

Note

MOLECULAR SIMULATION STUDY ON THE CHANGE OF POLYMER STRUCTURE DURING YIELDING*

Chen-guang Xu, Tai-ning Liang, Juan Sun and Xiao-zhen Yang**

State Key Laboratory of Polymer Physics and Chemistry, Center for Molecular Science, Institute of Chemistry,
Chinese Academy of Sciences, Beijing 100080 China

Abstract A better understanding of a recently raised argument on whether there occurs a structure change during yielding has been acquired by using molecular simulation. That is, when monitoring the displacements of all atoms before and after the yield, a structure transition does occur, which is the "atomic jump" that coordinates the amount of the atoms in the polymer and makes a large step beyond ~0.05 nm for all those atoms. Results indicate that the complex of polymer chain packing induces the multiple atomic jumps around the yield point. This explains why polymers have a broader yielding peak.

Keywords Polymer deformation, Yield, Structure transition, Atomic jump, Multiple yields

INTRODUCTION

In general, if stretching is performed before the yield point, after releasing the load, the sample will restore to its original structure. If a stretching has gone beyond the yield point, after releasing the stress the sample will not fully recover, since the original structure has been destroyed. Based on this, it is expected that a structural change should happen during a yielding process. However, a number of molecular simulation studies^[1-3] concluded that no specific structure change was found when the simulated elongation exceeded the yield point. This seems to infringe the conventionality. Therefore, clarification of such arguments was the motivation of the present work.

MODELS AND SIMULATION

A model polymer, atactic polypropylene containing 902 atoms, (150 repeating monomer units) was used in the present work. The methyl groups were replaced by "quasi-atoms". In the simulation, the commercial simulation software, Cerius² of Molecular Simulation Inc., was used. The Dreiding II force field was used to calculate the potential energies of the atoms.

Ten configurations of the model polymer were studied. Each of the configurations was confined in the periodic boundary condition cell, which was equilibrated at 800 K and then at 300 K by canonical ensemble (NVT) molecular dynamics (MD). During the simulation, the cells were kept at cubes, which was found viable under small deformation. The other average cell parameters of these structures are $a = 22.80475 \pm 0.18443$, $b = 23.19745 \pm 0.31856$, and $c = 23.08074 \pm 0.21945$. After equilibrating by MD and subsequently optimizing by molecular mechanics, the cell was stretched under the assumed Poisson's ratio. At each step, the side c of the cell was increased by 1% in length, but a and b were reduced correspondingly according to the calculation. The other parameters of the cell were kept constant. This procedure was repeated until the strain reached 15%. A total of ten structures were simulated independently. The properties of the model were the average of all ten

* This project has been supported by the Natural Science Foundation of China, 863 High Technology Project and the Special Funds for Major State Basic Research Project (G1999064800).

** Corresponding author: Xiao-zhen Yang (杨小震); E-mail: yangx@pplas.icas.ac.cn

Received May 10, 2001; Revised May 17, 2001; Accepted May 23, 2001

configurations.

RESULTS AND DISCUSSION

Figure 1 shows a typical stress-strain curve of the model glassy polymer averaged from ten samples in the simulation. The stress increases steeply and almost linearly with the strain (Hooke zone) before 3% strain and bends down slightly after 3% strain (non-Hooke zone), and reaches a maximum at 6% strain, which indicates the yielding point. Then the stress goes down and fluctuates. The curve appears as a typical stress-strain behavior around the yield point, even though averaged from ten samples. Because of adopting the three-dimensional period boundary, the results reflect the properties of the bulk polymer.

In the simulation, when the cell is stretched, the potential of the system makes the atoms move around on the energy surface to fit this change. The atoms will move from their old equilibrium locations to a more stable position. Figure 2 shows the energy changes of the sample under stretching. The van der Waals energy increases during the whole deformation process. The contribution of the total energy with strain is derived mainly from the intermolecular interaction. The change of the van der Waals energy accounts for about 95% of the total energy change. The same situation was found in the early studies^[1-5].

