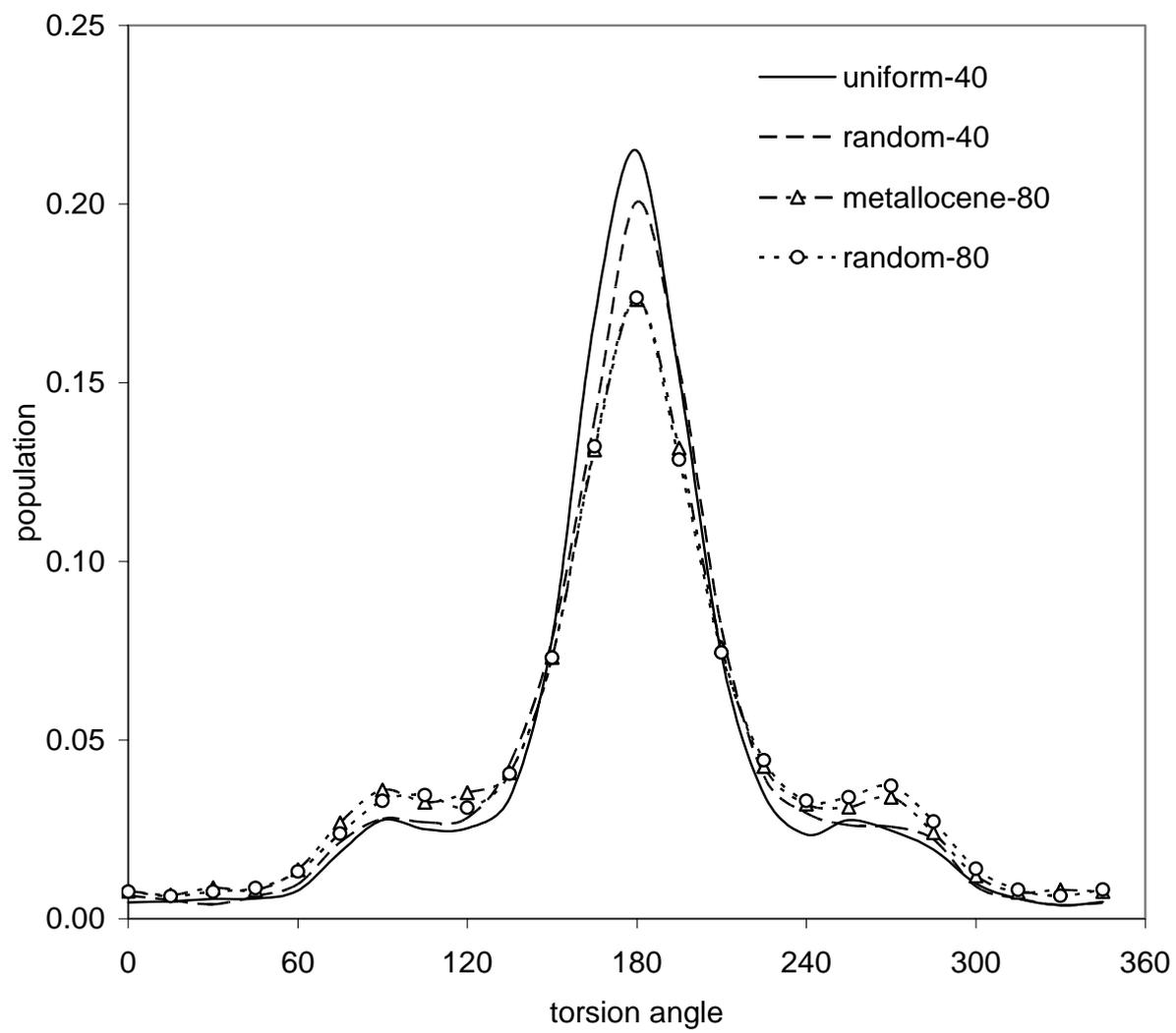


Figure 9.

