

# Diffusion Coefficient and Equilibrium Solubility of Water Molecules in Biodegradable Polymers

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**ABSTRACT:** The diffusion coefficient and solubility of water molecules were measured in polyglycolide (PGA), poly(L-lactide) (PLLA), poly[(R)-3-hydroxybutyrate] (PHB), poly( $\epsilon$ -caprolactone) (PCL), and Skygreen<sup>R</sup> (SG). The diffusion coefficient and equilibrium solubility decreased in the order SG > PCL > PLLA > PHB > PGA and PGA > SG > PLLA > PHB > PCL, respectively. The diffusion coefficient and solubility of water at low sorption temperature in PHB varied according to the initial crystallinity of the matrix polymer even though crystallization of PHB molecules took place during the sorption experiment. In contrast, the amorphous PLLA and the crystalline PLLA showed an almost identical diffusion coefficient and solubility of water, in spite of the fact that the amorphous PLLA remained practically amorphous during the whole sorption procedure. A strong correlation existed between the water solubility and the surface tension or contact angle of the polymer matrix. The water diffusivity in PGA was almost 2 orders of magnitude lower while water was more soluble in PGA with a lower heat of sorption than that corresponding to the other more hydrophobic polymers, indicating that the transport of water molecules in PGA followed the solution–diffusion model. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1716–1722, 2000

**Key words:** diffusion coefficient; solubility; water; biodegradable polymers

## INTRODUCTION

Microbial assimilation of polymers is frequently preceded by enzymatic or nonenzymatic hydrolysis. Much research has been done on the kinetics of nonenzymatic hydrolysis.<sup>1–11</sup> However, few data for the diffusion coefficient and solubility of water molecules in the biodegradable polymers are available to reveal whether the process of hydrolysis is reaction or diffusion controlled.<sup>12</sup>

The transport rate of diffusants is usually expressed in terms of permeability or a diffusion coefficient.<sup>13</sup> The permeability,  $P$ , is related to the diffusion coefficient,  $D$ , and equilibrium solubility,  $S$ , as in eq. (1).

$$P = S \cdot D \quad (1)$$

One of the simplest methods for the determination of the diffusion coefficient is the weighing method. The weight gain or weight loss of a specimen of known shape and size kept in an atmosphere of constant diffusant vapor pressure is measured from time to time. The diffusion coefficient is calculated from the weight variation of the film type specimen as shown in eq. (2).

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**Table I Characteristics of Biodegradable Polymers**

Sample	Structure	$M_n$	$M_n/M_w$
PLLA	$\left( \begin{array}{c} \text{CH}_3 \quad \text{O} \\   \quad    \\ \text{CH}-\text{C}-\text{O} \end{array} \right)_n$	138,800	3.5
PHB	$\left( \begin{array}{c} \text{CH}_3 \quad \text{O} \\   \quad    \\ \text{CH}-\text{CH}_2-\text{C}-\text{O} \end{array} \right)_n$	51,400	4.0
PCL	$\left( \begin{array}{c} \text{O} \\    \\ (\text{CH}_2)_5-\text{C}-\text{O} \end{array} \right)_n$	23,200	1.9
SG	$\left( (\text{CH}_2)_4-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O} \right)_x \left( (\text{CH}_2)_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_4-\overset{\text{O}}{\parallel}{\text{C}}-\text{O} \right)_y$	15,400	3.8
PGA	$\left( \begin{array}{c} \text{O} \\    \\ \text{CH}_2-\text{C}-\text{O} \end{array} \right)_n$	15,000 ± 1,000 <sup>a</sup>	

<sup>a</sup> Zero shear viscosity (in poise at 250°C).

$$D = \left( \frac{\pi}{16} \right) \left[ \frac{d \left( \frac{M_t}{M_\infty} \right)^2}{d \left( \frac{\sqrt{t}}{l} \right)} \right]^2 \quad (2)$$

where  $M_t$  and  $M_\infty$  are weight variations at time  $t$  and at equilibrium, respectively.

