Influence of Molecular Weight and Shape on Diffusion Coefficients of Small Molecules in Polyethylene Terephthalate

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Abstract: In this study, the diffusion coefficients of 13 kinds of small molecules with molecular weights ranging from 32 to 339 g.mol^{-1} in amorphous PET are calculated based on molecular dynamics (MD) simulation. The results suggest that diffusion coefficient of migrant depends not only the molecular weight but also the shape of migrant molecules. Further, the free volume of polymer matrix is calculated using Connolly surface method. The results show that some small free volume cavities conjoin together and form the larger cavities which facilitate the diffusion of migrant molecules in polymer matrix. The diffusion trajectories suggest that the molecules in first class move actively, but the molecules in class third class move limitedly and the movement mobility of molecules in second class is between that of first class and third class. The diffusion trajectories of small molecules strongly depend on the shape and molecular weight of migrant molecules, which is consistent with the diffusion coefficients.

Keywords: molecular dynamics simulation; diffusion coefficient; molecular weight; molecular shape

1. Introduction

Polyethylene terephthalate (PET) is a kind of excellent barrier material and has been widely used in food packaging engineering. A number of low-molecular-weight substances might migrate from the material into the food when PET packaging material contacts food. Diffusion coefficient is very important for migration models, which represents the migration rate and determines the process of migration dynamics. The experimental determination of the diffusion coefficient is very difficult. The literature has reported a series of sophisticated models for theoretical estimation of diffusion coefficients[1-4], however for non-polyolefin polymers such as PET, it seems not as reliable.

A computer simulation technique based on classical mechanics provides a new way to study the diffusion process. Over the last twenty years the molecular dynamics (MD) simulation technique on the basis of classical molecular mechanics has been widely used for the investigation of diffusion of small molecules in polymers[5-12]. Pavel and Shanks[9] applied the MD simulation technique to study the diffusion of oxygen and carbon dioxide in bulk amorphous PET and related aromatic polyesters and focused on the influence of free volume, temperature and number of

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aromatic rings on diffusion coefficients. Hahn and Mooney[10] investigated phenol diffusion in bisphenol-A-polycarbonate by means of MD simulation and obtained an approximate Arrhenius behavior for the diffusion coefficient. Li et al[11] used MD simulation to calculate the diffusion coefficients of small molecules with molecular weights ranging from 16.04 (methane) to 452.50 (fluocinolone acetonide) Daltons in four amorphous polymers and compared with the experiments in literatures. These studies provided results which agree qualitatively with experimental observations and suggested that MD simulation technique may be useful in obtaining relative diffusion coefficient. It has been recognized that in general the larger molecular weight, the lower its diffusion coefficient.

2. Methodology

However, a precise understanding is lacking for the influence of changes in molecular structure, such as size and shape of molecules, on the diffusion coefficient. For example, at a given molecular weight, linear molecules would diffuse faster than others, spherical molecules being the slowest.

Using MD simulations technique, we decided to measure diffusion coefficients of molecules selected on the basis of their molecular structure and functional groups, including compounds up to molecular weight 339 g/mol. The object of this paper is to reveal the influence of molecular weight and shape of molecules on diffusion.

Figure 1. Polyethylene terephthalate

Figure 2. 13 kinds of small molecules in PET

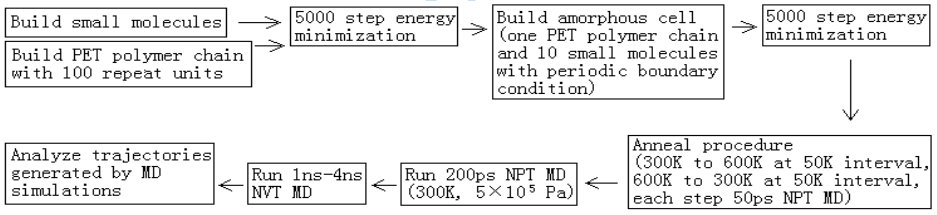

Figure 3. Schematic figure of MD simulation

The structure of PET is shown in Figure 1, and the structures of 13 kinds of small molecules with molecular weights ranging from 32 to 339 g.mol^{-1} in PET are shown in Figure 2. The model building and simulation procedure are similar to the authors' previous studies[13-15]. Here, the schematic figure of MD simulation is only given in Figure 3, and the details can refer to the references[13-15]. When the final NVT (the number of molecules *N*, volume *V* and temperature *T* of the system are kept constant) MD simulation is completed, the atomic trajectory is recorded every 5 ps for the subsequent analysis.

