Experimental and Simulation Study on the Dissolved Amount and Dissolution Rate of Supercritical CO2 in Polystyrene Melt

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ABSTRACT: The amount of supercritical CO2 dissolved in polystyrene (PS), dissolution rate, and solubility under static conditions at 170–190 °C and 7.5–9.5 MPa were calculated by utilizing volume-changing-method experiments and numerical simulations. By comparison, the instantaneous error can be guaranteed to be less than 15%. The two results are in good agreement, and the reliability of the simulation method is verified. Based on the obtained results, another parameter was added to the tested model, and the dissolution rate of supercritical CO2 in PS under different shear conditions was numerically simulated. The effects of temperature, pressure, and shear rate on dissolution were analyzed. The results show that when the temperature and pressure are constant, the dissolution rate of supercritical CO2 in PS with shear increases significantly compared with that without shear. The conditions that enable the maximum dissolution rate are 190 °C, 9.5 MPa, and a shear rate of 240/π. With the abovementioned pressure and shear rate conditions, the maximum solubility can be obtained under the temperature of 170 °C.

1. INTRODUCTION

Supercritical CO2 has a density similar to liquids and viscosity and diffusivity similar to gases.1 Meanwhile, because of its low price, abundant sources, and environmental friendliness, it can be used as a green alternative to traditional organic solvents. Supercritical CO2 has been widely used in polymer processing, such as extraction of contaminants from polymers,2 supercritical reactions,3,4 CO2-assisted polymer impregnation,5 particle preparation,6 and polymer blending.7 In recent years, the use of supercritical CO2 has attracted considerable attention from academia and industry. During the process of polymer foaming, if the solubility of CO2 in the polymer is known, then the maximum amount of CO2 dissolved in the polymer will be known. Similarly, if the rate of CO2 dissolution is known, then the time to reach the dissolution equilibrium will be known. CO2 dissolved in the polymer also affects the glass-transition temperature of the polymer and the physical properties such as melting point, fluidity, and crystallization behavior. The change of properties is directly related to the solubility of CO2, so the dissolved amount and dissolution rate of supercritical CO2 in polymers are the essential basis for controlling the processing conditions of supercritical CO2 auxiliary polymers.6–10 The key to the foaming process is whether the polymer/CO2 homogeneous phase can be formed in a very short time.11 It needs to be based on a deep understanding of the dissolution process of supercritical CO2 in polymer melts and accurate calculation of the dissolved amount and dissolution rate of supercritical CO2 in the polymer melt. The research on the dissolution of supercritical CO2 in polymer melts is of great significance in both academia and industry. However, the solubility and dissolution data of CO2 in polymer melts for the optional design of the foaming process are lacking.

Solubility and diffusivity data of gases in molten polymers have been investigated by many scholars. Sato12–15 studied the solubility of CO2 in polystyrene (PS), polypropylene, and high-density polypropylene by using the pressure decay method (PDM) at a temperature of up to 200 °C and a pressure range of 2.5–20 MPa. Boyer16 obtained the solubilities of supercritical CO2 in polymer melts with PDM. The study showed that the solubilities of CO2 almost linearly increased with pressure but decreased with temperature. Tang17 discussed the absorption and diffusion of supercritical CO2 in polycarbonate and polysulfone melts through the mass loss method. To avoid the error caused by desorption during sample removal, the quartz crystal microbalance technique18–20 was used instead in the experiment. Because of the shortcomings of the experiment, such as time consumption and high cost, some classical predicting methods have been widely used by some researchers. Chen21 applied the cubic and noncubic state equation to the
dissolution prediction model of the supercritical and subcritical fluids in polymers. Aionicesei\textsuperscript{22} put forward the predictive model for the solubility of supercritical CO\(_2\) in polymers by using the S−L equation of state. Merker\textsuperscript{23} studied the dissolution behavior using the molecular simulation method. Li\textsuperscript{24−27} used the neural network model to predict the solubility of supercritical CO\(_2\) in polymer melts. The existing studies in the literature focus on the solubility of CO\(_2\) in polymer melts, rather than on the whole dissolution process. Besides, all the studies are based on static conditions, which are relatively limited. This article will analyze the dissolution process under shear conditions.

