

# Sorption Studies of Volatile Organic Compounds in a Divinyl-Terminated Poly(dimethylsiloxane)-Oligo Polymer

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**ABSTRACT:** The sorption equilibria and kinetics of three volatile organic compounds (VOCs)—benzene, chloroform, and acetone—in a newly developed divinyl-terminated poly(dimethylsiloxane) (PDMS<sup>vi</sup>)-oligo polymer were studied. The PDMS<sup>vi</sup>-oligo polymer was prepared from a hexane solution consisting of PDMS<sup>vi</sup> as the polymer, oligosilylstyrene as the crosslinker, and a platinum-divinyltetramethyldisiloxane complex as the Karstedt catalyst. The sorption uptake of each VOC by the polymer was measured gravimetrically at different VOC partial pressures at a constant temperature and at different temperatures between 24 and 50°C. The rate of VOC sorption was monitored until equilibrium was established. The solubility coefficient increased when the VOC activity increased, and the results revealed that the PDMS<sup>vi</sup>-oligo polymer was a good sorbent for the three VOCs examined. Relatively high solubilities of these VOCs were obtained in this polymer in comparison

with those reported for conventional silicone rubbers. The Flory-Huggins model fit the observed equilibrium sorption isotherms of the benzene and chloroform systems very well, whereas the Koningsveld-Kleinjens variation law had to be combined with the Flory-Huggins model to describe the sorption isotherm of acetone in the polymer film. The rates of sorption of the three VOCs in the polymer samples were generally rapid and controlled by Fickian diffusion. The diffusivities of benzene, chloroform, and acetone at 24°C, determined with the diffusion equation, were approximately 10<sup>-6</sup> cm/s. The sorption and diffusion data revealed that the newly developed PDMS<sup>vi</sup>-oligo polymer was an excellent sorbent for the three VOCs examined. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 920–927, 2004

**Key words:** polysiloxanes; membranes; adsorption; diffusion

## INTRODUCTION

Volatile organic compounds (VOCs) are emitted from diverse sources, including automobiles, chemical manufacturing facilities, and some commercial and residential sources that use solvents and paints. The control of the atmospheric emissions of VOC-laden waste gas streams has become an issue of increasing importance because of the many adverse effects of these pollutants. At the same time, the venting of these organic compounds, particularly some valuable solvents, represents a significant waste of valuable materials and energy resources.

Vapor permeation, pioneered by Baker and coworkers,<sup>1,2</sup> is based on a thin-film composite membrane that has a high permeability for organics but is relatively impermeable to air and other permanent gases. Despite its relatively new development, vapor permeation is a well-recognized membrane separation technology, especially when valuable organic vapors such as reusable solvents and aroma and flavor essences are involved.<sup>3</sup> The removal of halogenated hydrocarbons,

gasoline vapors, and organic solvents from the air are among the major industrial applications.

Vapor permeation requires the membrane materials to be extremely permeable to the organic vapors and relatively impermeable to permanent gases. Conventional glassy polymeric membranes, such as cellulose acetate and polysulfone, are not suitable for VOC separation from air or nitrogen because they are size-selective. They favor smaller and lighter molecules. In contrast, rubbery polymers are more permeable to the bigger and heavier VOC molecules than to light gases. Most of the pioneering work in this area has focused on silicone-rubber-coated composite membranes with poly(dimethylsiloxane) (PDMS).<sup>2,4–7</sup>

Recently, a novel oligomer, used as a crosslinking material, was prepared and studied in our laboratory.<sup>8</sup> Divinyl-terminated poly(dimethylsiloxane) (PDMS<sup>vi</sup>), crosslinked by this novel oligomer, PDMS<sup>vi</sup>-oligosilylstyrene, has been found capable of efficiently separating chlorinated and aromatic hydrocarbons from liquid water by pervaporation<sup>9</sup> and aromatic hydrocarbons from nitrogen by vapor permeation.<sup>8</sup> Although this kind of material has excellent processing ability for making ultrathin composite membranes, the sorption characteristic of this material with respect to VOCs have not been well examined.

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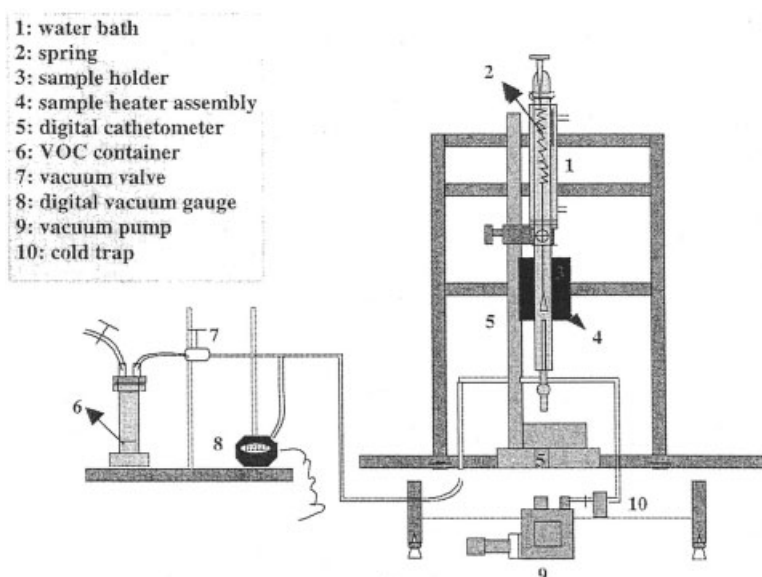


Figure 1 Sorption experimental setup.