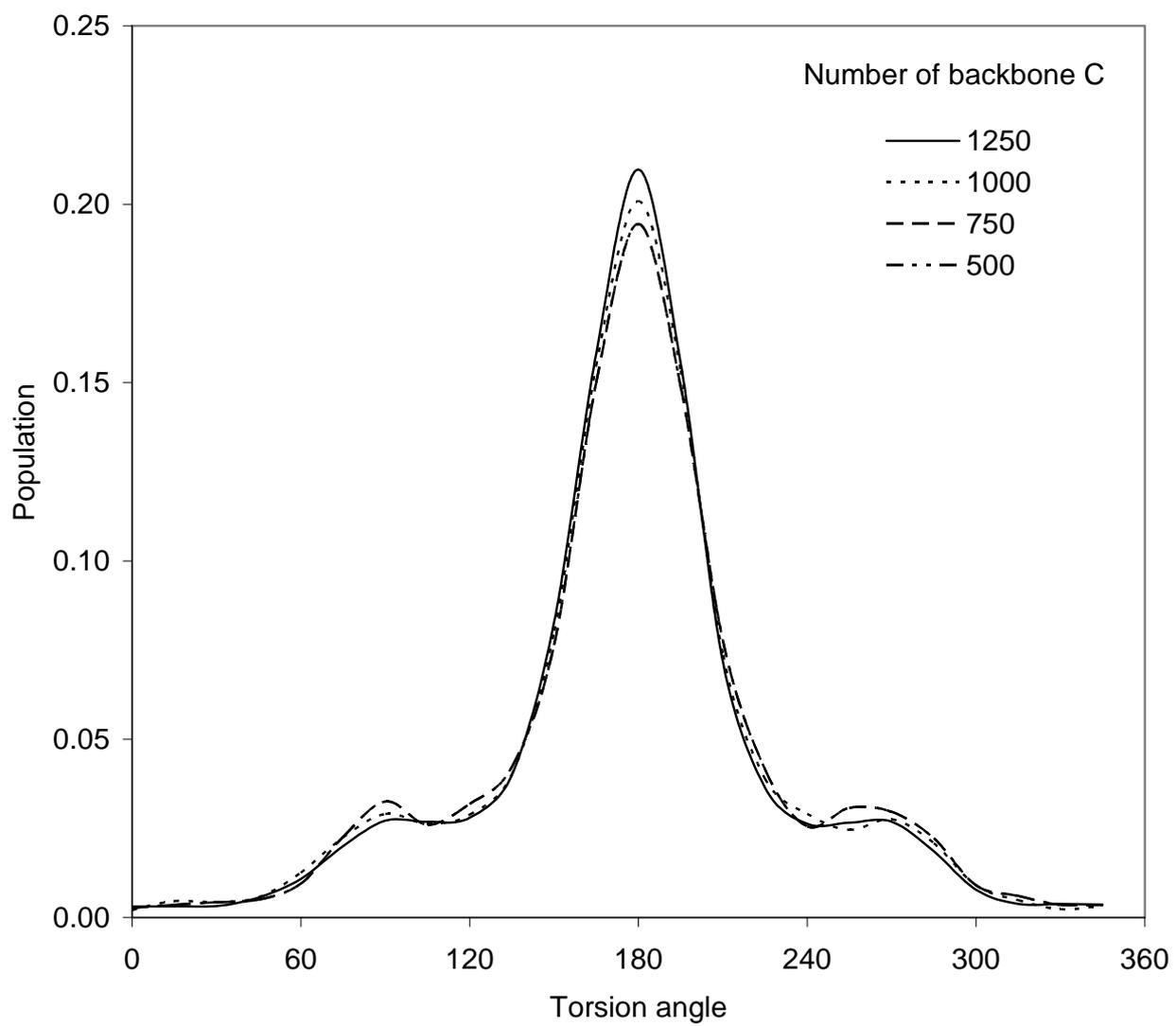


Figure 10.