This study has three main objectives. The first one is experimentally studying the dissolution processing of supercritical CO\(_2\) in polymer melts without shear. The experiments of molten PS with a given mass under different gas pressures and temperatures were carried out. In the experiments, the solubility, dissolved amount, and rate of supercritical CO\(_2\) dissolved under different pressures and temperatures are investigated. The second objective of this study is to reveal the amount of supercritical CO\(_2\) dissolved in PS under the conditions of different pressures and temperatures, with the help of the COMSOL simulation method. The third one is ascertaining the effects of pressure and temperature on the process of supercritical CO\(_2\) dissolved in PS under different shear rates with the additional conical shear device.

2. RESULTS AND DISCUSSION

2.1. Experimental Results and Discussion. Compared with the magnetic suspension balance method,\textsuperscript{29,30} the effect of shear rate on the dissolution process can be further studied. Furthermore, the wave of pressure change in the dissolution
process can be avoided compared with the PDM. Based on the analysis of the experimental process of the device, it has the following characteristics: (1) the dissolved amount and dissolution rate can be obtained by recording the change of displacement with time. (2) The dissolved amount and dissolution rate can be measured under different temperature and pressure conditions. (3) In each experiment, multiple groups of dissolution data can be obtained by changing the temperature and pressure of the system, which dramatically shortens the experimental period.

The dissolved amount and dissolution rate under different temperatures at 7.5, 8.5, and 9.5 MPa are shown in Figures 1, 2, and 3, respectively. (a) shows the change of dissolved amount with time, and (b) expresses the variation of the dissolution rate with time.

According to the abovementioned three figures, the following conclusions can be drawn. Dissolution always increases with time until the equilibrium is reached, at which time the dissolved amount reaches its maximum value, which is called solubility. In the early stage of the dissolution process, the dissolution rate is high. With time, the dissolution rate decreases gradually until reaching equilibrium; at this time, it becomes 0. When the pressure is constant, the increase in temperature shortens the time required for supercritical CO2 to reach equilibrium in PS, accelerates the initial dissolution rate, and reduces the solubility of supercritical CO2 in PS melt. When the temperature is invariant, the higher the pressure, the shorter the equilibrium time and the higher the dissolution rate and solubility. The results are consistent with the results in the literature, where the solubility of CO2 in polymers increases with increasing pressure and decreasing temperature.

The phenomena can be attributed to some aspects. First, this tendency can be explained by the plasticizing effect of CO2. By increasing the pressure, the gas molecules are forced between polymer chains, expanding the space between molecules, and thus increasing their mobility. The increased mobility of the chains allows more gas molecules to be absorbed once the pressure is further increased. Second, when the pressure is constant, the increase of temperature leads to the acceleration of the molecular movement rate and enhancement of intermolecular convection and diffusion. In the case of the same difference in the concentration inside and outside the PS, it is easy for CO2 to enter the polymer. The macroscopic feature is that the dissolution rate increases. As time goes on, the concentration difference decreases so that the dissolution rate decreases until reaching equilibrium. The higher the temperature, the stronger the expansion of CO2, the lower the density, the weaker the attraction of the polymer to gas molecules, and the smaller the number of CO2 molecules that can be accommodated in the voids of polymer chains. As a result, the solubility of supercritical CO2 in PS melt decreases. Third, when the temperature is unchanged, the increase of pressure leads to the increase of CO2 density, which makes the CO2 molecule easier to be pressed into the polymer. The result shows that the dissolution rate and solubility increase simultaneously. This conclusion keeps pace with the literature, in which the solubility of CO2 in polymers increases with increasing density at a constant temperature. At the same time, an increase in temperature accounts for a lower gas density, which can be correlated with lower solubility.

2.2 Static Simulation. The dissolution curves at different pressures and temperatures obtained by static simulation are shown in Figures 4, 5, and 6, where (a) and (b) represent the
dissolved amount curve and dissolution rate curve, respectively. By comparison, it can be found that the variation trend of the solubility and dissolution rate with time is consistent with the experimental results. When the pressure is constant, the higher the temperature is, the faster the initial dissolution rate is, but the smaller the solubility is. When the temperature is constant, the higher the pressure is, the faster the initial dissolution rate is, and the larger the solubility is. It also has a good agreement with the experimental result.

The effects of temperature and pressure on the dissolution under static conditions were studied through simulations. The results show that the increase in pressure and temperature can shorten the time needed to reach equilibrium and accelerate the initial dissolution rate. However, for solubility, it increases with the increase of pressure and decreases with the increase of temperature. The simulation results were analyzed, and it was found that the trend of the solubility and dissolution rate with time was consistent with the experimental result.

