Chinese Chemical Letters Vol. 12, No. 9, pp 827 – 828, 2001
http://www.imm.ac.cn/journal/ccl.html

Molecular Dynamics Simulation of Glass Transition Behavior of Polyimide Ensemble

Tai Ning LIANG, Xiang Yu ZHANG[2], Xiao Zhen YANG[1]*

[1]State Key Laboratory of Polymer Physics and Chemistry, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080
[2]Institute of Chemistry & Engineering, Heilongjiang University, Harbin 150089

Abstract: The effect of chromophores to the glass transition temperature of polyimide ensemble has been investigated by means of molecular dynamics simulation in conjunction with barrier analysis. Simulated Tg results indicated a good agreement with experimental value. This study showed the MD simulation could estimate the effect of chromophores to the Tg of polyimide ensemble conveniently and an estimation approach method had a surprising deviation of Tg from experiment. At the same time, a polyimide structure with higher barrier energy was designed and validated by MD simulation.

Keywords: Glass transition temperature, molecular dynamics simulation.

The prediction of glass transition temperature from chemical structure has a great significance to select and design new high-properties materials. However, for the estimation and correlation methods, the deficiency of parameters for newer groups will lead to invalidity of Tg prediction or greater deviation from experiment. In the present work, we predicted Tg for a polyimide (PI) ensemble with rigid moieties, and analyzed structural factor that regards to the rotation barrier of the bridging bonds between rings. The simulation work was performed on SGI workstation with R10000 with MSI production Cerius^{TM}. Each sample took about 15 days. The simulation theory and details can be found elsewhere[1-3].

In order to find the influence of chromophore structure upon T_g, three similar kinds of PI ensembles, PI1, PI2 and PI3, were selected as shown in **Figure 1**. As analogy in experiment, the T_g from MD is defined as the temperature at which the intersection of the specific volume slopes occurs, as described in other works[3]. The values of T_g thus simulated are shown in **Table 1**. For comparison, we use a correlation method to predict T_g for these ensembles. This correlation method is based on connectivity indices proposed by Bicerano[4]. The results thus predicted are listed in **Table 1**. Obviously, the much better prediction is from MD results consisting with the experimental observations[5], while the correlation method provides a surprising deviation.

The local conformational flexibility of polymer chains plays a more important role in glass transition temperature. The bridging group provides the flexibility of chains that decreases the T_g. Using the molecular mechanics, we investigated the heights of

* E-mail: yangx@pplas.icas.ac.cn

the rotation barriers of the bridging bonds labeled as *ϕ1*, *ϕ2*, *ϕ3*, and *ϕ4* shown in **Figure 1**. Two different kinds of bonds at this site in PI3 are labeled as *ϕ3* and *ϕ4*. The optimized heights of the rotational barrier for these four bonds are 0.98, 4.43, 1.74, 1.81 kcal/mol, which are in the same order to their T_g values. This result may encourage one to increase the barrier height to enhance T_g. A new structure PI4 is therefore designed by substituting two phenyl groups for the two hydrogen atoms of the bridging bond of PI1. Using the MD simulation, the Tg of PI4 is found to be 612K. The relation between rotational barrier and Tg was proven validated. So the design was found efficient for the polymers with high T_g.

Figure 1 The structure of PI1, PI2, PI3

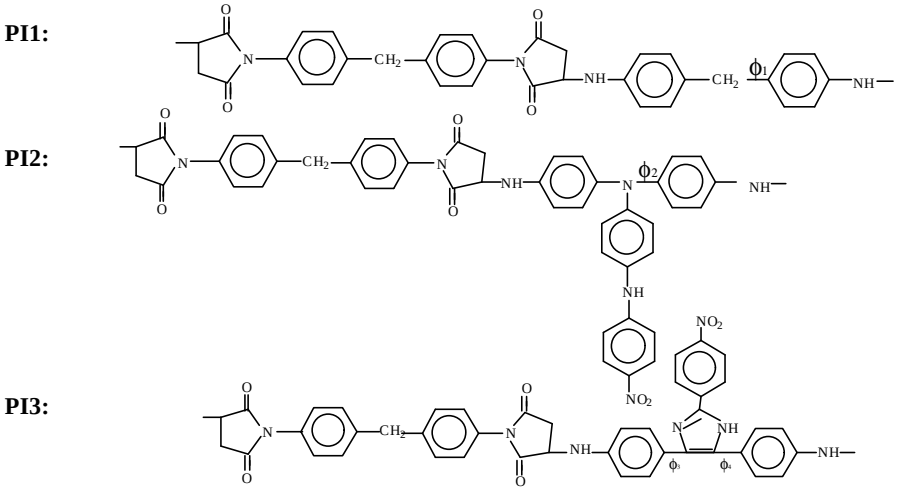

Table 1 Glass transition temperature by means of MD simulation, correlation prediction and experiment

	T_g (MD simulation)	T_g (Correlation method)	T_g (Experiment)
PI1	563 K	468 K	549 K
PI2	601K	460 K	597 K
PI3	549 K	467 K	535 K

Acknowledgments

This project has been supported by the National Natural Science Foundation, China Special Funds for Major State Basic Research Project (G1999064800). The authors wish to thank Prof. Ye Cheng for providing the experiment data.

References

1. R. H. Boyd, *Trends Polym. Sci.*, **1996**, *4*, 12.
2. R. J. Roe, *Computer Simulation of Polymer,* Prentice Hall, New Jersey, **1991**.
3. T. Liang, Y. Yang, D. Guo, X. Yang, *J. Chem. Phys.*, **2000**, *112*, 2016.
4. J. Bicerano, *Predictions of Polymer properties*, Marcel Dekker: New York, **1993**.
5. C. Wang, C. Zhang, P. Wang, P. Zhu, *et al. Polymer*, **2000**, *41*, 2583.

Received 10 January, 2001