The membrane separation of VOCs from air involves the sorption and permeation of VOCs in composite membranes. In vapor permeation, the sorption and diffusion of VOCs in a polymer control the permeability of the VOCs. Sorption generally plays a more important role than diffusion because the diffusion of bulky VOC molecules is always slower than the transport of light gases. Therefore, the effective separation of VOCs from permanent gases requires the VOCs to be much more easily dissolved in the polymer than light gases to compensate for their inferior diffusivity. VOC solubility is, therefore, a key factor governing a membrane's permeability to a VOC, and sorption studies will provide an understanding of the intrinsic relationship between penetrating VOCs and a membrane. In this work, the sorption equilibria and kinetics of various VOCs in PDMS<sup>vi</sup>-oligo have been studied. Various sorption models have been used to explain and predict the performance of VOC sorption in this polymer.

## EXPERIMENTAL

### Materials

The polymer samples were prepared from solutions consisting of oligosilylstyrene as the crosslinker, PDMS<sup>vi</sup> (analytical-grade; 1000cs, UCT, Bristol, PA) as the polymer, and platinum-divinyltetramethyldisiloxane complex as the Karstedt catalyst (analytical-grade; UCT). An optimal PDMS<sup>vi</sup>/oligomer ratio of 4 : 1 gave the desired rate of crosslinking and the product properties. Based on this ratio, 10 wt % PDMS<sup>vi</sup> coating solutions were prepared with a catalyst concentration of 16 w/v %. Each of the three

components was prepared individually with hexane (analytical-grade; J.T. Baker, Phillipsburg, NJ) as a solvent. They were then mixed thoroughly in a shaker assembly until homogeneity was achieved. The mixed polymer solution was left standing for about half an hour to ensure complete desorption of the entrapped air bubbles. For samples used in the equilibrium studies, thin polymer films were cast in a shallow plastic container with a flat bottom. A thin gel film that formed after evaporation was placed in an oven kept at 50°C for about 12 h to ensure complete crosslinking. The PDMS<sup>vi</sup>-oligo polymer film eventually obtained was in the form of a dense, transparent gel film with a uniform thickness of 0.33 mm and a density of 0.99 g/cm<sup>3</sup>. Spherical PDMS<sup>vi</sup>-oligo polymer samples (4 mm in diameter) were prepared for use in the sorption kinetic studies. The samples were prepared from the same polymer formulation and with a procedure similar to that described previously. A dense, transparent, circular gel layer, which formed after crosslinking overnight in the oven at 50°C, was carefully carved into a sphere 4 mm in diameter with a density of 0.99 g/cm<sup>3</sup>.

The three VOCs selected for this research were benzene (analytical-grade; J.T. Baker), chloroform (analytical-grade; J.T. Baker), and acetone (analytical-grade; J.T. Baker). They were directly used for VOC sorption studies.

### Sorption studies

Sorption experiments were carried out with the conventional McBain spring balance system shown as Figure 1. The whole system was supplied by Ruska

Laboratories, Inc. (Houston, TX). The apparatus contained a glass chamber that could withstand a high vacuum. A PDMS<sup>vi</sup> sample was suspended from a delicate helical quartz spring (Ruska Laboratories) with a sensitivity range of 0.3–0.5 mm of extension/mg of load. The change in the sample weight as a result of the sorption and desorption of the film could be monitored through the measurement of the elongation and contraction of the spring by a microscope, which was attached to a large vernier caliper perpendicular to the ground. A heater (Ruska Laboratories) was mounted around the lower part of the sorption chamber in which the sample was located.

In a sorption isotherm experiment, a sample of the thin polymer film weighing about 10–50 mg was hung on a selected quartz spring of the desired sensitivity. The sorption chamber was then evacuated and maintained at a vacuum of about 5 mbar for at least 12 h to ensure the complete removal of air and other contaminated gases or vapors. The liquid VOC reservoir and delivery system was maintained at the desired temperature. The VOC delivery line was also evacuated before each experiment. The polymer sample in the chamber was then exposed to a certain pressure of a pure VOC vapor registered by a digital vacuum gauge (V2, Vacuumbrand, Cedar Grove, NJ) at a desired temperature  $T$ . The elongation of the spring as a result of a weight change of the film was magnified by a microscope and recorded with a digital cathetometer. The change in the weight of the polymer sample due to VOC sorption was monitored until a constant weight was obtained when equilibrium was established for each experiment. This procedure was repeated while the partial pressure of VOC was increased in stages until the saturated vapor pressure was reached at the experimental temperature. Sorption studies for the different VOCs and at different temperatures (24–50°C) were performed according to the procedure already described. These equilibrium sorption data were used to determine the sorption isotherm curve and to calculate the sorption coefficients.