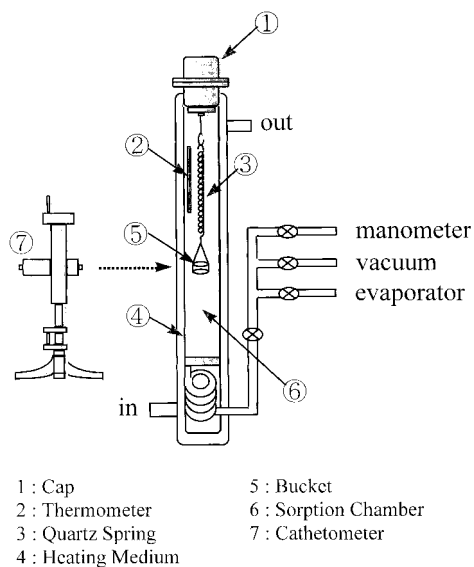
The diffusion coefficient of a diffusant/polymer matrix system was reported to be a strong function of the diffusant concentration, as well as the temperature, which can be predicted by the free volume theory.<sup>14-16</sup> The diffusion coefficient determined from eq. (2) should thus be the average value between  $t = 0$  and  $t = t$ . However, it was found that for many diffusant/polymer matrix systems the initial  $M_t/M_\infty$  versus  $t^{1/2}/l$  plot yielded a good straight line so that the diffusion coefficient could be easily determined experimentally.<sup>16</sup>

In this study the diffusion coefficient and solubility of water molecules in polyglycolide

(PGA), Skygreen<sup>R</sup> (SG), poly(L-lactide) (PLLA), poly[(R)-3-hydroxybutyrate] (PHB), and poly(ε-caprolactone) (PCL) were explored using the weighing method. A comparison was made to investigate the effect of crystallinity and hydrophilicity of the polymers on the diffusivity and solubility of water molecules.

## EXPERIMENTAL

The PHB and PLLA were obtained from ICI and Shimadzu, respectively. The SG (an aliphatic polyester of succinic acid/adipic acid-1,4-butanediol/ethylene glycol) was obtained from SKI (Korea). The PGA was donated by Samyang (Korea). The PCL was purchased from Aldrich. The molecular weight was measured by GPC [Waters model 410, RI detector, chloroform eluent at 1.0 mL/min, 30°C, column (porosity of 10 μm, styragel HR1,



**Figure 1** The sorption apparatus.

HR 2, HR 4, linear)]. The PGA was hardly soluble in many organic solvents and the zero shear melt viscosity at 250°C was measured in place of the molecular weight (Table I).

A Perkin–Elmer DSC-7 was used to measure the thermal properties. Samples were initially heated to 30°C higher than the respective melting temperature ( $T_m$ ) at a rate of 10°C/min to determine the  $T_m$ , and then they were quenched using liquid nitrogen. The crystallization and glass-transition temperatures ( $T_c$  and  $T_g$ ) were obtained by reheating those samples at 10°C/min.

Film specimens were prepared by hot pressing at the respective melting temperature under 250 atm. Quenched polymer samples were made by quenching them from the melt state using liquid nitrogen (subscript Q); crystallized ones were obtained by slow cooling under the hot press (about  $-1^\circ\text{C}/\text{min}$ ) to the respective  $T_c$ , where additional crystallization was continued for 24 h (subscript C). The crystallinity of the quenched polymer after sorption at 45°C for 2 days was also measured with WAXD (subscript S).

