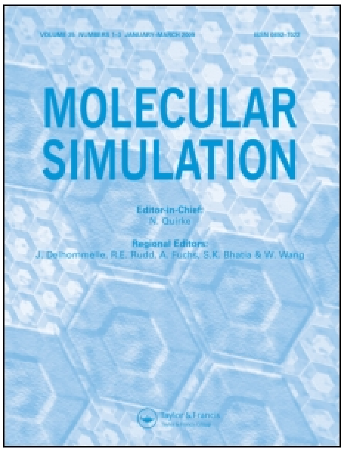

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# Sorption Mechanism of Aromatic Molecules in the Interface between Liquid and Polymer Crystal

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# Sorption Mechanism of Aromatic Molecules in the Interface between Liquid and Polymer Crystal

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**A molecular dynamics simulation was performed for the interface between liquid benzene and the $\delta$ form of crystalline syndiotactic polystyrene in order to investigate the sorption–desorption mechanism of the aromatic molecules in the $\delta$ form. In the single crystal of the $\delta$ form, no translational diffusion of benzene was observed. In the crystal/liquid interface, on the other hand, the sorption of the benzene molecules was observed. Sorption is likely to occur on the (1 0 0) surface rather than the (0 1 0) surface. It was found that the ordering of the liquid on the surface of the polymer crystal plays an important role in the sorption mechanism.**

*Keywords*: Crystal; Sorption; Polystyrene; Molecular dynamics; Simulation

## INTRODUCTION

Syndiotactic polystyrene (s-PS) (Fig. 1) is known for the complex polymorphic behavior, as a consequence of its stereo-regularity [1,2]. The $\delta$ form of crystalline s-PS is a clathrate molecular compound with various solvents, e.g. toluene [3], iodine [4] and 1,2-dichloroethane [5]. The emptied $\delta_e$ form [6] can be obtained by the extraction of the solvent molecules from the $\delta$ form. The $\delta_e$ form is rather stable below 400 K and is transformed into the $\gamma$ form at higher temperatures [7,8]. The stability of the $\delta_e$ form and the structural phase transition from the $\delta_e$ to $\gamma$ forms were investigated by a molecular dynamics (MD) simulation in our previous study [9].

The density of the $\delta_e$ form ($0.977\,g/cm^3$) [6] is significantly lower than that of the amorphous s-PS ($1.045\,g/cm^3$). This implies the existence of large cavities in the crystal. Both experimental and simulation studies have been performed to clarify the cavity structures in the $\delta_e$ form [10–12]. A more detailed and precise study of the cavity structures in the polymorphs of s-PS, using the MD simulation, was reported in our previous paper [13]. Cluster analysis of the free volume in the $\delta_e$ form clearly reveals the cavity structures; large individual holes are in an orderly manner connected by narrow channels. We call such a cavity structure a molecular cavity. The smart membranes, which have a precisely controlled molecular cavity, may be used as high-performance separation membranes. For example, *p*-xylene is preferentially absorbed from the mixed solvents of *m*- and *p*-xylene, which are chemically alike, by membranes containing the $\delta_e$ form crystal [14].

The understanding of the sorption–desorption mechanism of the organic solvents and gases in the $\delta$ form is essential in order to apply the s-PS crystal to the separation membranes. In this study, MD simulations have been performed for the interface between liquid benzene and crystalline s-PS in order to investigate the sorption–desorption mechanism of the aromatic molecules in the $\delta$ form. The sorption phenomenon of the small molecules into the crystals is much interesting also from the standpoint of the fundamental science because it is contrary to the common wisdom that the polymer crystals are virtually impermeable to the gas transport.

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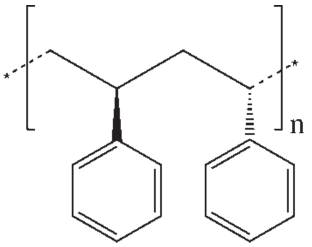

FIGURE 1 Molecular structure of s-PS.