Spherical polymer samples were used in VOC sorption kinetic studies at 24°C. Before each experiment, the sorption chamber was evacuated for about 12 h for the removal of air and other contaminated vapors. The sample was then exposed to a VOC at a constant pressure and temperature. The change in the spring elongation with the time was recorded continuously until saturation occurred. Thereafter, desorption was effected by the exposure of the VOC-saturated polymer sample to vacuum (pressure = 5 mbar), and the decrease in the spring length with time was also recorded until a constant length was obtained. The curve of the VOC sorption kinetics was used to compute the VOC diffusivity in the PDMS<sup>vi</sup>-oligo polymer ( $D$ ).

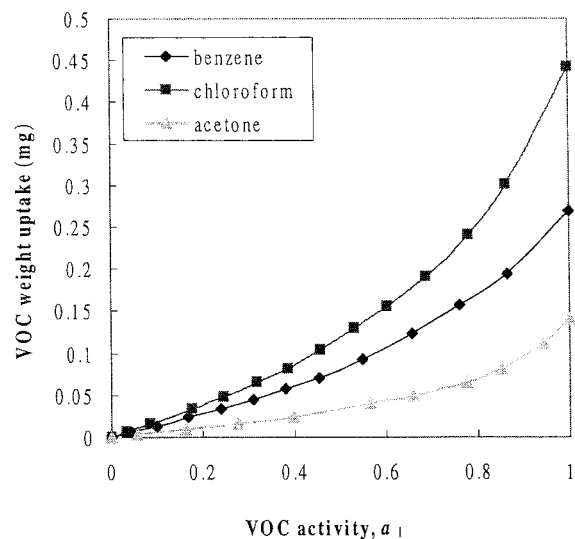


Figure 2 VOC isotherms in PDMS<sup>vi</sup> films at 24°C.

## RESULTS AND DISCUSSION

### Sorption equilibrium and VOC solubility in PDMS<sup>vi</sup>-oligo films

Sorption isotherm experiments were conducted with three VOCs—benzene, chloroform, and acetone—at temperatures ranging from 24 to 50°C. The VOC weight uptake has been plotted against the VOC activity ( $a_1$ ) in the membrane film. At low operating pressures, the vapor phase was assumed to behave as an ideal gas, and  $a_1$  is defined as the ratio of the partial pressure to the saturated pressure of the VOC at the sorption temperature. The isotherm covers the entire range of the VOC partial pressures studied.

Sorption isotherms of benzene, chloroform, and acetone at 24°C are illustrated in Figure 2. Initially, the VOC uptake closely follows a linear relationship with the VOC vapor activity and then increases progressively with the vapor activity until the partial pressure reaches its saturation value at the operating temperature ( $a_1 = 1$ ). The convex shape of the observed sorption curve is typical for the sorption of organic vapors in rubbery materials. This phenomenon is due to an increase in the polymer free volume when the polymer swells and vapor sorption occurs. This increased free volume enhances the sorption capacity of the polymer for VOC molecules. Therefore, more vapor sorption induces more free volume and, therefore, a greater capacity for vapor molecules. Among the three VOCs examined, chloroform has the highest sorption capacity, whereas acetone has the lowest sorption capacity, at their saturation states when unit activity is reached.

Sorption experiments of the VOCs were also performed at two other temperatures: 37 and 50°C. As illustrated in Table I, VOC sorption is not favored at higher temperatures. The sorption capacities of the

**TABLE I**  
Sorption Uptake of VOCs at Different Temperatures

	VOC uptake (mg) <sup>a</sup>		
	24°C	37°C	50°C
Benzene	4.477	0.933	0.523
Chloroform	16.365	2.323	1.012
Acetone	1.798	0.478	0.241

<sup>a</sup> The activity was 1.

VOCs in a polymer film decline dramatically at higher temperatures. For example, the benzene uptake at 24°C is 4.5 mg, but the uptake drops drastically to only 1.0 mg at 37°C and to 0.52 mg at 50°C. This illustrates the significant temperature dependence of the VOC sorption in the PDMS<sup>vi</sup>-oligo polymer film. Because of the exothermic nature of the sorption process, the polymer swelling effect becomes weaker, and this results in a reduction in the polymer free volume; therefore, its sorption capacity is lower.