3. Results

The mean-squared displacement (MSD) curves for long times are obtained by analyzing the atomic trajectories. MSD curves for 13 kinds of small molecules in PET at different temperatures are shown in Figure 4.

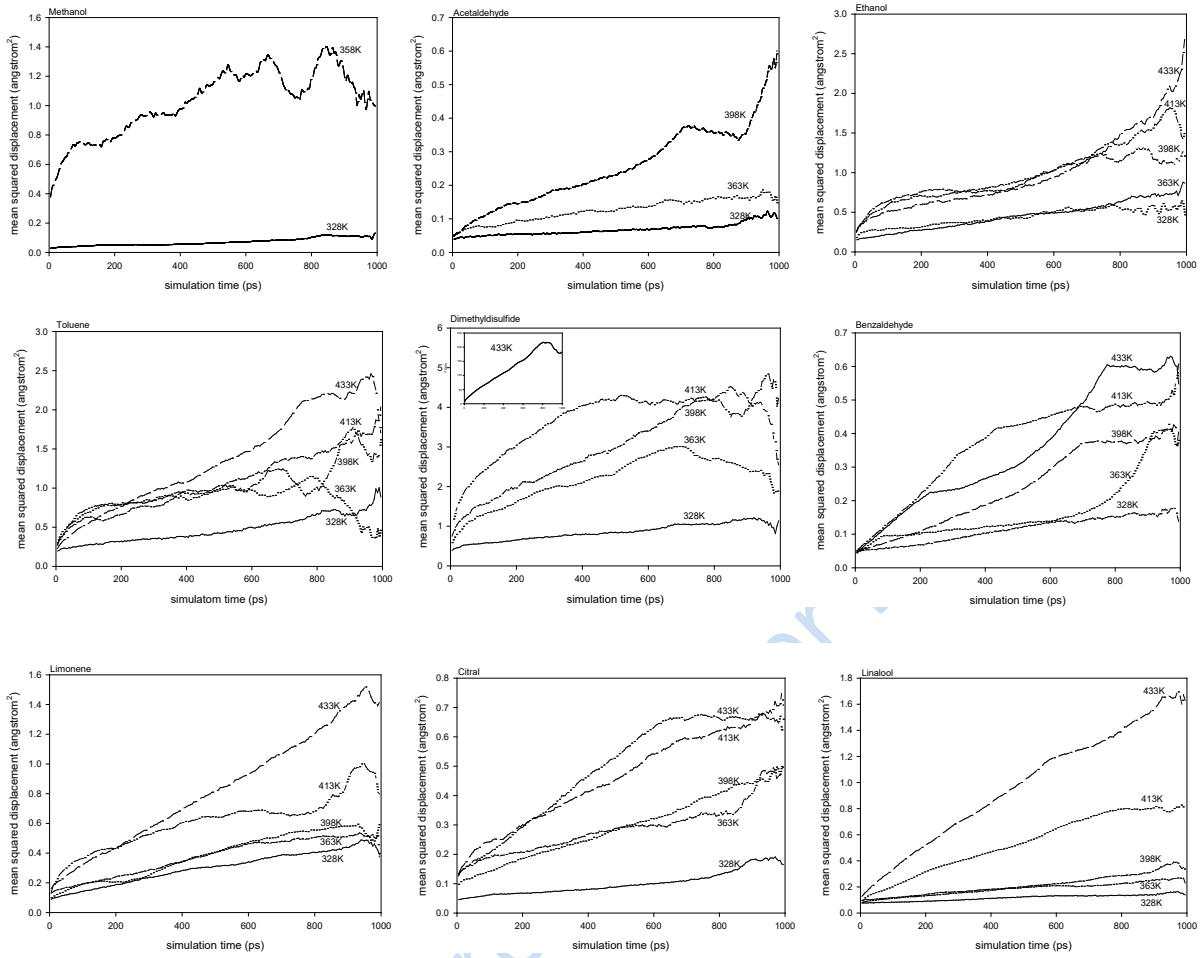

Figure 4 MSD curves for small molecules in PET at different temperatures

It can be observed from Figure 4 that the MSD curves for m-Xylene, limonene, linalool and tetracosane at five temperatures are almost linear, but for other molecules the curves are not satisfactorily linear. In order to obtain perfect linear MSD curves, longer simulation times are required. This may be results from the stronger interactions between the small molecules and the polymer matrix, such as hydrogen bond.