## SIMULATION DETAILS

### MD Simulation

The procedure for the MD simulation is the same as that used in previous studies [9,13,15,16]. The bonded interactions of the bond angle, torsion angle and improper torsion angle and the nonbonded interactions of Lennard–Jones and Coulomb were included in the potential function. The bond lengths were constrained by the SHAKE method [17]. The potential parameters were taken from the all-atom force field, AMBER [18]. The weak partial charges were assigned only to the aromatic hydrogen (+0.085e) and aromatic carbon which is bonded to the hydrogen (−0.085e), following the *ab initio* calculation of Smith *et al.* [19]. The potential parameters of the noble gases were taken from the literature [20]. The long-range nonbonded interactions were smoothly cut off at 14 Å. Temperature and pressure tensors were controlled by the Nosé [21] and Parrinello–Rahman [22] methods, respectively. The equations of motion were solved by a variant of the Verlet algorithm [23,24] with a time step of 1 fs, which is sufficiently short for the conservation of the Hamiltonian.

A cluster machine with 28 processors (Pentium 4 and Xeon) was used for the simulation along with the molecular simulation program PAMPS [25,26] coded and developed by one of the authors (Y. Tamai).

### Single Crystal Model

The initial structure of the $\delta_e$ form was generated on the basis of an X-ray diffraction experiment [6]. The space group is $P2_1/a$ and the main chain conformation is TTGG. The atomic coordinates are generated from the fractional coordinates of atoms in a asymmetric unit, which are listed in the paper [6], according to the space group symmetry [27]. An MD unit cell contains $3 \times 4 \times 6$ crystal units. The three-dimensional periodic boundary condition was applied. The crystal was modeled as a single crystal in which the monomer units are infinitely connected along the *c*-axis. The MD simulations were performed for 150 ps at 300 K under ambient pressure. As for the single crystal model, all the edge lengths and the angles between the edges were allowed to fluctuate. The crystal structure of the $\delta$ form, which is the complex with benzene, was also obtained similarly.

### Interface Model

The interface model was constructed by elongating one of the crystal axes approximately two times and filling the vacant space with liquid benzene (Fig. 2). The number of benzene molecules is 576; the total number of atoms in the unit cell is 16,128. We simulated the two crystal/liquid interfaces, i.e. the (1 0 0) and (0 1 0) faces, which were obtained by elongating the *a*- and *b*-axes, respectively, 2.2 times. The MD simulation was performed under the constant NPT condition. To prevent any unusual deformation of the unit cell, which is usually caused by the flexibility of the liquid region, only the edge lengths were allowed to fluctuate; the angles between the edges were constrained. After the equilibration run of 0.3 ns, the MD simulation was performed for 5 ns at 300 K.

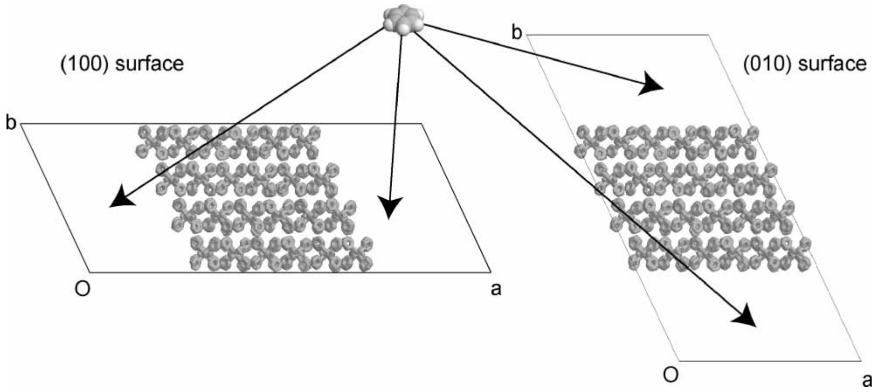

FIGURE 2 Schematic representation of the modeling procedure of interface between the s-PS $\delta$ form and liquid benzene.

