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Effect of tacticity of PMMA on gas transport through membranes: MD and MC simulation studies

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Abstract

The effects of tacticity of poly methyl methacrylate (PMMA) on the morphology and size distribution of free volume and gas molecules transport through PMMA matrix were conducted by molecular simulation techniques. How the spatial structure of PMMA affects the glass transient temperature T_g of stereoregular PMMA membranes and the solution and diffusion mechanisms in the stereoregular PMMA membranes were conducted by molecular simulation techniques and were compared with experimental data. The polymer chains conformation, gas diffusion mechanism, the time course of the accessible free volume, free volume size distribution, free volume morphology and glass transient temperature, in the various stereoregular PMMA were obtained by a molecular dynamics simulation technique, while the gas solubility in different stereoregular PMMA was calculated by a Monte Carlo technique. A comprehensive comparison of the physical and transport properties of the stereoregular PMMA membranes between simulated and experimental results are provided based on a microscopic interpretation of chain flexibility, free volume morphology and size distribution of free volume in the stereoregular PMMA membranes and gas molecule transport mechanisms through the stereoregular PMMA membranes.

Keywords: Free volume; Diffusion; Molecular dynamics simulation; Monte Carlo simulation; PMMA membrane; Sorption; Tacticity

1. Introduction

Gas separation has become a major application of membrane technology during the past two decades. In the next five years, gas separation by selective permeation through membranes is still one of the fastest growing segments of the membrane processes [1]. Polymeric membranes play a vital role in the membrane-based separation processes, such as oxygen enrichment, nitrogen purification, natural gas treatment, hydrogen separation and carbon dioxide recovery. The polymeric membranes for gas separation can be comprised from a variety of polymers, such as polyimide, polysulfone, polysiloxane, poly ether-ether-ketone (PEEK), or poly methyl methacrylate (PMMA), etc. In recent years, some of the research efforts on the development of polymeric membrane for gas separation have been focused on the conformations of polymeric chains and related interactions of the matrix. For instance, stereoregular conformation of polymeric membranes has been regarded to be one of the predominant factors affecting the membrane permeability.

Previous research on the tacticity of PMMA can be divided into two categories of experimental and simulation approaches. In the experimental approach, syntheses of stereoregular PMMA membranes [2–5], vibrational spectra of stereoregular PMMA [6–8], stereostructure effect on glass transition temperature properties [9,10] and free volume size distribution probed by using PALS [11–13] and the photochromy method [14] were the main issues. In order to examine the effects of spatial structure of PMMA on the transport [2,3] and permeation [4] of small molecules, various stereoregularity of PMMA stereocomplexes have been synthesized. Pilcher and Ford [5] used the cationic surfactant as emulsifier and investigated the structure and properties of

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the PMMA microlatex. They used a microemulsion process to analyze the rich syndio-PMMA (s-PMMA) component in the solution. Allen et al. [6] studied the rotational barriers of α-methyl group in stereoregular PMMA by NMR and Neutron and reported that the energy of α-methyl dihedral angle barrier is 32 and 23 kJ/mol in s- and i-PMMA, respectively. This experimental result has later been elucidated by Koinuma et al. [15] using a statistical mechanical method which consists of conformational analysis of the polymer chain and shielding calculation. Bywater and Toporowsky [9] showed the relationship between T_g and matrix interaction. Grohens et al. [10] found s-PMMA content to be the major parameter on glass transition temperature T_g property of the polymer. Consolati et al. [11] have reported the time dependence of free volume distributions and sizes or shapes of free volume variation from positron annihilation lifetime spectrum experimental data. Although there are some experimental methods to conduct the variances in free volume of membrane, such as PALS, and the photochromy method, the morphology of free volume and diffusion mechanism of gas molecule is still unknown. Soldera and Grohen [12] proposed that the relationship between the effect of the tacticity on the free volume and the T_g variance of PMMA membranes existed. Wright and Paul [16] indicated the α-methyl side chain group appeared to be more effective for hindering backbone motion, and the carboxylate ester side chain will disrupt polymer chain packing.

