



## Molecular simulations of fragility of linear and ring polymers



Yijing Nie, Xubo Ye, Xiaoyan Qiu, Tongfan Hao, Rongjuan Liu, Zhiping Zhou\*, Ya Wei, Zhouzhou Gu, Wenming Yang, Songjun Li

Institute of Polymer Materials, School of Materials Science and Engineering, Jiangsu University, 301 Xuefu Road, Zhenjiang 212013, China

### ARTICLE INFO

#### Article history:

Received 2 May 2017

Received in revised form 1 September 2017

Accepted 3 October 2017

#### Keywords:

Monte Carlo simulations

Fragility

Ring polymer

Glass transition

### ABSTRACT

Nowadays, investigation on fragility in glass-forming liquids is a hot topic in the field of condensed matter physics, since the understanding of its microscopic mechanism is useful to uncover the underlying mechanism of the glass transition. In the present paper, we performed dynamic Monte Carlo simulations to explore the correlations between fragility index and conformational changes in linear and ring polymer chains. Compared with ring chains, linear chains exhibit a higher fragility index. In addition, for both ring and linear chains, during approaching the glass transition temperature ( $T_g$ ), the fraction of segments with trans-conformation increased significantly. To reveal the effect of conformational changes on segmental dynamics during relaxation, a new parameter, the aggregation region of segments with trans-conformation (ARST), is proposed. The maximum ARST has the lowest mobility, which determines the relaxation time of polymers. The fragility index has a strong relationship with the maximum ARST. For linear chains, during approaching  $T_g$ , the maximum ARST grew more abruptly, resulting in the larger fragility index.

© 2017 Elsevier B.V. All rights reserved.

### 1. Introduction

The glass transition is an important feature of amorphous materials [1]. Large changes occur in mechanical properties, volume characteristics, thermodynamic properties and electrical properties of polymer materials near the glass transition temperature ( $T_g$ ), which have a significant impact on the applications of polymer materials. Therefore, the glass transition is still an important research topic in polymer science. In the past 50 years, scientists have established several theoretical models for the glass transition [2–7]. However, all the theories have limitations. There is still insufficient understanding of the physical nature of the glass transition mechanism [8–12].

In 1985 Angell proposed the concept of “fragility”, which can be used to characterize how quickly transport coefficients or relaxation times increase with the decrease of temperature ( $T$ ) in a glass-forming system [7]. As the glass transition temperature is approached, some liquids show a strongly non-Arrhenius temperature dependence, and are considered as “fragile” liquids [7]. Specifically, the deviation from the Arrhenius temperature dependence is traditionally quantified by the fragility index  $m$ , which is the slope of  $\log \tau$  vs.  $T_g/T$  at  $T_g$  [1]

$$m = \left. \frac{d \log \tau}{d(T_g/T)} \right|_{T=T_g} \quad (1)$$

where  $\tau$  is the relaxation time.

Nowadays, it is widely accepted that fragility is closely correlated with the microscopic mechanism of the glass transition [7,13–17]. In other words, understanding of the microscopic mechanism of fragility is important for a full comprehension of the mechanism of the glass transition. Up to now, numerous researches have been carried out to investigate the relationships between fragility and the glass transition [14–26]. Theories to explain fragility are, for example, dynamic and thermodynamic theories [3,18,19,27], potential energy map [3,28–31], and mode coupling theory [32]. However, some questions about fragility still exist and wait for solution. For instance, to which phenomenon is fragility connected [20]? Questions like these encourage researchers to make further efforts on fragility.

In liquids, structural relaxation time exhibits a simple Arrhenius behavior when the temperature is high. However, at lower temperatures, the relaxation time increases much faster than that predicted by the Arrhenius law. This means that the apparent activation energy of the structural relaxation increases during cooling toward  $T_g$ . Following the Adam–Gibbs theory [3], many researchers ascribe this non-Arrhenius temperature dependence of relaxation time to a significant increase in molecular cooperativity involved in the structural relaxation.

\* Corresponding author.

E-mail address: [zhouzp@ujs.edu.cn](mailto:zhouzp@ujs.edu.cn) (Z. Zhou).

Many experiments [18–23] and simulations [24–26] have been carried out at temperatures near the glass transition to reveal the relationship between fragility and cooperativity. Unfortunately, a unified answer has not been achieved. Some studies [19,20,22,24–26] indicated that cooperativity increases with fragility, which is in accord with our intuitive expectation. Based on the bond strength coordination number fluctuation model, Aniya et al. [24] concluded that cooperativity increases with increase of fragility. However, others [18,21,23] stated that a clear correlation does not exist. Hong et al. [18] reported that although fragility of glass-forming liquids is related to cooperativity in molecular motion, the connections between cooperativity length scale and fragility index remain unclear. This contradiction implies that further investigations performed from different points of view are necessary.

Recently, we have performed molecular simulations, including molecular dynamics simulations and dynamic Monte Carlo (MC) simulations, to investigate the micro-structural evolution of polymers during glass transition [33–37]. It was found that conformational transitions occur during cooling [33,35,37]. We demonstrated the existence of a strong correlation between conformational transitions and cooperativity [33,34] and also revealed the key factors determining the distribution of local  $T_g$ s in ultrathin polymer films and polymer nanocomposites [38,39]. In addition, we investigated the effect of chain topology on dynamical heterogeneity [36]. Binder et al. [40] and de Pablo et al. [41] also performed MC simulations to study the polymer glass transition behavior.