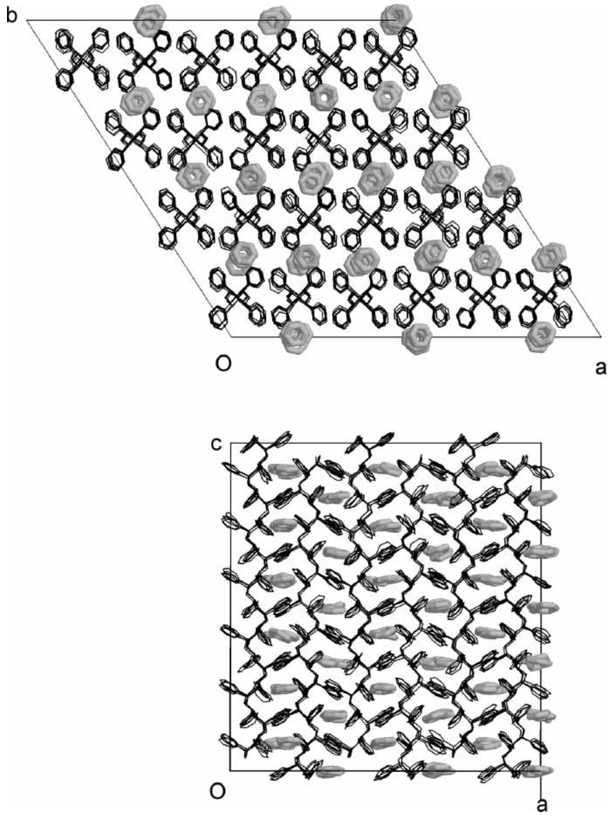

FIGURE 3 Snapshot of the s-PS $\delta$ form with benzene. Polystyrene and benzene are indicated by black lines and gray bonds, respectively. Only the carbon atoms are shown for simplicity. The polymer main chains are infinitely connected along the *c*-axis.

## RESULTS AND DISCUSSION

### Crystal Structure

The crystal structures of the $\delta$ and $\delta_e$ forms were stable during the simulation runs. The snapshot of the $\delta$ form is shown in Fig. 3. The benzene molecules are clathrated in the s-PS crystal. The densities and the lattice constants obtained from the simulation are listed in Table I, compared with the experiments. The experimental values were satisfactorily reproduced by the simulation. Therefore, the application of the present model to the simulation of s-PS crystals is justified.

TABLE I Density and lattice constants of s-PS crystals

| *Crystal* | *$\rho$ (g/cm$^3$)* | *a (Å)* | *b (Å)* | *c (Å)* | *$\gamma$ (deg.)* |
|---|---|---|---|---|---|
| *Simulation* | | | | | |
| $\delta$* | 1.075 | 17.51 | 13.34 | 7.75 | 122.4 |
| $\delta_e$ | 0.959 | 17.38 | 11.74 | 7.81 | 115.0 |
| *Experiment* [3,6] | | | | | |
| $\delta^\dagger$ | 1.11 | 17.58 | 13.26 | 7.71 | 121.2 |
| $\delta_e$ | 0.977 | 17.4 | 11.85 | 7.70 | 117 |

*Complex with benzene. †Complex with toluene.

### Mobility in Single Crystal

The mobility of small molecules in the single crystals of the $\delta$ and $\delta_e$ forms was examined. After the noble gas molecules were inserted in the cavities of the emptied $\delta_e$ form, the MD simulation was performed up to 5 ns at each temperature of 300–500 K. The diffusion coefficients of He, Ne and Ar in the crystal were calculated from the mean-square displacements. The temperature dependence of the diffusion coefficient, *D*, is shown in Fig. 4. The small gases can diffuse translationally. The diffusion mechanism consists of the large-amplitude oscillation in the cavities and the long-distance jumping between the cavities through the narrow channels. The main diffusion path of small gases in the $\delta_e$ form was the (1 0 1) direction. The diffusion along the *b*-axis was also observed, though the jump probability was low.

The mobility of larger molecules, such as benzene, was also examined. As for benzene, no translational diffusion was observed during 5 ns even at the highest temperature 500 K. In order to investigate the reorientational motion of benzene in the $\delta$ form, in which each cavity is occupied by a benzene molecule, the long-time simulation was also performed for the $\delta$ form. Two types of unit vectors, (1) the unit vector along the chord from the $C_1$ to $C_4$ carbons, $\mathbf{u}_\parallel$, and (2) the unit vector perpendicular to the ring plane, $\mathbf{u}_\perp$, were embedded on the phenyl rings of benzene, and time evolution of these vectors were observed. The reorientational relaxation time, $\tau$, was calculated by fitting the time correlation function $C_1(t) = \langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle$ to the sum of the Gaussian and exponential functions. The short relaxation times, $\tau_s \sim 0.5$ ps, were almost constant for all the temperatures, while the main (long) relaxation times, $\tau$, increased by decreasing the temperature. The $\tau$ values are well described by the Arrhenius law, as shown in Fig. 5.