In order to describe the error between the simulation and experiment of dissolution, the following formula is used to calculate it at the t moment.

\[
\delta_t = \frac{|S_{\text{sim}} - S_{\text{exp}}|}{S_{\text{exp}}} \times 100\%
\]  

(1)

where \(\delta_t\) represents the instantaneous error between simulated and experimental dissolution at t-time, \(S_{\text{sim}}\) is a simulated value of dissolution at t-time, and \(S_{\text{exp}}\) is an experimental value of dissolution at t-time. The instantaneous errors obtained at each time are connected with a smooth curve, and the instantaneous error curves of simulated and experimental values of dissolution are obtained, as shown in Figure 7. Figure 7a, b, and c corresponds to 7.5, 8.5, and 9.5 MPa, respectively. It can be seen that the error between simulated and experimental solubility is significant at the initial stage of dissolution. The reason for the sizeable instantaneous error in the early stage of dissolution can be summarized as follows. At the beginning of
Figure 9. Dissolution curves under different shear rates at 170 °C, 8.5 MPa. (a)—Dissolved amount; (b)—dissolution rate.

Figure 10. Dissolution curves under different shear rates at 170 °C, 9.5 MPa. (a)—Dissolved amount; (b)—dissolution rate.

Figure 11. Dissolution curves under different shear rates at 180 °C, 7.5 MPa. (a)—Dissolved amount; (b)—dissolution rate.

Figure 12. Dissolution curves under different shear rates at 180 °C, 8.5 MPa. (a)—Dissolved amount; (b)—dissolution rate.
Figure 13. Dissolution curves under different shear rates at 180 °C, 9.5 MPa. (a) — Dissolved amount; (b) — dissolution rate.

Figure 14. Dissolution curves under different shear rates at 190 °C, 7.5 MPa. (a) — Dissolved amount; (b) — dissolution rate.

Figure 15. Dissolution curves under different shear rates at 190 °C, 8.5 MPa. (a) — Dissolved amount; (b) — dissolution rate.

Figure 16. Dissolution curves under different shear rates at 190 °C, 9.5 MPa. (a) — Dissolved amount; (b) — dissolution rate.
At present, there is only the comparison of solubility, rather than the instantaneous errors during the dissolution process. The errors between the predicted and experimental values of solubility tend to be between 10 and 20%.

To calculate the error at 12.1% when the temperature was 100 °C, and the error would further expand as the temperature increased. In this experiment, except that the instantaneous error is relatively large at the beginning, the error of dissolution can be maintained within 15% for the rest of the time, which is in good agreement with the experimental result.

2.3. Shear Simulation. The dissolution curves of supercritical CO2 in PS melt at different pressures, temperatures, and shear rates obtained by shear simulation are shown in Figures 8–16, where (a) and (b) represent the dissolved amount curve and dissolution rate curve, respectively. Figures 8, 9, and 10 show the dissolution curve at 170 °C. Figures 11, 12, and 13 show the dissolution curve at 180 °C. Figures 14, 15, and 16 show the dissolution curve at 190 °C.

The dissolution curves under static and shear conditions were compared, and we can conclude that the solubility under shear conditions is the same as the one under static conditions. In other words, increasing the shear force will not affect the solubility of supercritical CO2 in molten PS. However, the most significant advantage of shearing is that the dissolution rate can be greatly improved. Under static conditions, it takes tens of minutes to reach the equilibrium of dissolution. For shear conditions, it only takes a few minutes.

With the increase of shear rate, the dissolution rate of supercritical CO2 in PS melt is also increasing, especially at the initial stage of dissolution. It can be seen that when the shear rate changes from 0 to 60/π, the dissolution rate increases the most obvious. The subsequent dissolution rate increases with the increase of shear rate, but the increase margin decreases. The above phenomena are not accidental. The specific causes can be summarized as follows: PS, as an incompressible non-Newtonian viscous fluid, has the characteristics of shear thinning. Under the action of shear stress, within a certain shear rate range, the viscosity of the polymer decreases rapidly and increases the flowability of the polymer. In other words, it can heighten the entanglement rate of polymer chains, which can accelerate the passage of CO2 molecules therein and make it easy for CO2 to enter PS melt in the direction of the concentration gradient. As a result, the dissolution rate of supercritical CO2 in PS melt is increased. It is not difficult to see from Table 4 that when the shear rate of PS changes from 0 to 60/π, the viscosity increase of PS is enormous. As the shear rate continues to increase, the viscosity of PS also increases, but the difference becomes smaller and smaller, which explains the dissolution rate of supercritical CO2 in PS melt with the increasing shear rate, but the growth trend gradually slows down.

