Supporting Information

Synthesis of polyimides containing Tröger's Base and triphenylmethane moieties with tunable fractional free volume for CO_2 separation

Xiaochen Xu, Jie Dong*, Xiuting Li, Xin Zhao, Qinghua Zhang*

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, P. R. China

*Corresponding author: dj01@dhu.edu.cn, qhzhang@dhu.edu.cn

Atomistic simulation protocol. In this paper, the establishment of molecular cell, adsorption and analysis of copolyimides with CO_2 were completed by Material Studio 6.0 software (MS) based on the previous reports [1-3]. The binding energy between TPM-derived structures and CO_2 molecules was calculated by Gaussian 09W software. The specific operations were as followed:

1. Establishment of amorphous cell

In this step, four kinds of copolyimides were simulated, and Compass II force field was selected for molecular optimization and kinetic simulation. Ewald mode was used to calculate electrostatic interaction, and atom based method was used to calculate van der Waals force. The amorphous cell was shown in Figure S1.

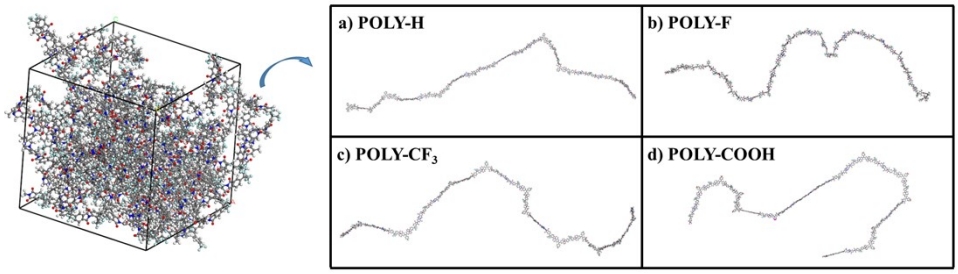

Figure S1. Probable chain conformation of copolyimides resulted by molecular

simulation.

Firstly, the molecular chain of the corresponding copolymer was established and optimized by MS. In order to ensure the accuracy of simulation and shorten the calculation time as much as possible, the designed molecular chain length was set to one fifth of the actual measured molecular weight. Amorphous cells including 10 molecular chains were established after further geometric optimization. In order to avoid the problems of ring chain and fork branch, the initial density of the simulation unit is then set to 0.1 g/cm. According to the literature [4], the forcite module was used to perform the following steps to optimize the model:

I. Calculate 10 ps at high temperature (800 K) and high pressure (0.5 GPa) under NPT (fixed molecular number, pressure, temperature) ensemble to make the density of amorphous cells close to the actual density;
II. Annealing at 598 K and 298 K for 20 ps under NVT (fixed molecular number, cell volume, temperature) ensemble;
III. Under normal temperature (298 K) and pressure (0.0001 GPa), let the cell relax for 20 ps under NPT ensemble until the cell density remains stable;
IV. Continue to relax 300 ps under NVT ensemble to stabilize the amorphous cell.

2. Molecular dynamics simulation and free volume calculation

After establishing the appropriate model, the free volume fraction (FFV) was estimated by Monte Carlo (MC) simulation. The probe was randomly inserted into the simulation unit. If the probe did not overlap with any polymer atom, the insertion was considered successful. The ratio of successful inserts to the total number of inserts gave the FFV. In this study, the probe radius used was 1.0 Å.

3. Radial distribution function (RDF) and binding energy between CO_2 molecules and TPM-derived structures

RDF and binding energy were commonly used to measure intermolecular interactions. The specific optimization and analyze processes were as followed: firstly, sorption module in material studio was used to introduce 300 CO_2 molecules

into the three amorphous cells of POLY-H, POLY-F, POLY-CF_3 and POLY-COOH. The NPT ensemble was used to calculate 300 ps at 0.0001 GPa and 298 K to stabilize the whole cell. NVT ensemble was then used to calculate the RDF between CO_2 molecules and TPM-derived structures. The binding energy between CO_2 and bulky TPM-derived structures was calculated by using M062M energy level in Gaussion 09W and the optimized positions with the lowest energies could be obtained.

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[2]. Ghasemnejad-Afshar, E.; Amjad-Iranagh, S.; Zarif, M.; Modarress, H. Effect of side branch on gas separation performance of triptycene based PIM membrane: A molecular simulation study. *Polym. Test.* **2020,** *83*, 106339.

[3]. Fang, W.; Zhang, L.; Jiang, J. Gas permeation and separation in functionalized polymers of intrinsic microporosity: A combination of molecular simulations and ab initio calculations. *J. Phys. Chem. C* **2011,** *115* (29), 14123-14130.

[4]. Heuchel, M.; Hofmann, D. Molecular modelling of polyimide membranes for gas separation. *Desalination* **2002,** *144* (1-3), 67-72.

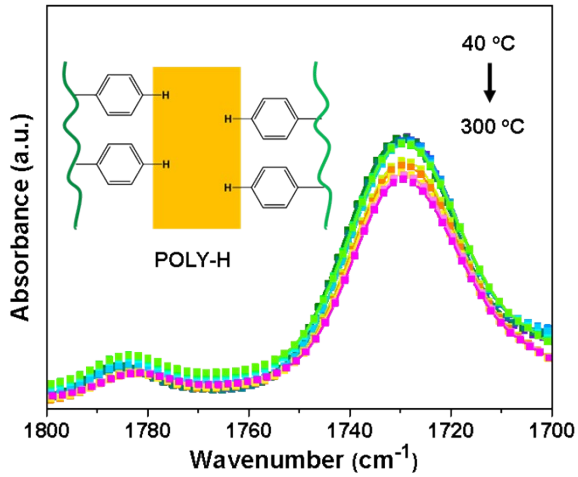

Figure S2. Temperature-dependent FTIR spectra of POLY-H upon heating from 40 to 300 °C