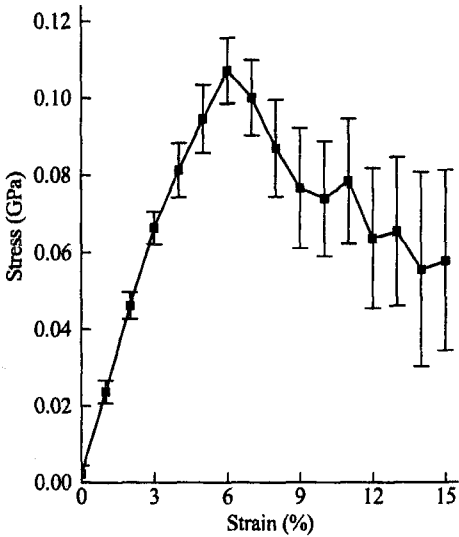


Fig. 1 The stress-strain curve of the model polymers

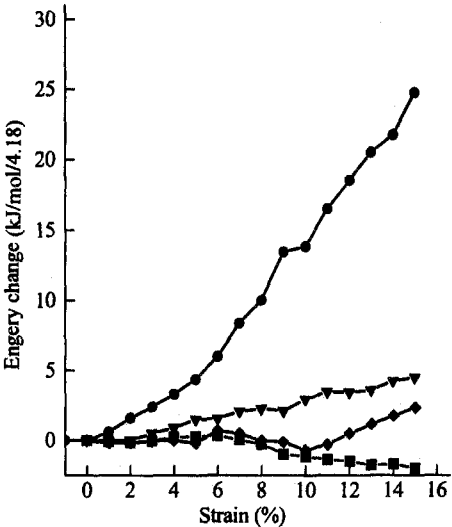


Fig. 2 Change of the energy components for the model cell
● van der Waals energy; ◆ Bond angle energy;
■ Bond energy; ▼ Torsion energy

The energy components of the bond stretching and the valence angle bending change little, especially before the yielding point. Also the torsion energy contributes insignificantly. These results confirm that Suter's assumption^[6-9] about the fixed bonds and bond angles in simulation of small deformation is valid. The torsion then seems to be significant to coordinate the atoms moving around for responding to the strains.

When we were examining the yielding process through a different window, which is the displacement of atoms during the deformation, we found a structural transition. Since in a stretching step each of the atoms can just share about 0.003 nm of the extension increment. When the window is selected for the displacement beyond ~ 0.05 nm, a kind of atom jumps will appear clearly in front of us. Figure 3 shows the amounts of this "atomic jump" for individual deformation beyond 0.003 nm, 0.03 nm, and 0.05 nm of one specific configuration sample. Most atom jumps are beyond 0.003 nm. No specific change will be found at this level. But the displacement beyond 0.03 nm begins to show some relationship with the bends of the stress-strain curves. The atomic jumps

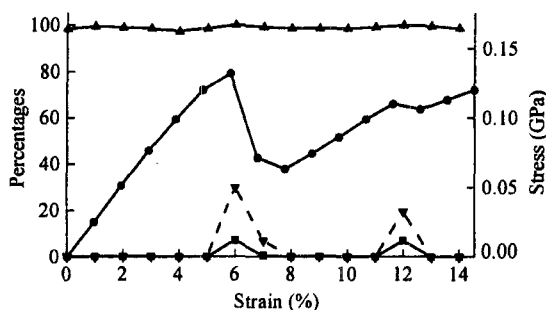


Fig. 3 Atom's displacements during deformation

▲: Atom's displacements larger than 0.003 nm

▼: Atom's displacements larger than 0.03 nm

■: Atom's displacements larger than 0.05 nm

●: Stress-strain curve

correspond to the bends in the stress-strain curves in the following two points. (1) The “atomic jump” relates to the bends, and (2) the amount of the atomic jumps does not relate to the degree of the bend. The first point sets up a significant correlation, which indicates that such an “atomic jump” alters the energy-increasing rate. The “atomic jump” obviously induces a structural transition, where the distribution of all atom pairs of van der Waals interaction is updated with a quite different one. The second point shows a feature of the atomic jumps that the hardcore atoms for the structural transition are in the minority while their locations count for much. It is observable from the ten contour maps, the atomic jumps mainly occur around the averaged yield point at 6% strain. Besides, some yields locate ahead and behind around the yield point, and therefore, the yield peak becomes broadened. This result manifests that the multiple-yielding behavior found in the present study may be the reason why a “non-Hooke zone” appears in polymer deformation. And this is attributed to the complexity of the polymer chain packing produced from different configurations.

REFERENCES

- 1 Fan, C.F., *Macromolecules*, 1995, 28: 5215
- 2 Jang, S.S. and Jo, W.H., *Macromol. Theory Simul.*, 1999, 8: 1
- 3 Jang, S.S., *J. Chem. Phys.*, 1999, 110: 7524
- 4 Fan, C.F. and Hsu, S.L., *Macromolecules*, 1991, 24: 6244
- 5 Fan, C.F. and Hsu, S.L., *Macromolecules*, 1992, 25: 266
- 6 Theodorou, D.N. and Suter, U.W., *Macromolecules*, 1985, 18: 1467
- 7 Theodorou, D.N., and Suter, U.W., *Macromolecules*, 1986, 19: 139
- 8 Theodorou, D.N. and Suter, U.W., *Macromolecules*, 1986, 19: 379
- 9 Huntlik, M., Argon, A.S. and Suter, U.W., *Macromolecules*, 1993, 26: 1097