By directly monitoring the orientation of benzene, the reorientational jumping motion of 60°

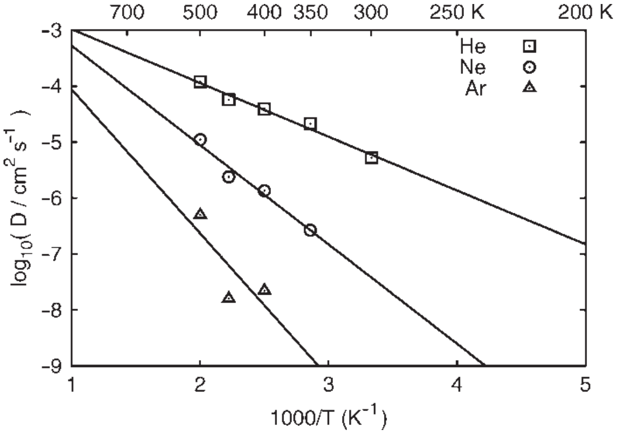

FIGURE 4 Temperature dependence of diffusion coefficient, *D*, of He, Ne, and Ar in the $\delta_e$ form crystal.

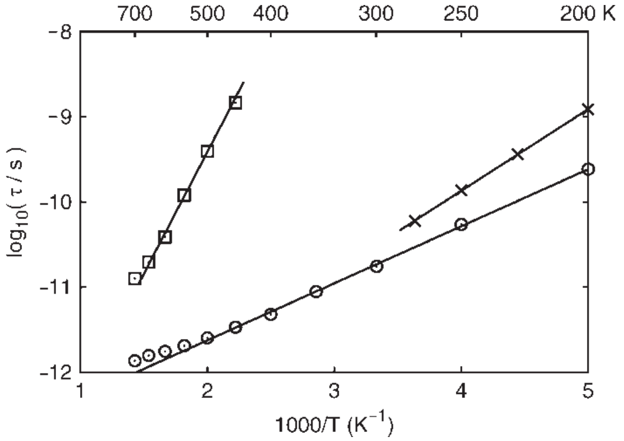

FIGURE 5 Temperature dependence of reorientational relaxation time, $\tau$, of benzene: (square) $\boldsymbol{u}_{\perp}$ in the $\delta$ form, (circle) $\boldsymbol{u}_{\parallel}$ in the $\delta$ form, and (cross) experiment for $\boldsymbol{u}_{\parallel}$ in the solid benzene [30].

cycles about the $C_6$ symmetry axis was observed. This kind of motion is also experimentally observed in pure crystalline benzene [30] and many benzene clathrates [28,29]. The fast reorientation of benzene in the $\delta$ form was also observed in the $^2$H NMR experiment of Trezza *et al.* [31].

The fact that no translational diffusion was observed for benzene contradicts to the experimental results that the aromatic molecules, which are clathrated in the $\delta$ form, can be extracted from the crystal and can be absorbed by the crystal.

## Sorption at Interface

Figure 6 shows the projection of the (1 0 0) interface model on the *a*–*b* and *a*–*c* planes after the MD simulation of 5 ns. In this model, benzene molecules occasionally jumped into the crystal membrane and were trapped in a first layer cavity. The insertion path of benzene in the interface agrees with the diffusion path of the small gases, i.e. the (1 0 1) direction. In order to directly observe the absorption of benzene, an animation was prepared by Quick Time movie (see the Molecular Simulation Website at http://www.tandf.co.uk/journals/titles/08927022.asp). The polymer chains and the benzene molecules are colored light green and orange, respectively. One of the benzene molecules is colored red. The motion of atoms in a cubic region with edge length 20 Å during 200 ps is shown in the movie. The red-colored benzene molecule diffuses around the surface of the crystal. The molecule occasionally jumps into the molecular cavity, after interacting with the two phenyl rings of s-PS.

Figure 7 shows the snapshot of the (0 1 0) interface model, which is projected on the *a*–*b* and *b*–*c* planes. In the (0 1 0) interface, no benzene molecules entered into the crystal region. In the first layer of the liquid phase, the benzene molecules are clearly aligned on the surface of the crystal. This is contrasted to the liquid structure on the (1 0 0) surface, in which the benzene molecules are randomly oriented. The small gases are also able to diffuse along the *b*-axis, though