**Table II** Thermal Properties of Biodegradable Polymers

	PLLA	PHB	PGA	SG	PCL
$T_g$ (°C)	61	5	42	-40	-60
$T_c$ (°C)	105	110	150	10	5
$T_m$ (°C)	172	175	219	95	60

**Table III** Degree of Crystallinity of Biodegradable Polymers

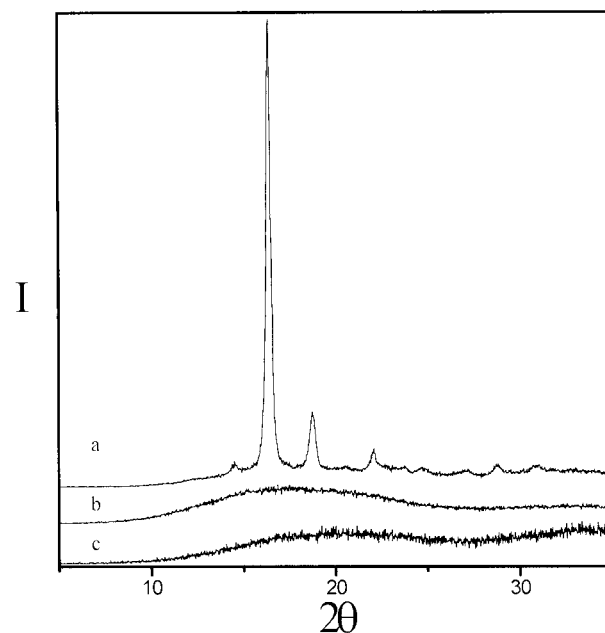
		Degree of Crystallinity <sup>a</sup>
PLLA	PLLA <sub>Q</sub>	0 (0) <sup>b</sup>
	PLLA <sub>C</sub>	78.5
PHB	PHB <sub>Q</sub>	44.5 (76.4) <sup>b</sup>
	PHB <sub>C</sub>	76.2
PGA	PGA <sub>Q</sub>	7.5 (39.1) <sup>b</sup>
	PGA <sub>C</sub>	68.5
SG	SG <sub>C</sub>	21.1
PCL	PCL <sub>C</sub>	61.8

<sup>a</sup> Measured by WAXD.

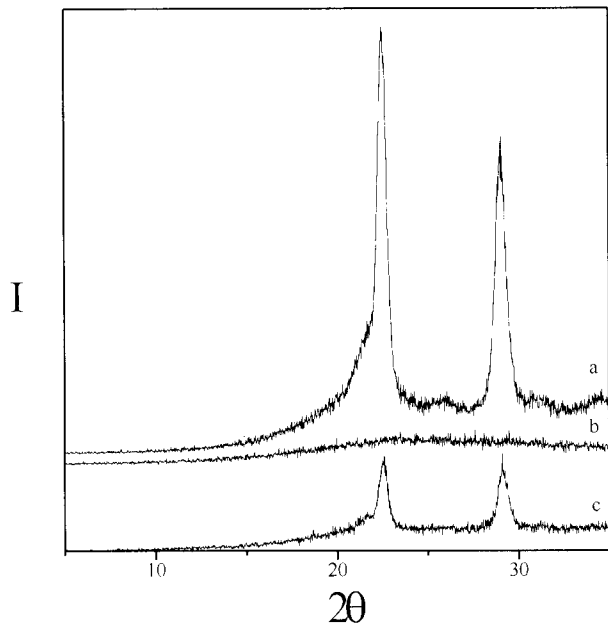
<sup>b</sup> Quenched sample after sorption of water vapor at 45°C for 2 days.

The WAXD was acquired by a Philips X'Pert-MPD diffractometer at about 18°C (CuK $\alpha$ , Ni filtered, 40 kV, 20 mA). The crystallinity was calculated from the WAXD by approximating each diffraction peak to the Gaussian function.

The contact angle was obtained with water by a dynamic contact angle analyzer (CHAN, DCA-315) at 36.5°C. Polymer specimens for the contact angle measurements were prepared by hot pressing in the melt state followed by slow cooling to the  $T_c$  and additional crystallization for 24 h. An average of the three measurements was taken.