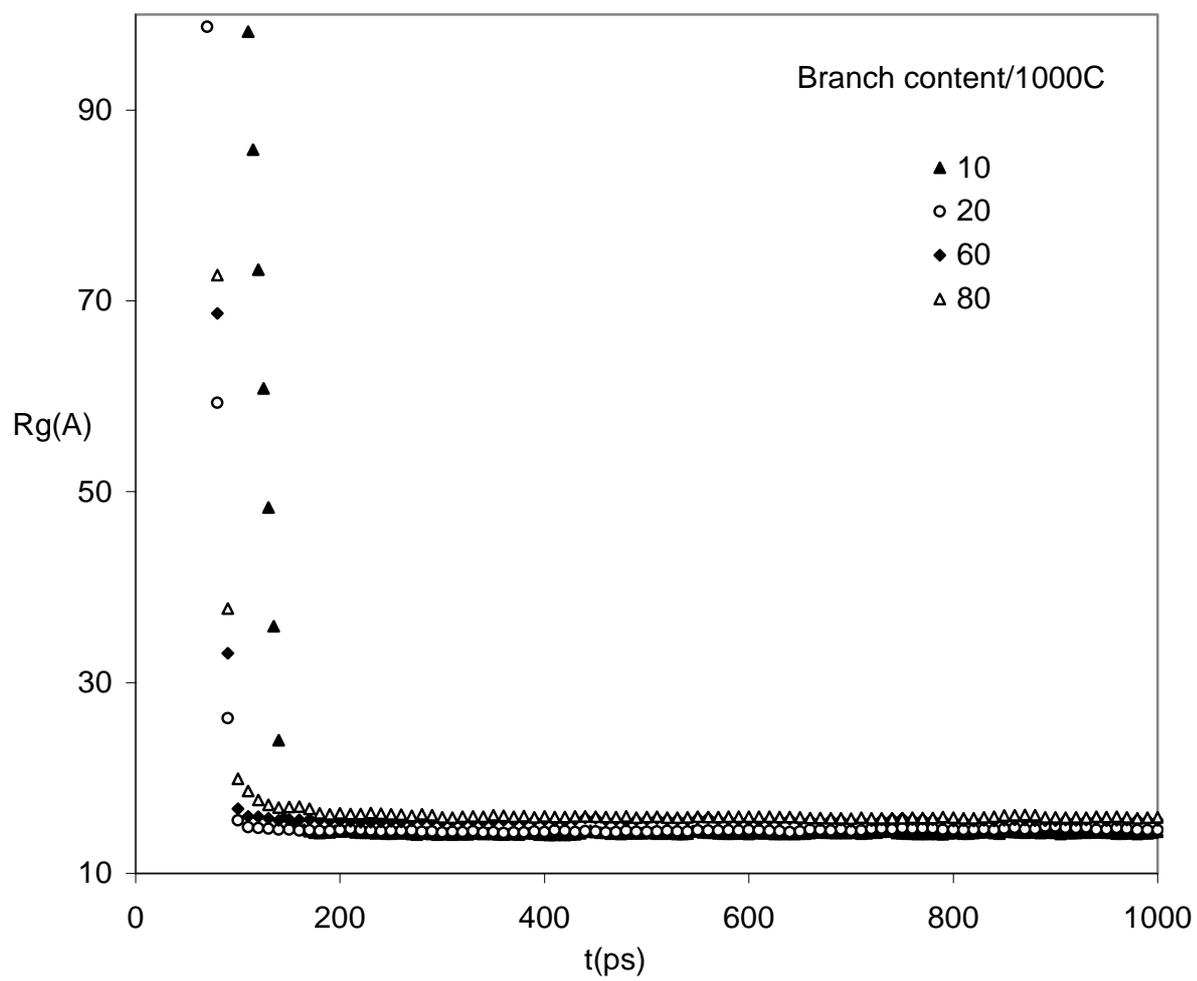


Figure 11.