4. EXPERIMENTAL SECTION

4.1. Materials. PS (>99.7% purity, Tg = 108.25 °C, Mw = 105) was supplied by Tai Hua Polystyrene Co. Ltd (Ningbo, China). All the details of PS were given by the supplier. CO2 (>99.5% purity) was obtained from Guohui Gas Co. Ltd. (Nanchang, China). All chemicals were used as received.

4.2. Apparatus and Methods. The dissolved amount and dissolution rate of the gas (supercritical CO2) in the polymer (PS) melt were measured by using the apparatus, which is designed by this group. The measurement method used by the equipment is the volume-changing method.

In this method, the amount of the gas dissolved in the polymer sample is determined from the difference between the initial displacement reading of the piston and the final one after equilibration. To this end, our team developed a set of devices to measure the solubility of supercritical CO2 in polymer melts, as shown in Scheme 1. The experiment is conducted with the temperature range 170–190 °C and the pressure range 7.5–9.5 MPa. The piston pressure vessel and the high-pressure reaction vessel are made in stainless steel with the sizes Φ105 mm × 360 mm and Φ120 mm × 180 mm, respectively, and the maximum pressure that can be reached is 30 MPa. In the heating system, the heating oil is supplied by TAIYAO Chemical Co., Ltd. (Dongguan, China) and can be heated up to 300 °C, and the accuracy of the temperature sensor is ±0.1 °C. The oil bath is controlled by the lifting platform so that the two cells can be heated evenly and flexibly. The accuracy of each pressure sensor and displacement sensor are ±0.01 MPa and ±0.05 mm, respectively.
respectively. The displacement information of the piston is transmitted to the computer via the displacement sensor, and the frequency at which the computer collects the signal is one time/sec.

The main structure of the apparatus is shown in Scheme 2. The piston pressure vessel and the reaction vessel are connected with a pipe with the inflow valve. The temperature of them can be held by the oil bath, and the pressure in the reaction vessel can be kept constant by the movement of the piston. Most important is that these two cells must be well sealed. The principle of this experiment can be described as follows: a certain amount of the polymer sample is placed in cell 2; meanwhile, keep valve 3 between cell 1 and cell 2, valve 4 open, and valves 1 and 2 closed. Cell 1 and cell 2 are evacuated with a rotary pump. Then, close the two valves until the piston reaches the bottom of cell 1. Next, the sample gas (supercritical CO2) is introduced into cell 1, and it will make the piston stay at the top until the pressure reaches a particular value (close valve 2).

At this moment, the amount of substance of supercritical CO2 can be evaluated by the following equation

\[ n_T = \frac{p_i V_i}{zRT} \]  

where \( T, p_i, \) and \( z \) are the temperature, initial pressure, and the compressibility factor, respectively, of the gas at \( T \) and \( p_i \). \( V_i \) is the inner volume of cell 1.

After reaching a certain pressure in cell 1, valve 3 is opened to start the dissolution of gas into the polymer in cell 2. By controlling the upper pressure of the piston in cell 1, the piston moves to maintain the gas pressure constant in cell 2. Supercritical CO2 is dissolved in polymer melts under the circumstances of constant temperature and pressure, and the volume reduction in cell 1, \( \Delta V_1 \), can be achieved by the change of the position of the piston. \( \Delta V_2 \) represents the volume of undissolved CO2 in cell 2, and it can be determined by using the following equation.

\[ \Delta V_2 = V_2 - V_p \]  

where \( V_2 \) is the volume of cell 2 and \( V_p \) represents the volume of the polymer in cell 2.

As a result, the volume of the CO2 dissolved in the polymer under the conditions of pressure \( P \) and temperature \( T \) can be described as

\[ \Delta V = \Delta V_1 - \Delta V_2 \]  

Based on the PVT equation, the amount of dissolved CO2 can be obtained. \( V \) is acquired by the piston displacement through reading the change in the displacement meter in the experiment, so the dissolving amount of CO2, \( S \), is related to the reading, which changes with time.