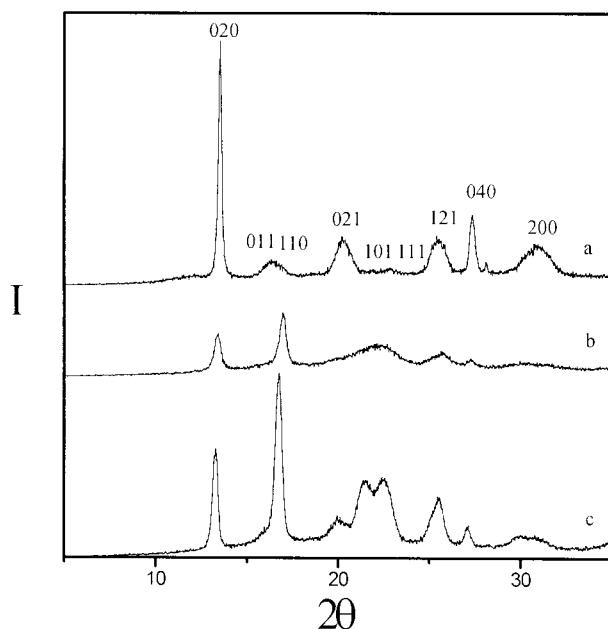


**Figure 2** Wide-angle X-ray spectra of (a) PLLA<sub>C</sub>, (b) PLLA<sub>Q</sub>, and (c) PLLA<sub>S</sub>.



**Figure 3** Wide-angle X-ray spectra of (a)  $PGA_C$ , (b)  $PGA_Q$ , and (c)  $PGA_S$ .

The diffusion coefficient and solubility were measured by monitoring the extension of a quartz spring (0.5 mm/mg of modulus) due to the weight variation accompanied by the sorption. The sorption chamber (Fig. 1) was kept under a vacuum at a sorption temperature until all the volatile substances were removed from the sample to attain a



**Figure 4** Wide-angle X-ray spectra of (a)  $PHB_C$ , (b)  $PHB_Q$ , and (c)  $PHB_S$ .

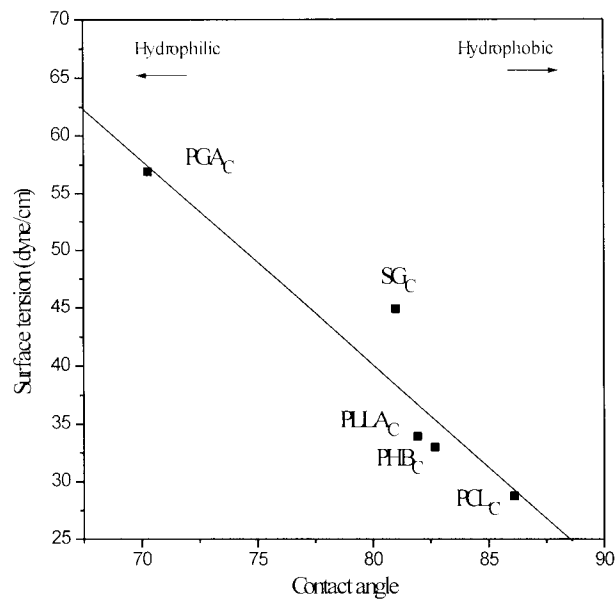
**Table IV** Surface Tension and Contact Angle of Biodegradable Polymers

	Surface Tension (dyne/cm)	Contact Angle (Advancing)
$PLLA_C$	33.9	82.0°
$PHB_C$	33.0	82.7°
$PGA_C$	56.9	70.3°
$SG_C$	44.9	81.0°
$PCL_C$	28.7	86.1°

constant weight. The water vapor was introduced into the sorption chamber and the weight gain was followed with a cathetometer having a 10- $\mu$ m precision. The sorption temperatures were controlled to  $36.5 \pm 0.1$ ,  $45 \pm 0.1$ , and  $60 \pm 0.1^\circ\text{C}$ .