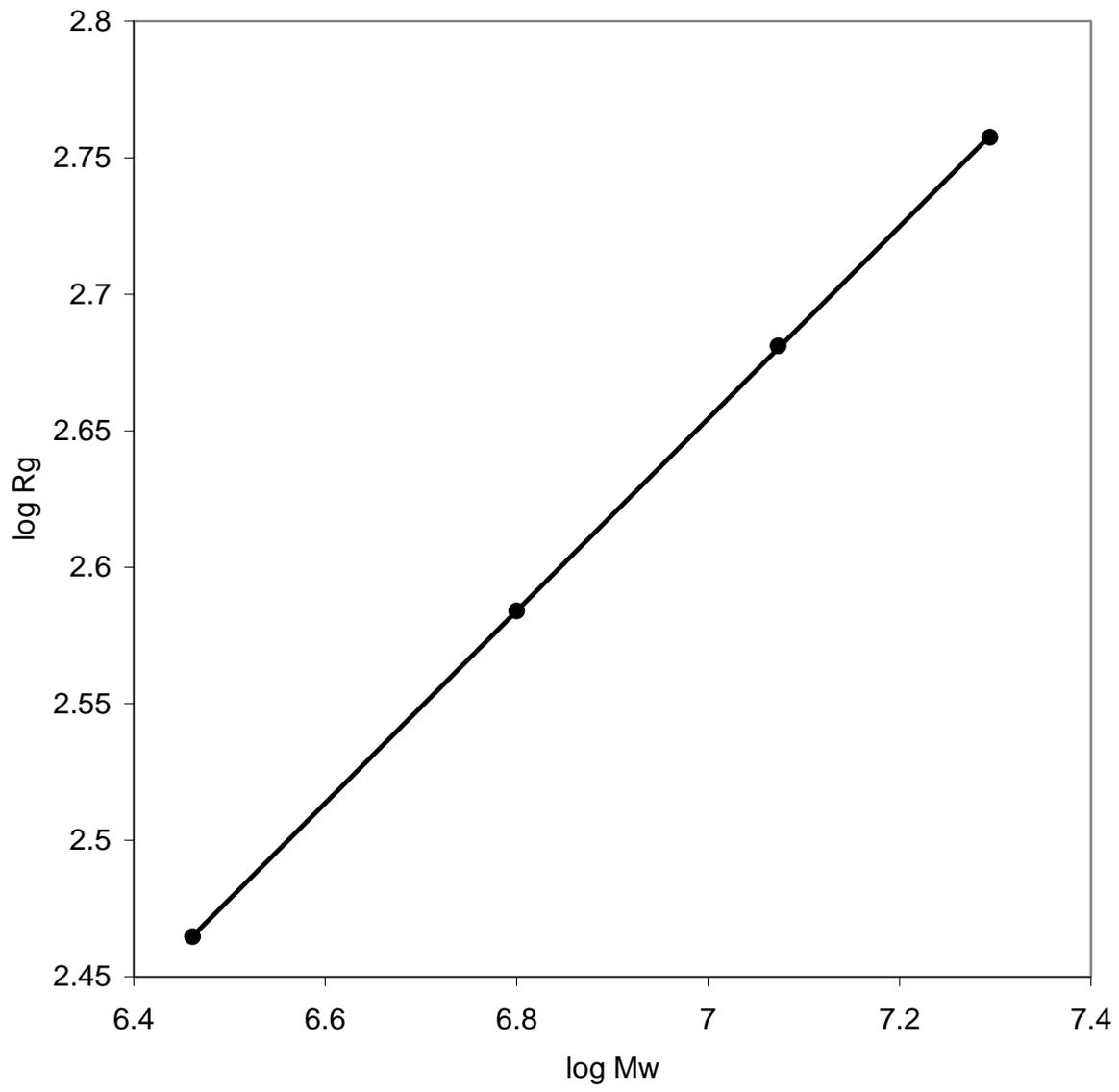


Figure 12.