5. NUMERICAL SIMULATIONS

5.1. Static Model Based on the Transport of Diluted Species. The geometry model and finite element mesh of the static state based on the transport of diluted species are shown in Figure 17. A cylindrical geometry model is established according to the shape of the polymer melt in the cell. The size of the model is consistent with that in experiments, and it is determined by the shape of the reaction vessel and the quality of the polymer. The radius of the model is the same as that of the reaction vessel. The model height can be calculated as follows

\[ h = \frac{m}{\pi A^2 \rho} \]  

where \( m \) represents the mass of the polymer, \( A \) is the radius of the reaction vessel, and \( \rho \) is the density of polymer melt. Given that the model is the shape of the rule, the mesh is constructed by the automatic generation of the physical field control, and in order to improve the accuracy, the mesh unit size selected is ultrafine.

5.2. Shear Model Based on Rotating Machinery and Laminar Flow Module. The mixing element is a cone, as shown in Figure 18; the radius \( B = 50 \) mm and the cone angle is \( 3^\circ \). The design of the mixing element adopts the principle of the cone–plate rheometer, which means when the cone-top angle is tiny (generally less than \( 3^\circ \)), the shear rate in the flow field remains constant. The relationship between the shear rate and the speed of the mixing element is as follows.
For all boundaries, the initial concentration of supercritical CO2 and PS, the concentration of supercritical CO2 after equilibrium, and the fluid velocity field are mainly taken into account. According to the process of dissolution, the initial conditions and constraint conditions are set as follows:

Initial conditions: the initial concentration of CO2 and PS in the geometric model before dissolution is taken as the initial condition, and the upper surface of the geometric model is regarded as the inflow surface of CO2. The initial concentration of CO2 is 0. The initial concentration of PS is determined by the ratio of its mass to its density. In the shear simulation, the initial velocity field is set to 0.

Constraint conditions: concentration is taken as a constraint condition, including the concentration of CO2 and PS after dissolution equilibrium. The concentration of CO2 is calculated by the S–L equation of state for binary mixtures, which is shown in Table 1. As for the concentration of PS after dissolution equilibrium, the concentration of PS is equal to that before dissolution because the amount of PS does not change during dissolution.

5.5. Material Parameters. In the static numerical simulation, the parameters needed include the molar mass of PS and CO2, the density of PS, and the diffusion coefficient of CO2 in PS melt. The molar mass of PS and CO2 are 105 and 44 g/mol, respectively. The densities of PS under different conditions are calculated by the S–L state equation, which is shown in Table 2. The diffusion coefficient of CO2 in PS melt is based on the experiment.37

### Table 1. Prediction Values of the Solubility of Supercritical CO2 in PS by the S–L Equation

| Temperature | 170 °C | 180 °C | 190 °C |
|-------------|--------|--------|--------|
| p MPa       | solubility g g⁻¹ | p MPa       | solubility g g⁻¹ | p MPa       | solubility g g⁻¹ |
| 7.5         | 0.0259 | 7.5     | 0.0236 | 7.5     | 0.0217 |
| 8.5         | 0.0293 | 8.5     | 0.0268 | 8.5     | 0.0246 |
| 9.5         | 0.0328 | 9.5     | 0.0300 | 9.5     | 0.0275 |

### Table 2. Density of PS

| Temperature | 170 °C | 180 °C | 190 °C |
|-------------|--------|--------|--------|
| p/MPa       | ρ/g cm⁻³ | p/MPa       | ρ/g cm⁻³ | p/MPa       | ρ/g cm⁻³ |
| 7.5         | 0.9899 | 7.5     | 0.9838 | 7.5     | 0.9776 |
| 8.5         | 0.9908 | 8.5     | 0.9847 | 8.5     | 0.9786 |
| 9.5         | 0.9917 | 9.5     | 0.9857 | 9.5     | 0.9796 |

Based on the reasonable hypotheses mentioned above, the governing equations are presented as follows by combining the rheology of the polymer process

\[
\frac{\partial C_i}{\partial t} + \nabla \cdot N_i = \nu_i
\]

(7)

\[
N_i = -D_i \nabla C_i + \vec{v} C_i
\]

(8)

where \( N_i \) denotes the diffusion flux, \( \nu_i \) is the number of materials \( i \) produced by the chemical reaction, and \( \vec{v} \) is the fluid flow velocity. No chemical reaction occurs in the simulation process, so \( \nu_i = 0 \). Under static conditions, the dissolution of supercritical CO2 in PS proceeds spontaneously along the direction of the concentration gradient without convection. As a result, \( \vec{v} C_i = 0 \), the equation becomes a continuity one.