**RESULTS AND DISCUSSION**

The glass-transition ( $T_g$ ), crystallization ( $T_c$ ), and melting temperatures ( $T_m$ ) of the biodegradable polymers are summarized in Table II. PLLA has a higher  $T_g$  and PGA shows a similar  $T_g$  while PHB, SG, and PCL have a lower  $T_g$  compared to the sorption temperature. Therefore, quenched PHB, SG, and PCL made by quenching from the melt state into liquid nitrogen were susceptible to crystallization during the sorption experiments. SG and PCL have very low glass-transition and



**Figure 5** The surface tension and contact angle of the biodegradable polymers.

**Table V** Diffusion Coefficient of Biodegradable Polymers ( $\text{cm}^2/\text{s}$ )

Samples	External Pressure of Water Vapor (atm)			
	0.024	0.042	0.060	0.072
36.5°C				
PLLA <sub>Q</sub>	$8.04 \times 10^{-8}$	$8.81 \times 10^{-8}$	$9.62 \times 10^{-8}$	$11.04 \times 10^{-8}$
PLLA <sub>C</sub>	$6.61 \times 10^{-8}$	$7.07 \times 10^{-8}$	$7.31 \times 10^{-8}$	$8.04 \times 10^{-8}$
PHB <sub>Q</sub>	$1.23 \times 10^{-8}$	$2.41 \times 10^{-8}$	$6.16 \times 10^{-8}$	$8.04 \times 10^{-8}$
PHB <sub>C</sub>	$0.87 \times 10^{-8}$	$1.04 \times 10^{-8}$	$1.33 \times 10^{-8}$	$1.54 \times 10^{-8}$
PGA <sub>Q</sub>	$16.11 \times 10^{-11}$	$19.63 \times 10^{-11}$	$23.76 \times 10^{-11}$	$26.42 \times 10^{-11}$
PGA <sub>C</sub>	$4.42 \times 10^{-11}$	$7.85 \times 10^{-11}$	$12.27 \times 10^{-11}$	$15.39 \times 10^{-11}$
PCL <sub>C</sub>	$17.35 \times 10^{-8}$	$18.10 \times 10^{-8}$	$19.24 \times 10^{-8}$	$22.90 \times 10^{-8}$
SG <sub>C</sub>	$25.97 \times 10^{-8}$	$41.85 \times 10^{-8}$	$74.66 \times 10^{-8}$	$104.77 \times 10^{-8}$
45.0°C				
PLLA <sub>Q</sub>	$8.55 \times 10^{-8}$	$11.95 \times 10^{-8}$	$14.52 \times 10^{-8}$	$18.86 \times 10^{-8}$
PLLA <sub>C</sub>	$6.83 \times 10^{-8}$	$8.04 \times 10^{-8}$	$10.46 \times 10^{-8}$	$16.98 \times 10^{-8}$
PHB <sub>Q</sub>	$5.73 \times 10^{-8}$	$6.38 \times 10^{-8}$	$8.04 \times 10^{-8}$	$12.57 \times 10^{-8}$
PHB <sub>C</sub>	$0.95 \times 10^{-8}$	$1.54 \times 10^{-8}$	$2.41 \times 10^{-8}$	$2.84 \times 10^{-8}$
PGA <sub>Q</sub>	$17.67 \times 10^{-11}$	$24.05 \times 10^{-11}$	$31.42 \times 10^{-11}$	$34.73 \times 10^{-11}$
PGA <sub>C</sub>	$16.51 \times 10^{-11}$	$22.70 \times 10^{-11}$	$29.86 \times 10^{-11}$	$33.01 \times 10^{-11}$
PCL <sub>C</sub>	$18.86 \times 10^{-8}$	$32.67 \times 10^{-8}$	$40.72 \times 10^{-8}$	$58.09 \times 10^{-8}$
SG <sub>C</sub>	$31.67 \times 10^{-8}$	$58.77 \times 10^{-8}$	$84.13 \times 10^{-8}$	$123.70 \times 10^{-8}$