3.1 Diffusion Coefficients

The glass transition temperatures Tg of pure and amorphous PET are about 80°C and 65°C, respectively. Above Tg, polymer segmental motions occur, whereas below Tg, they are frozen. Diffusion of small molecules in a rubbery polymer can be safely calculated by employing MD simulation and invoking the Einstein relation. In this paper, simulation temperatures are all above the Tg of amorphous PET except for one temperature 328K. The diffusion coefficients of small molecules in PET are calculated from the slope of the linear fitting of MSD curves by Einstein relation. The simulated diffusion coefficients are listed in Table 1.

Table 1. Simulated diffusion coefficients (cm^2/s) of 13 kinds of small molecules

Molecules	No	Molecular weight	328K	363K	398K	413K	433K
Methanol	1	32	1.33E-09	8.06E-09			
Acetaldehyde	2	44	7.32E-10	1.61E-09	6.02E-09		
Ethanol	3	46	5.89E-09	5.92E-09	1.07E-08	1.09E-08	1.57E-08
Toluene	4	92	1.52E-09	2.30E-09	2.32E-09	2.45E-09	7.31E-09
Dimethyl disulfide	5	94	1.15E-08	5.05E-08	6.57E-08	1.00E-07	4.06E-06
Benzaldehyde	6	106	1.01E-10	1.16E-10	1.07E-09	2.44E-09	3.88E-09
m-Xylene	7	106	2.59E-10	1.21E-09	3.19E-09	8.85E-09	6.41E-08
Ethyl-butyrate	8	116	3.17E-09	5.01E-09	9.55E-09	1.03E-08	1.15E-08
Chloroform	9	119	7.83E-09	8.28E-09	3.78E-08	3.10E-08	6.37E-08
Limonene	10	136	4.17E-09	4.26E-09	4.39E-09	4.75E-09	2.19E-08
Chitral	11	152	1.58E-09	1.12E-09	3.53E-09	8.21E-09	9.06E-09
Linalool	12	154	1.31E-10	1.43E-10	1.48E-10	5.73E-10	8.95E-09
Tetracosane	13	339	2.52E-09	6.33E-09	1.07E-08	1.13E-08	1.66E-06

Reynier[16-17] defined three different diffusion behaviors: (1) diffusion behavior is the same as that of linear alkanes with the same molecular weight; (2) diffusion behavior is lower than that of linear alkanes with the same molecular weight; (3) intermediate behavior. Molecules behaving as the first class diffusion behavior are linear or approximately linear molecules, the second class molecules are spherical molecules, and the third class molecules have both linear parts and spherical parts. Linear molecules diffuse faster than spherical molecules with the same molecular weight, which has been confirmed. According to the classification, 13 small molecules studied in this paper can be divided such that molecules 1, 2, 3, 5, 8 and 13 belong to the first class, molecules 4, 6, 7 and 9 the second class, and molecules 10, 11, 12 the third class. For molecules 1, 2 and 3, three linear molecules and smallest molecules in this paper, the diffusions are relative to their structures of linear molecules, and the diffusion coefficients by simulation are very close to their corresponding theoretical predictions and experimental values[18]. The molecules 4 and 5, with almost similar molecular weight, have quite different diffusion coefficients and the diffusion of the molecule 5 is much faster than that of the molecule 4 because the molecule 5 is a linear one and the molecule 4 is a spherical one. The molecules 6 and 7 are observed to have almost the same diffusion coefficients, which is probably because they have the same molecular weight and similar shape (spherical molecule). This case also occurs among molecules 10, 11 and 12. The molecular 13, in spite of the largest molecular weight, doesn't show the smallest diffusion coefficient because it is linear alkane and diffuses faster.

3.2 Free Volume

Polymer matrix consists of the occupied volume and free volume. The volume which is not occupied by the matrix atoms is usually defined as "free volume". Free volume plays an important role in the diffusion behavior of small molecules in the polymers. The calculation of free volume adapts the Connolly surfaces methods. The Connolly surface is calculated when the probe molecule with the radius rolling over the Vander Waals surface, and the free volume is defined as the volume on the side of the Connolly surface without atoms. The morphology of free volume is shown in Figure 5.