According to the convection–diffusion characteristics of polymer melt and gas in rotating machinery and laminar flow module, we propose the following several hypotheses for the numerical simulation. (1) Satisfying all the static assumptions, (2) no wall slip, and (3) the mixing element used in the simulation process provides a constant shear rate. The flow of the fluid is laminar.

The following governing equation shows high performance in combination with the rheology of the polymer process and the equations of the static model

\[
\rho \frac{d\vec{v}}{dt} = -\nabla p + \eta \nabla \cdot \vec{v} + \rho F
\]

(9)

where \( \eta \) is dynamic viscosity of the polymer and \( F \) is an external force on the fluid.

### 5.4. Boundary Conditions. For all boundaries, the initial concentration of supercritical CO2 and PS, the concentration of supercritical CO2 after equilibrium, and the fluid velocity field are mainly taken into account. According to the process of dissolution, the initial conditions and constraint conditions are set as follows:

Initial conditions: the initial concentration of CO2 and PS in the geometric model before dissolution is taken as the initial condition, and the upper surface of the geometric model is regarded as the inflow surface of CO2. The initial concentration of CO2 is 0. The initial concentration of PS is determined by the ratio of its mass to its density. In the shear simulation, the initial velocity field is set to 0.

Constraint conditions: concentration is taken as a constraint condition, including the concentration of CO2 and PS after dissolution equilibrium. The concentration of CO2 is calculated by the S–L equation of state for binary mixtures, which is shown in Table 1. As for the concentration of PS after dissolution equilibrium, the concentration of PS is equal to that before dissolution because the amount of PS does not change during dissolution.
In addition to the abovementioned four parameters, the shear rate of the mixing element and dynamic viscosity of PS are also needed in shear simulation. The shear rate range is 0–4 circles per second. The dynamic viscosity of PS is calculated by using the Cross–Carreau model

$$\eta = \frac{\eta_0}{1 + \left(\frac{\dot{\gamma}}{\dot{\gamma}_c}\right)^{n-1}}$$  \hspace{1cm} (10)

$$\eta_0 = G \cdot \exp\left(\frac{\alpha}{T - T_r} + \beta \rho\right) \hspace{1cm} (11)$$

where $\eta_0$ represents zero shear viscosity of the polymer. $\dot{\gamma}$, $\eta$, $G$, $\alpha$, $n$, $T_r$, and $\beta$ are characteristic parameters of the polymer, as shown in Table 3. The dynamic viscosity of PS is shown in Table 4.

### Table 3. Characteristic Parameters of the Cross–Carreau Model for PS

| $T$ (°C) | $\dot{\gamma}$ (1/s) | $\dot{\gamma}_c$ (1/s) | $\eta_0$ (106 Pa·s) | $\alpha$ (°C) | $n$ | $G$ (104 Pa·s) | $T_r$ (°C) | $\beta$ (1/°C) |
|----------|---------------------|---------------------|---------------------|----------------|-----|----------------|----------------|------------|
| 60       | 60                  | 10                  | 1.2                 | 1.5            | 0.5 | 100            | 100            | 0.1         |
| 120      | 120                 | 10                  | 2.4                 | 3.0            | 0.5 | 500            | 500            | 0.2         |
| 180      | 180                 | 10                  | 3.6                 | 4.5            | 0.5 | 1000           | 1000           | 0.3         |
| 240      | 240                 | 10                  | 4.8                 | 6.0            | 0.5 | 3000           | 3000           | 0.4         |

### Table 4. Dynamic Viscosity of PS

| Shear Rate (°C) | Dynamic Viscosity (106 Pa·s) |
|-----------------|-------------------------------|
| $T = 170$ °C, $p = 7.5 \times 10^3$ Pa | 10.56 |
| $T = 180$ °C, $p = 9.5 \times 10^3$ Pa | 12.31 |
| $T = 190$ °C, $p = 1.1 \times 10^4$ Pa | 14.08 |

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**Author Contributions**

X.H. and M.L. proposed the concept of the paper. S.W. and L.W. conducted experiments. D.W. and W.W. performed the theoretical computations. D.W. and Z.C. analyzed the results and wrote the paper.

**Notes**

The authors declare no competing financial interest.

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