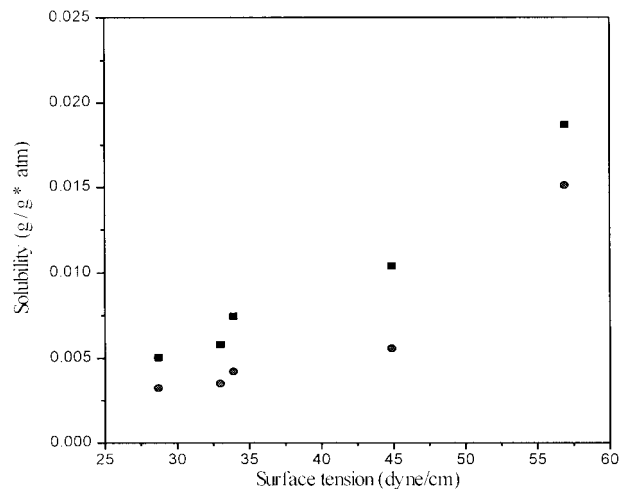
crystallization temperatures. Therefore, the sorption experiments were run for SG and PCL that were completely crystallized by annealing at each  $T_c$  for 24 h. In contrast, the crystallization rate of PLLA, PGA, and PHB was expected to be slow at the sorption temperature, so that experiments were initially carried out for these polymers in a quenched state and a crystallized state. Table III shows the degree of crystallinity of the biodegradable polymers measured by WAXD. It can be seen that the quenched PLLA remained amorphous even after water sorption at 45°C for 2 days (Fig. 2). PGA quenched from the melt state gave 7.5% crystallinity, and it approached 39.1% after the water sorption as shown in Figure 3.

PHB crystallized so fast that the crystallinity was raised to 44.5% during the quenched sample preparation for WAXD. The quenched PHB after the sorption at 45°C for 2 days showed almost the same level of crystallinity as the PHB annealed at 110°C for 24 h (Fig. 4). However, the 020 reflection of the latter PHB was more intense than the 011 or 110 reflection as compared with that of the former PHB, indicating that the crystalline morphology was changed during the sorption experiment.

Table IV and Figure 5 present the surface tension and contact angle of the biodegradable polymers. It can be observed that the hydrophilicity decreased in the order of PGA > SG > PLLA > PHB > PCL.

The diffusion coefficients of the water molecules determined from the initial slope of  $M_t/M_\infty$  as a function of  $t^{1/2}/l$  are summarized in Table V. The diffusion coefficients decreased as SG > PCL > PLLA > PHB > PGA.

The glass-transition temperature of SG was -40°C, and water molecules could easily penetrate into the SG matrix at the sorption temperature. Water diffused slower in PCL than in SG,



**Figure 6** The solubility of water as a function of the surface tension of the biodegradable polymers; sorption at (■) 36.5°C and (●) 45.0°C.