The solubility coefficient ( $S$ ) is an important parameter used to determine the permeability of a membrane. It is calculated from the VOC sorption isotherm with the following equation:

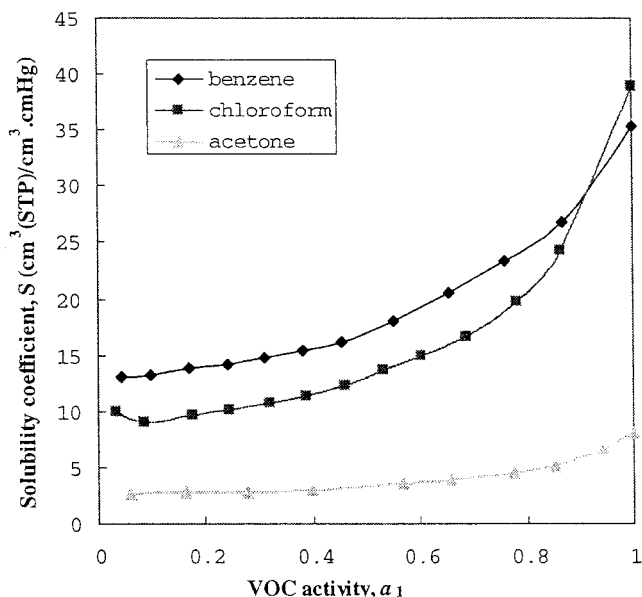
$$S_1 = c_1/p_1 \quad (1)$$

where  $c_1$  is the VOC concentration in the polymer phase and  $p_1$  is the VOC partial pressure in the vapor phase.  $c_1$  can be calculated from the molar uptake ( $M_p$ ).

The  $S$  values of benzene, chloroform, and acetone are plotted with the VOC activity in Figure 3.  $S$  increases continuously when the activity of VOC increases. As explained previously, this is the result of increasing free volume due to the swelling of the polymer exposed to a VOC. Among the three VOCs investigated, benzene has the highest values of  $S$  over the entire activity range, except at unit activity, and it is followed by chloroform and acetone. The  $S$  values for both benzene and chloroform increase drastically over the complete range of VOC activity, whereas that of acetone remains rather insensitive to increasing activity. The solubility of a VOC in a polymer film may be considered to be affected by three factors: (1) the molecular weight (a higher molecular weight VOC tends to condense more easily on the polymer surface), (2) like-dissolves-like theory (a VOC exhibiting structures or functional groups similar to those of the polymer is more easily dissolved in the polymer), and (3) cohesive energy theory (two components with close solubility parameters tend to dissolve each other much more easily).

An analysis of the three VOCs and the polymer examined in this research shows that the VOC molecular weight follows the order of chloroform  $\approx$  ben-

zene > acetone; their solubility parameters suggest the order of benzene > chloroform > acetone because of the ease of interaction with the polymer and the structural similarity. Benzene is favored over the other two VOCs because the benzene ring exists in the polymer molecular chain. A combination of the effects of these factors explains the high  $S$  values of benzene and chloroform observed in this study. Some of the solubility data obtained for the three VOCs in PDMS<sup>vi</sup>-oligo are listed in Table II and compared with reported results for the same VOCs, but with different polymers under similar experimental conditions. The data presented in this table illustrate that the  $S$  values obtained in PDMS<sup>vi</sup>-oligo are all much higher than the published results. Although the operation conditions are slightly different, the large difference in the solubility data of the same VOCs suggests that the developed PDMS<sup>vi</sup>-oligo polymer possesses a much higher sorption capacity than other conventional PDMS polymers. This may be due to the use of the novel functional oligomer as the crosslinker for PDMS<sup>vi</sup>. The oligomer structure produces more free volume and functional groups that have a special affinity to VOCs. The high VOC solubility of this polymer material suggests that PDMS<sup>vi</sup>-oligo is a good sorbent for VOCs and is ideal for use in preparing composite hollow-fiber membranes through the coating of the PDMS<sup>vi</sup>-oligo film on suitable porous supporting hollow-fiber membranes such as polysulfone, poly(ether sulfone), and poly(vinylidene fluoride). The use of these PDMS<sup>vi</sup>-oligo-based composite membranes for VOC separation by vapor permeation has been studied and will be reported separately.



**Figure 3** VOC solubility versus the VOC activity at 24°C.



TABLE II  
Comparison of  $S_1$  Values

	$S_1$ this work [cm <sup>3</sup> (STP)/cm <sup>3</sup> cmHg]	$S_1$ from the literature [cm <sup>3</sup> (STP)/cm <sup>3</sup> cmHg]
Benzene	30.5 (24°C, $a_1 = 0.92$ )	12.7 (27°C, $a_1 = 0.92$ – $0.95$ ) <sup>18</sup>
Chloroform	4.5 (37°C, $a_1 = 0.5$ )	2.5 (40°C, $a_1 = 0.5$ ) <sup>17</sup>
Acetone	3.73 (24°C, $a_1 = 0.5$ )	1.2 (28°C, $a_1 = 0.5$ ) <sup>13</sup>

### Modeling of the sorption isotherm

A Flory–Huggins (F–H) model has been applied to describe VOC sorption isotherms.<sup>10–14</sup> For a binary polymer–VOC system, the F–H model can be written as follows:

$$\ln \alpha_1 = \ln \phi_1 + (1 - \phi_1) + \chi_{12} (1 - \phi_1)^2 \quad (2)$$

where  $\chi_{12}$  is the F–H interaction parameter between a VOC (component 1) and a polymer (component 2) and  $\phi_1$  is the VOC volume fraction in the polymer film.  $\phi_1$ , which is related to the solubility of a VOC in the polymer, is generally expressed in terms of the VOC  $M_p$  value (mmol/g) by the polymer:

$$\phi_1 = \frac{M_p V_1}{M_p V_1 + 1/\rho_2} \quad (3)$$

where  $\rho_2$  is the polymer density (g/cm<sup>3</sup>) and  $V_1$  is the VOC molar volume (cm<sup>3</sup>/mmol). Many authors have already observed the validity of the classic F–H model for VOC sorption in silicone rubbers<sup>10–13</sup> as well as other elastomers.<sup>15</sup>