Then, some new questions appear. Whether some connections exist between the conformational transitions and fragility? Or what is the molecular structural origin of fragility in polymers? Our previous paper [36] showed that the differences in dynamical heterogeneity between ring and linear polymers can be attributed to differences in their topologies. In this paper, the microscopic mechanism of fragility was studied from the viewpoint of conformational changes. We comparatively study the fragility of ring and linear polymers by using dynamic MC simulations. Linear polymers show a higher fragility index compared with ring polymer. We demonstrated that fragility is closely correlated with the Aggregation Region of Segments with Trans-conformation (ARST). During approaching  $T_g$ , the polymer system that exhibits a faster growth of ARSTs has the higher fragility index.

## 2. Simulation details

In the current paper, on-lattice MC simulations were carried out. Firstly, a cubic lattice box, whose side length was 32 lattice sites, was established. In order to improve simulation efficiency, 512 ring and linear chains were placed into the lattice space, respectively, in which one segment can only be located on one lattice site, and each chain consists of 32 segments. Thus, the occupation density of polymer chains in the lattice space is 0.5 high. Although the linear chain length is the same as the box side length, the values of X-axis, Y-axis and Z-axis parts of mean-square radius of gyration of the relaxed chains ( $\langle R_{gx}^2 \rangle$ ,  $\langle R_{gy}^2 \rangle$ ) and ( $\langle R_{gz}^2 \rangle$ ) are around 4 lattice sites, much smaller than the box side length. Thus, in this condition, the effect of the box side length on the simulation results can be ignored. The simulations of the system with higher occupation density (0.875) were also performed, and the difference in fragility between ring and linear polymers was almost unaffected by the change of occupation density. Therefore, only the simulation results of the systems with the occupation density of 0.5 were displayed. Taking into the account of excluded volume effects, the crossing among bonds was not allowed. In the lattice space, a bond (formed by two consecutive segments) could be oriented along lattice sides or along face diagonals or along body

diagonals, and thus the length of the single bond could be 1 or  $\sqrt{2}$  or  $\sqrt{3}$  lattice sites, as illustrated in Fig. S1a in supporting information. Obviously, the coordination number in our system that contained 3 sides, 6 face diagonals and 4 body diagonals was 26. Two collinear adjacent bonds constitute a trans-conformation; otherwise, the conformation is considered as a gauche-conformation. In order to improve the simulation efficiency and avoid boundary effects, periodic boundary conditions were adopted in the simulation process. In one MC step all the chain segments tried to move once on average. In our system, the chain segment primarily moved in two ways: jumping of a single segment and slipping of partial segments [42]. This micro-relaxation model was used by de Gennes to investigate the  $T_g$  of polymer films [43,44]. A similar motion mode was also adopted to study the structural relaxation in ultrathin polymer films by Hu et al. based on dynamic MC simulations [45,46]. The Metropolis sampling method was used to decide whether the motion can be accepted. The acceptance probability ( $p$ ) of a new state was calculated as follows:

$$p = \min\{1, \exp(-\Delta E/kT)\} \quad (2)$$

$$\Delta E = cE_c + lE_{LJ} + \sum f_i E_f \quad (3)$$

where  $k$  represents Boltzmann's constant,  $E_c$  is the energy change for non-collinear connection of consecutive bonds along the chain, which can be used to reflect the flexibility of chains,  $c$  is the net change of non-collinear connection pairs of consecutive bonds,  $E_{LJ} = 4\varepsilon \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$  is Lennard-Jones potential energy, representing the interactions between all non-bonded segments ( $\varepsilon$  is the characteristic energy potential well,  $\sigma$  represents the lattice spacing considering the excluded volume, and  $r$  is the distance between two segments. The distance can be achieved based on the three-dimensional coordinates of the corresponding two non-bonded segments, as shown in Fig. S1b),  $l$  is the net change of Lennard-Jones interaction pairs between non-bonded segments within the cut-off distance,  $E_f$  denotes the frictional barrier for chain sliding imposed by other neighboring segments, reflecting the frictional effect of local packing density on segmental mobility, and  $\sum f_i$  is the number of neighboring segments around the moving segment along the local sliding diffusion path. In the present simulation, the value of  $4\varepsilon/E_c$  is 1 and  $\sigma$  is 1 lattice site. When the distance between two non-bonded segments was greater than 3 lattice sites, the Lennard-Jones potential energy between them was be ignored. We use  $kT/E_c$  to represent the reduced system temperature (below abbreviated as  $T^*$ ). Ring and linear polymers were relaxed for  $10^6$  MC cycles to prepare an initial equilibrium state at  $T^* = 8$ . After that, the initial equilibrium state was cooled from  $T^* = 8$  to  $T^* = 0.05$  at a rate of 0.01 unit of  $T^*$  per 100 MC cycles.

## 3. Results and discussion

In order to obtain the fragility curves of the ring and linear chains, the  $T_g$ s and the relaxation times at several typical temperatures should be obtained. In our previous paper [33], a new parameter, the probability of segment movement (PSM), was proposed to reflect segmental mobility. PSM was defined as the probability of each chain segment moving to the neighboring vacancy lattice site by jumping or sliding motion in one MC step:

$$\text{PSM} = \min \left[ 1, \sum_{j=1}^n \exp \left( \frac{-\Delta E_{ij}}{kT} \right) \right] \quad (4)$$

where  $n$  is the number of vacancy lattice sites in the neighborhood of the corresponding segments, and  $\Delta E_{ij}$  is the energy change of the system due to the movement of a segment from site  $i$  to site  $j$ .

Download English Version:

<https://daneshyari.com/en/article/7958389>

Download Persian Version:

<https://daneshyari.com/article/7958389>

[Daneshyari.com](https://daneshyari.com)