**Table VI Equilibrium Water Content in Biodegradable Polymers (g/g of Polymer)**

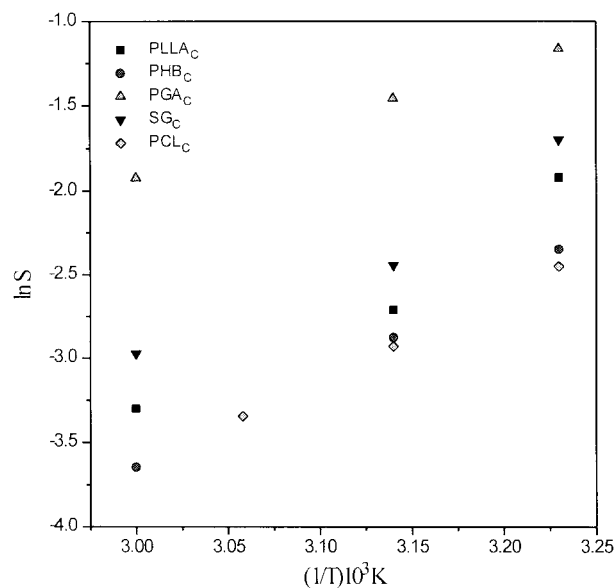
Samples	External Pressure of Water Vapor (atm)			
	0.024	0.042	0.060	0.072
<b>36.5°C</b>				
PLLA <sub>Q</sub>	$3.87 \times 10^{-3}$	$6.39 \times 10^{-3}$	$9.80 \times 10^{-3}$	$13.32 \times 10^{-3}$
PLLA <sub>C</sub>	$2.90 \times 10^{-3}$	$5.03 \times 10^{-3}$	$7.44 \times 10^{-3}$	$11.15 \times 10^{-3}$
PHB <sub>Q</sub>	$3.08 \times 10^{-3}$	$5.47 \times 10^{-3}$	$8.78 \times 10^{-3}$	$11.03 \times 10^{-3}$
PHB <sub>C</sub>	$2.84 \times 10^{-3}$	$4.20 \times 10^{-3}$	$5.79 \times 10^{-3}$	$7.10 \times 10^{-3}$
PGA <sub>Q</sub>	$11.24 \times 10^{-3}$	$20.50 \times 10^{-3}$	$27.21 \times 10^{-3}$	$35.10 \times 10^{-3}$
PGA <sub>C</sub>	$9.91 \times 10^{-3}$	$14.95 \times 10^{-3}$	$18.67 \times 10^{-3}$	$23.52 \times 10^{-3}$
PCL <sub>C</sub>	$2.01 \times 10^{-3}$	$3.35 \times 10^{-3}$	$5.03 \times 10^{-3}$	$6.29 \times 10^{-3}$
SG <sub>C</sub>	$5.23 \times 10^{-3}$	$7.70 \times 10^{-3}$	$10.36 \times 10^{-3}$	$13.91 \times 10^{-3}$
<b>45.0°C</b>				
PLLA <sub>Q</sub>	$2.13 \times 10^{-3}$	$3.23 \times 10^{-3}$	$4.49 \times 10^{-3}$	$5.53 \times 10^{-3}$
PLLA <sub>C</sub>	$1.89 \times 10^{-3}$	$2.86 \times 10^{-3}$	$4.21 \times 10^{-3}$	$4.77 \times 10^{-3}$
PHB <sub>Q</sub>	$1.98 \times 10^{-3}$	$2.82 \times 10^{-3}$	$3.51 \times 10^{-3}$	$4.39 \times 10^{-3}$
PHB <sub>C</sub>	$1.85 \times 10^{-3}$	$2.80 \times 10^{-3}$	$3.50 \times 10^{-3}$	$4.19 \times 10^{-3}$
PGA <sub>Q</sub>	$9.92 \times 10^{-3}$	$13.58 \times 10^{-3}$	$15.39 \times 10^{-3}$	$18.16 \times 10^{-3}$
PGA <sub>C</sub>	$9.85 \times 10^{-3}$	$13.00 \times 10^{-3}$	$15.11 \times 10^{-3}$	$17.83 \times 10^{-3}$
PCL <sub>C</sub>	$1.67 \times 10^{-3}$	$2.59 \times 10^{-3}$	$3.23 \times 10^{-3}$	$3.99 \times 10^{-3}$
SG <sub>C</sub>	$3.66 \times 10^{-3}$	$4.64 \times 10^{-3}$	$5.72 \times 10^{-3}$	$6.61 \times 10^{-3}$
<b>60.0°C</b>				
PLLA <sub>C</sub>	$1.84 \times 10^{-3}$	$2.06 \times 10^{-3}$	$2.27 \times 10^{-3}$	—
PHB <sub>C</sub>	$1.27 \times 10^{-3}$	$1.46 \times 10^{-3}$	$1.60 \times 10^{-3}$	—
PGA <sub>C</sub>	$9.57 \times 10^{-3}$	$12.11 \times 10^{-3}$	$14.82 \times 10^{-3}$	—
PCL <sub>C</sub> <sup>a</sup>	$1.45 \times 10^{-3}$	$1.81 \times 10^{-3}$	$2.15 \times 10^{-3}$	—
SG <sub>C</sub>	$1.86 \times 10^{-3}$	$2.73 \times 10^{-3}$	$3.70 \times 10^{-3}$	—

<sup>a</sup> Sorption at 54°C.

in spite of the fact that PCL had lower a  $T_g$  than SG. This seems to have been due to the fact that PCL was more crystalline than SG.