The F–H model has been applied to describe the sorption isotherms observed for the VOC–polymer systems used in this study. The volume fraction has been plotted against the vapor activity for both the experimental data and the calibrated data from the F–H model.  $\chi_{12}$  has been determined from curve fitting to be 1.058, 0.734, and 1.669 for benzene, chloroform, and acetone, respectively. Figure 4 compares the experimental sorption isotherms of benzene, chloroform, and acetone (at 24°C) and the predicted isotherms based on the F–H model. The F–H model fits the sorption isotherm data of the benzene and chloroform systems perfectly.

However, large discrepancies exist between the predictions based on the F–H model and the experimental isotherm data of acetone. This means that the hypothesis, which assumes a constant value of  $\chi_{12}$ , is not valid for acetone. To account for the variation of  $\chi_{12}$ , we have applied the Koningsveld–Kleinjens (K–K) variation law,<sup>12</sup> which assumes that the enthalpy of mixing is related to the VOC interaction surface fraction rather than the volume fraction. The interaction parameter is described as follows:

$$\chi_{12} = \alpha + \frac{\beta(1 - \omega)}{[1 - \omega(1 - \phi_1)]^2} \quad (4)$$

where  $\alpha$  is an empirical constant,  $\beta$  is linked to the enthalpy of mixing, and  $\omega$  is a function of the coordination number of the network. The parameter values in eq. (4) for acetone have been determined from the curve fitting of the experimental data with the least-square method to be  $\alpha = 0.7$ ,  $\beta = 0.394$ , and  $\omega = 0.727$ . This variation law, when combined with the F–H equation, yields a very good fit for the acetone isotherm, as shown in Figure 5. The predicted values from the modified F–H model agree very well with the experimental data.

$\chi_{12}$  for acetone decreases from 2.12 to 1.46 continuously as the VOC activity increases from 0 to 1.0.  $\chi_{12}$  represents the interaction force between the membrane and the vapor. The smaller  $\chi_{12}$  is, the more easily the vapor is dissolved in PDMS<sup>vi</sup>. The interaction parameter for acetone shows a decreasing trend with the vapor activity. This phenomenon has also been observed in other polymer/penetrant systems. Singh et al.<sup>13</sup> reported a similar decreasing trend of  $\chi_{12}$  with increasing vapor activity. For instance, they observed that for acetone sorption in PDMS, the values

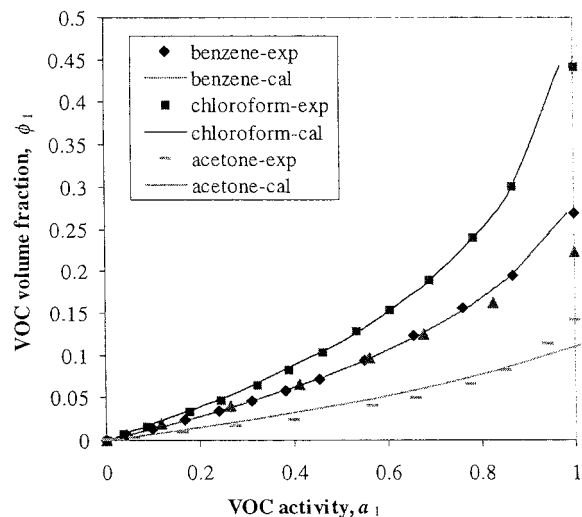
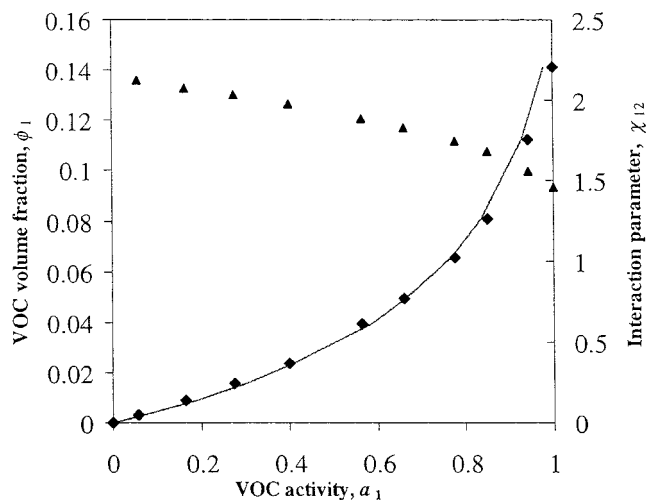


Figure 4 Comparison of the VOC isotherms and the F–H model predictions at 24°C.