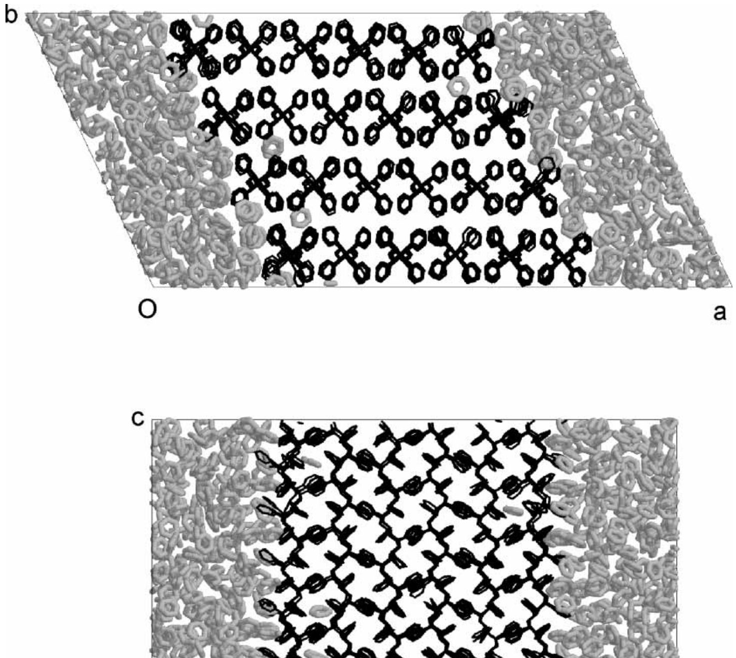

FIGURE 6 Snapshot of the (1 0 0) interface model between the $\delta_e$ form crystal and liquid benzene projected on the *a*–*b* and *a*–*c* planes. The polymer chains and benzene are indicated by black lines and gray bonds, respectively. Only the carbon atoms are shown for simplicity.

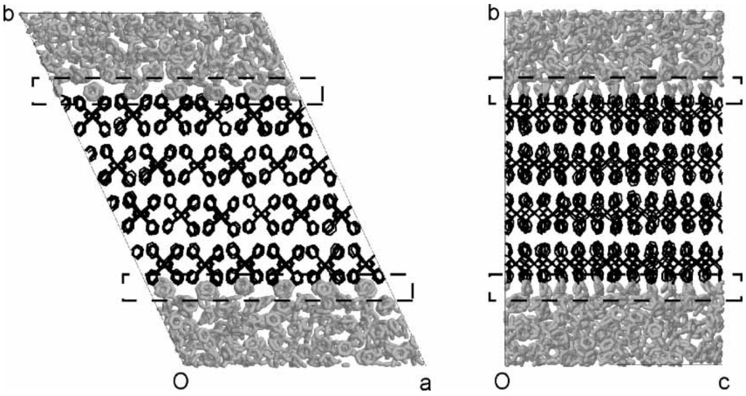

FIGURE 7 Snapshot of the (0 1 0) interface model between the $\delta_e$ form crystal and liquid benzene projected on the $a-b$ and $b-c$ planes. The polymer chains and benzene are indicated by black lines and gray bonds, respectively. Only the carbon atoms are shown for simplicity. The first layer of the liquid is indicated by dashed lines.

the jump probability is low. On the (0 1 0) surface, the benzene molecules are trapped by the polymer chains. The trapped positions are different from the diffusion channels, which are located between two chains. Therefore, the benzene molecules cannot be absorbed by the crystal across the (0 1 0) surface.

The sorption mechanism of the aromatic molecules is summarized below. On the (1 0 0) surface, the solvent molecules are randomly oriented and are faced by the diffusion channels. The benzene molecules can enter into the cavity by the cooperative motion with the polymer chains. On the (0 1 0) surface, on the other hand, the crystal-like order of the liquid is observed. The solvent position does not face the diffusion channels. Therefore, the aromatic molecules are preferentially absorbed on the (1 0 0) surface.

## CONCLUSIONS

In summary, a MD simulation was performed for interface between liquid and s-PS crystal. In the single crystal of the $\delta$ form, no translational diffusion of benzene was observed. In the crystal/liquid interface, on the other hand, the sorption of benzene molecules was observed. The sorption is likely to occur on the (1 0 0) surface rather than the (0 1 0) surface. The ordering of the liquid on the surface of the polymer crystal was found to play an important role on the sorption mechanism. Role of the fluctuation of polymer chains in the crystal and the mobility of benzene molecules in the liquid phase is also of much interest. In order to clarify this, a further study, including the long-time simulation, the temperature dependence and the effect of solvent species, is now in progress.

### *Acknowledgements*

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