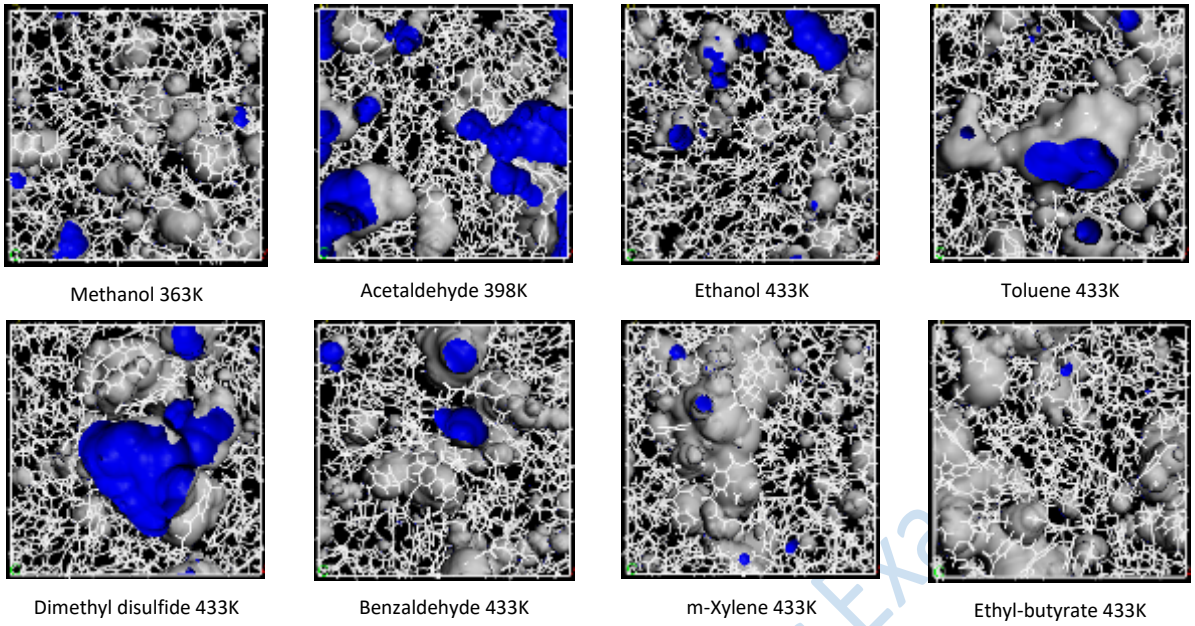

Figure 5. The simulated morphology of free volume: “blue” for high-energy surface and “gray” for low-energy surface of free volume (*to reduce the size of the file, some pictures have been taken out*)

Figure 6 Diffusion trajectories of migrant molecules in packing models during 1ns MD simulation

4. Discussion

The simulated morphology consists of many different shapes and size free volume cavities, and these free volume cavities are mutually connected. Some of them are connected to flaky area, such as Acetaldehyde, Toluene, Dimethyl disulfide, Limonene, Linalool. When small molecules move into the flaky free volume cavities, they tend to move forward rather than coming back and forth, which is available to diffuse from one cavity to another cavity of free volume. The movement of migrant molecules strongly depends on two aspects. One is the properties of free volume, such as the shapes, size, and amount of free volume. Another is temporary channels between adjacent cavities in the polymer matrix. The frequency of temporary channels forming is determined by the mobility of polymer segment. The channel changes faster when the segment moves faster. With the segment movement, some smaller cavities of free volume have more chance to conjoin one larger cavity enough to accommodate the migrant molecule. At the same time the migrant molecule uses temporary channels to diffuse from one cavity to another cavity.

Figure 6 shows the diffusion trajectories of migrant molecules during 1ns MD simulation. The diffusion trajectories of small molecules show the difference of species. The movement trajectories of molecules 1, 2, 3, 5, 8 and 13 distribute very widely, which suggests that the movements of these molecules in polymer are very vigorous. The movement trajectories of small molecules 4, 6, 7 and 9 overlap densely, which suggests that the movements of these molecules in polymer are not vigorous. The movement trajectories of molecules 10, 11, 12 are between

those of the first class and the second class and have a wide range of distribution with some overlap. The diffusion trajectory strongly depends on the molecular shape and weight, which is consistent with the simulated diffusion coefficient.

5. Conclusion

The diffusion coefficients of 13 kinds of small molecules with molecular weights ranging from 32 to 339 g/mol in amorphous PET are calculated based on molecular dynamics simulation. The results suggest that diffusion coefficient of migrant depends not only its molecular weight but also its molecular shape. Connolly surface method is used to calculate free volume of polymer matrix. The results show that some small free volume cavities conjoin together and form the larger cavities which exactly accommodate migrant molecules. Thus, it facilitates the diffusion of migrant molecules in polymer matrix. The diffusion trajectories suggest that the molecules in first class move actively, but the molecules in third class move limitedly. The movement mobility of molecules in second class is between that of first class and third class. The diffusion trajectory of small molecules strongly depends on the shape and molecular weight, which is consistent with the simulated diffusion coefficient.

6. References

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7. Acknowledgments:

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