**Figure 5** Comparison of the acetone isotherm and the modified F-H model prediction at 24°C.

of  $\chi_{12}$  declined from 1.9 to 1.3 as the acetone activity increased from 0.1 to 1.0. Table III shows that chloroform has the strongest interaction with the PDMS<sup>vi</sup> membrane.  $\chi_{12}$  also affects the sorption pattern; the higher  $\chi_{12}$  is, the less convexity there is in the sorption isotherm.

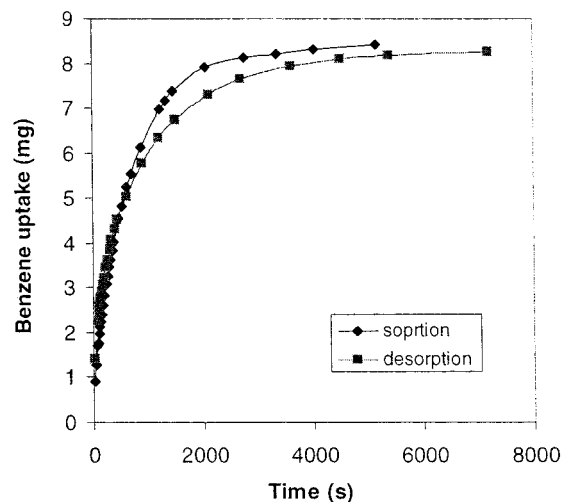
The maximum volume fraction ( $\phi_{\max}$ ) represents the degree of swelling of a polymer in the presence of a vapor as a solute. The results reveal that chloroform is a very good solute for PDMS<sup>vi</sup>-oligo ( $\phi_{\max}$  for chloroform can be as high as 0.45, as shown in Fig. 4). However, acetone is a poor solute because of its small molecular weight and the big difference in the solubility parameters between PDMS (7.3–7.6) and acetone (10.0). In general, the closer the solubility parameters are, the more easily the one component is dissolved in the other according to the like-dissolves-like theory. These results further verify that the F-H model performs well for good solutes such as benzene and chloroform, the  $\phi_{\max}$  of which are 0.26 and 0.45, respectively. However, a poor solute, such as acetone ( $\phi_{\max} = 0.125$ ), requires more sophisticated approaches. In the test determining the swelling degree of the PDMS<sup>vi</sup>-oligo polymer in different kinds of VOCs, the polymer did not appear noticeably swollen in acetone and alcohol.

### Sorption kinetics

The sorption kinetics of a VOC in the PDMS<sup>vi</sup>-oligo polymer were investigated via the transient weight

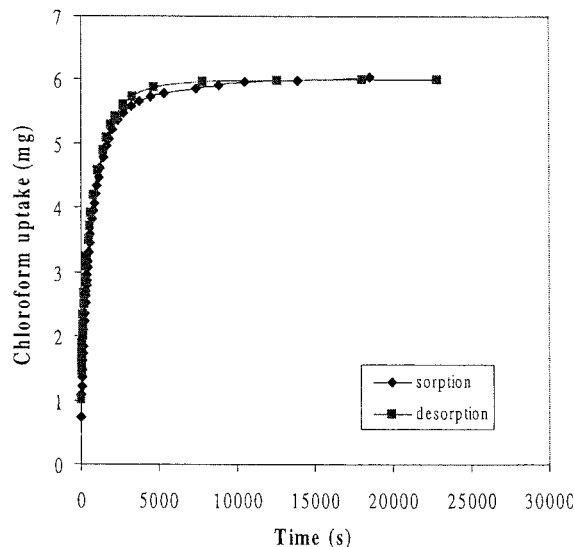
**TABLE III**  
 $\phi_{\max}$  and  $\chi_2$  Values of VOCs in PDMS<sup>vi</sup>

	$\phi_{\max}$	$\chi_{12}$
Benzene	0.269	1.058
Chloroform	0.443	0.734
Acetone	0.141	1.835

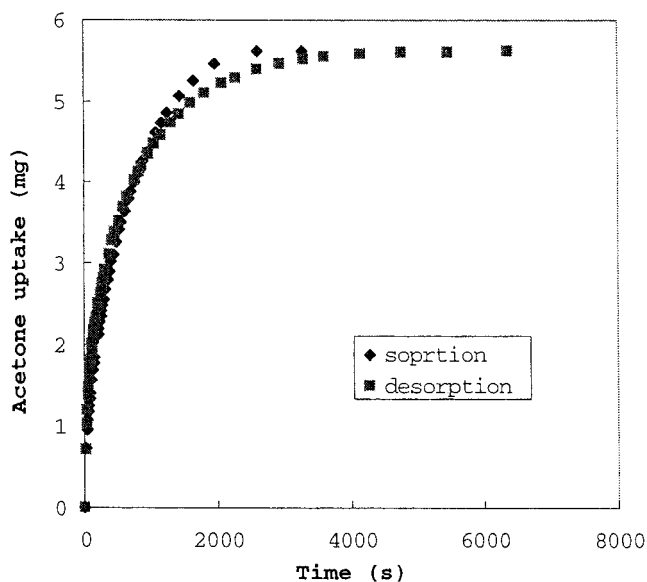


**Figure 6** Sorption and desorption of benzene in PDMS<sup>vi</sup> samples at 24°C (vapor pressure = 110 mmHg, sample weight = 50.5 mg).