In the past decade, it was pointed out that the applicable and successful development of theory and high-performance computing [17] on molecular simulation enabled the matrix interaction study to be carried out by the molecular dynamics (MD) simulation technique. MD simulation includes both molecular mechanics (MM) and quantum mechanics (QM) league. The molecular mechanics suitable for the membrane structure simulation is attributed to the lack of chemical reactions and lower calculating cost [18]. The use of the *pcff* force field on a polymeric simulation is also validated by Soldera and Grohens [12]. The force constants in the *pcff* and *cff91* force fields are corrected with proper quantum mechanics data [19–21]. In the *pcff* force field, the inclusion of inner gases and rare metal force constants can be found. As the apparent macromolecular interaction function in the force field exists, the *Lennard-Jones 12-6* potential function must be replaced with the *9-6* potential function (or *Lennard-Jones 9-6* potential function) [22]. Molecular simulation research of gas diffusion through membranes has also been reported. Smit et al. [23] reported the jumping and trapping mechanisms of carbon dioxide in polyimide matrices. Tocci et al. [24] showed the dominant jump motion of N_2, O_2 and H_2 molecules inside the PEEK membrane. However, despite the application of molecular simulation on a polymeric membrane (Sok et al. [25]; Krishna Pant and Boyd [26]) and the successful development of a molecular mechanism in a polymeric membrane (Sun et al. [20]), the physical meanings of the differences between gas transfer mechanisms exhibited by various tacticities of PMMA are not fully understood. According to the solution–diffusion model, the performance of a separation membrane is defined as being permeable. The crucial factors on permeability of a separation membrane are diffusivity and solubility measurements. For the improvement of diffusivity, a great amount of free volume or cavities are promoted in the membrane. Hofmann et al. [27] discussed the transport of small molecules and the dynamic behavior of free volume in rubbery and glassy polymers. Hofmann et al. [28] also used a novel technique V_connect and R_max for analyzing the free volume size distribution by using molecular simulation. Recently, Lu and Tung [29] simulated the time course of the free volume size variation in the various stereoregular PMMA by a MD simulation technique with an emphasis on examining the chain flexibility, chain interaction and end-to-end distance of a chain. Simulation results depict that the less flexibility and longer end-to-end distance in the s-PMMA matrix causes the shapes and sizes of s-PMMA free volume to be longer and larger than those in an i-PMMA membrane. Nevertheless, how the morphology of free volume in PMMA membranes will affect the gas transport as well as the performance of the membrane is still not fully revealed.

In this study, the effect of tacticity of PMMA on the morphology and size distribution of free volume and gas molecules transport through PMMA matrix were conducted by molecular simulation techniques. By adopting conformation energy minimization and molecular dynamics simulation techniques, various tacticity models of PMMA were constructed and their effect on the trajectories of gas molecules movement was analyzed. How the effects of spatial structure of PMMA on the diffusion and sorption of oxygen molecules in PMMA membranes were conducted using molecular dynamics simulation and Monte Carlo (MC) simulation method, respectively. Finally, the simulated diffusion and solubility coefficients were compared with the experimental values to verify the validity of the MD and MC simulation and the reliability of the simulation.

2. Theoretical models

In this theoretical study, both molecular dynamics simulation and Monte Carlo simulation methods were adopted to analyze how the spatial structure of PMMA will affect on the diffusion and sorption of oxygen molecules in PMMA membranes, respectively. Firstly, three types of membrane matrixes were generated for calculating the T_g values of the membranes and diffusivity and solubility of gas molecules in the membranes. As indicated in Fig. 1, 10 amorphous cells (TsM1–5/TiM1–5) were constructed for the estimation of the T_g values of s- and i-PMMA membranes. In order to estimate the gas diffusivity in various spatial structures of PMMA membrane, another 10 amorphous models (AsM1–5/AiM1–5) were also constructed. All atoms in amorphous model were defined by using *all-atoms* model. Furthermore, the interface cells (IsM1–5/IiM1–5)