As in many other volatile substance/polymer systems,<sup>16</sup> the diffusion coefficients of the water molecule increased with the external pressure of the water vapor.

It is interesting to observe that the water diffusivity and the water solubility were nearly independent of the crystallinity of the PLLA (Tables V, VI), even though, in the case of the water/PCL and water/SG systems, the crystallinity seemed to have a strong influence on the water diffusivity. Siparsky et al.<sup>12</sup> varied the crystallinity of PLA by quenching and annealing or by copolymerizing with D-lactide units. They also reported the permeability and solubility of water had little connection with the crystallinity of the PLA, which was ascribed to the fact that the transportation of water molecules in the PLA matrix followed the water-cluster model rather than the solution-diffusion model. Water molecules sorbed in the polymer matrix associate with each



**Figure 7** The plot of the  $\ln(S)$  vs.  $1/T$  for the biodegradable polymers.

**Table VII Heat of Sorption of Water in Biodegradable Polymers**

Samples	$\Delta H$ (kJ/mol)
PLLA <sub>C</sub>	-48.4
PHB <sub>C</sub>	-46.8
PGA <sub>C</sub>	-27.4
PCL <sub>C</sub>	-43.2
SG <sub>C</sub>	-44.7

other and form clusters through preferential binding to each other by hydrogen bonding. Water molecules are not necessarily soluble in the polymer and permeate through the polymer in the cluster form. According to the solution-diffusion model, water molecules dissolve in the polymer matrix and pass through it by diffusion in response to a concentration gradient.

The diffusivity of water molecules in PHB annealed at 110°C for 24 h was lower than that in PHB quenched from the melt state. The solubility of water in PHB at 36.5°C depended on the initial crystallinity while it was nearly independent of the initial crystallinity at 45°C. This was because the final crystallinity attained by the quenched PHB after the sorption at 45°C was almost equal to that of PHB annealed at the  $T_c$  for 24 h, and it should be higher than that obtained at 36.5°C. Therefore, the equilibrium solubility at 45°C, which was determined after the sorption was completed, became independent of the initial crystallinity. In contrast, the diffusion coefficient was measured from the sorption data of the initial stage, thus depending on the initial crystallinity.

Observe that the equilibrium water uptake of PHB of similar crystallinity was almost the same, irrespective of the different thermal history leading to nonidentical crystalline morphology.

The question remains unanswered as to why differences in crystallinity drastically change the water diffusion coefficient in PHB while the diffusion coefficient in PLLA is nearly independent of crystallinity, even though PHB is more hydrophobic than PLLA. Thus, the water cluster type transport in PHB is expected to be more probable than that in PLLA.

The water diffusivity at 36.5 and 45°C and water solubility at 36.5°C in PGA were dependent of the initial crystallinity of PGA, while the solubility in PGA at 45°C was independent of the initial crystallinity as was the water/PHB system.

Figure 6 shows that a strong correlation exists between the water solubility and surface tension of the biodegradable polymers.

The heat of sorption of water molecules in the polymers were determined by the following equation<sup>12</sup>:

$$S = S_0 \exp(-\Delta H/RT) \quad (3)$$

Figure 7 is the plot of the  $\ln S$  as a function of  $1/T$ , and the heat of sorption determined from the slope is summarized in Table VII. Highly hydrophilic PGA gave a heat of sorption of -27 kJ/mol, and the other polymers had a heat of sorption of -45 kJ/mol. Siparsky et al.<sup>12</sup> measured the heat of sorption of water in PLA and found it to be -40 kJ/mol. They presented this result evidence for the water-cluster model, because this value was almost identical to the heat of condensation of water.

The water solubility in PGA had relatively lower activation energy (-27 kJ/mol) and the water diffusivity was almost 2 orders of magnitude lower than that of the other plastics. Hence, the water transport in PGA seemed to follow the solution-diffusion model.

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