changes of the membrane sample with time during both sorption and desorption stages at 24°C. The rates of the sorption and desorption of benzene, chloroform, and acetone were monitored, and the results are illustrated in Figures 6–8. As shown, all the sorption curves for the three VOCs generally follow the same trend. There is a very fast initial rate of VOC uptake; thereafter, the rate declines rapidly to zero when equilibrium is reached. Most of the free volume in the polymer is occupied in a very short time, and the sorption kinetics, which are controlled by Fickian diffusion, approach equilibrium very quickly. This type of kinetic behavior has often been observed for organic vapor sorption in polymers.



**Figure 7** Sorption and desorption of chloroform in PDMS<sup>vi</sup> samples at 24°C (vapor pressure = 540 mmHg, sample weight = 0.0446 g).



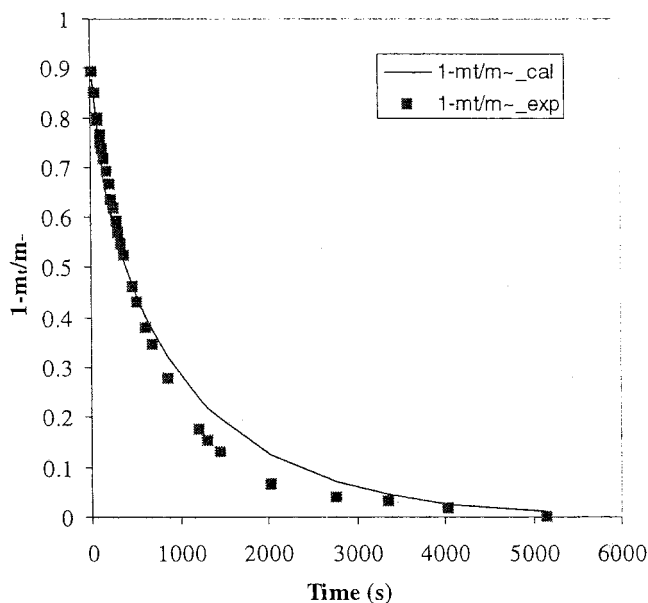
**Figure 8** Sorption and desorption of acetone in PDMS<sup>vi</sup> samples at 24°C (vapor pressure = 280 mmHg, sample weight = 0.0446 g).

For the sorption of chloroform in a membrane sample, the data on sorption and desorption, as shown in Figure 7, are in perfect agreement. This suggests that the diffusivity of chloroform is a constant and is independent of the concentration. However, the uptake curves for the sorption and desorption of benzene and acetone, which do not quite agree with each other, may suggest a concentration dependence of  $D$ .

For a spherical sample, the diffusion of VOCs in the PDMS<sup>vi</sup>-oligo polymer is three-dimensional. A solution to the partial differential equation describing such a three-dimensional diffusional process is given by the following expression:<sup>16</sup>

$$\frac{m_t}{m_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D t}{r^2}\right) \quad (5)$$

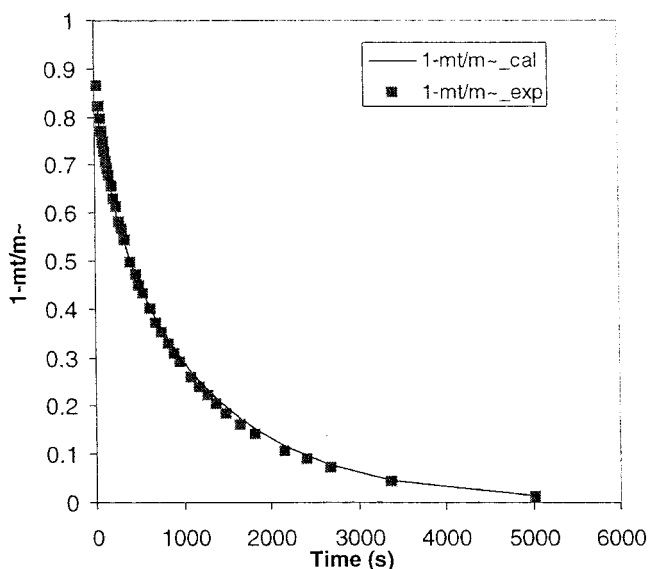
where  $m_t$  (mg/mg) is the VOC uptake at time  $t$  (s),  $m_\infty$  (mg/mg) is the VOC uptake at saturation, and  $r$  (cm) is the sample radius. Based on the sorption data obtained in the experiments, plots of  $1 - m_t/m_\infty$  versus  $t$  for benzene, chloroform, and acetone in the PDMS<sup>vi</sup>-oligo polymer at 24°C are given in Figures 9–11.  $D$  has been derived by the regression of the experimental data with the least-square method in Excel internal programs. The  $D$  values for benzene, chloroform, and acetone in PDMS<sup>vi</sup>-oligo are  $3.17 \times 10^{-6}$ ,  $3.084 \times 10^{-6}$ , and  $4.2 \times 10^{-6}$  m<sup>2</sup>/s, respectively, at 24°C. These values have the same order of magnitude as those reported for vapor diffusivity in other rubbery polymers.<sup>12,17,18</sup>



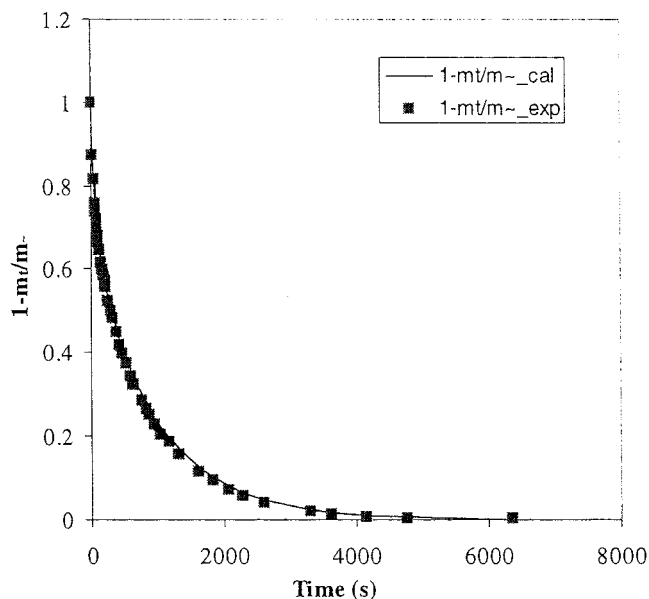
**Figure 9** Comparison of the experimental and theoretical uptake curves of benzene at 24°C (vapor pressure = 110 mmHg, sample weight = 50.5 mg).

## CONCLUSIONS

The equilibria and kinetics of sorption of three VOCs—benzene, chloroform, and acetone—in PDMS<sup>vi</sup>-oligo polymer films have been studied from 24 to 50°C. The observed  $S$  values for these VOCs in the polymer film are significantly higher than the reported data for conventional silicone rubbers. The F–H model very well describes the observed equilibrium sorption isotherms for benzene and chloroform. The K–K vari-



**Figure 10** Comparison of the experimental and theoretical uptake curves of chloroform at 24°C (vapor pressure = 540 mmHg, sample weight = 0.0446 g).



**Figure 11** Comparison of the experimental and theoretical uptake curves of acetone at 24°C (vapor pressure = 280 mmHg, sample weight = 0.0446 g).

ation law, combined with the F–H model, has been applied to represent the sorption isotherm data for acetone because the interaction parameter of acetone and the polymer,  $\chi_{12}$ , is not a constant according to the experimental data. The rates of sorption of the three VOCs in the polymer are rapid and are controlled by Fickian diffusion. A comparison of the sorption and desorption data reveal that the results are in good agreement, especially for the chloroform–polymer system. The rates of VOC uptake in spherical polymer samples are well described by the three-dimensional diffusion equation. The diffusivity data of benzene, chloroform, and acetone, determined from the diffusion equation, agree reasonably well with reported values. The sorption and diffusion data reveal that the newly developed PDMS<sup>vi</sup>-oligo polymer is an excellent sorbent for all three VOCs examined. The polymer appears to be a good candidate for the fabrication of composite hollow-fiber membranes for use in VOC separation by vapor permeation.

## NOMENCLATURE

### Symbols

$a_1$  ratio of the partial pressure to the saturated pressure at the sorption temperature

$c_1$  VOC concentration in the polymer phase [ $\text{cm}^3(\text{STP})/\text{cm}^3$ ]  
 $D$  VOC diffusivity in the polymer ( $\text{m}^2/\text{s}$ )  
 $p_1$  VOC pressure in the vapor phase (cmHg)  
 $m_\infty$  VOC uptake at saturation (mg/mg)  
 $M_p$  molar uptake (mmol/g)  
 $m_t$  VOC uptake at time  $t$  (mg/mg)  
 $r$  sample radius (mm)  
 $S$  solubility coefficient [ $\text{cm}^3(\text{STP})/\text{cm}^3 \text{cmHg}$ ]  
 $S_1$  VOC solubility coefficient in the membrane [ $\text{cm}^3(\text{STP})/\text{cm}^3 \text{cmHg}$ ]  
 $t$  time (s)  
 $T$  temperature ( $^\circ\text{C}$ )  
 $V_1$  VOC molar volume ( $\text{cm}^3/\text{mol}$ )

### Greek letters

$\alpha$  empirical constant given in eq. (4)  
 $\beta$  constant linked to the enthalpy of mixing given in eq. (4)  
 $\rho_2$  polymer density ( $\text{g}/\text{cm}^3$ )  
 $\phi_1$  VOC volume fraction in the polymer film  
 $\phi_{\text{max}}$  maximum volume fraction of VOC  
 $\chi_{12}$  VOC–polymer interaction parameter  
 $\omega$  function of the coordination number of the network given in eq. (4)

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