NOTES

Effects of Annealing on the Sorption of Propane in Polycarbonate

INTRODUCTION

The effect of sub-T_g annealing on the equilibrium sorption and diffusion behavior of cast bisphenol-A polycarbonate films with propane as the penetrant was investigated using a finite-bath sorption apparatus. Most results are interpreted in terms of a dual sorption model, which has become standard for analyzing equilibrium sorption and diffusion in glassy polymers.[1–5] The model ascribes the penetrant concentration C to two components

$$C = C_D = C_H = k_D p + C'_H bp/(1 + bp) \tag{1}$$

where C_D is the concentration attributed to the Henry's law term and C_H is the concentration attributed to the Langmuir isotherm term. The parameters are the Henry's law constant k_D, the Langmuir capacity C'_H, the affinity constant b, and the pressure p.

The glass transition T_g of bisphenol-A polycarbonate is ~150°C making thermal treatment above and below T_g and sorption measurements well below T_g readily accessible to investigators. Norton[6] measured permeabilities and time lags of several gases across amorphous, glassy polycarbonate. Vieth and Ellenberg[7] investigated diffusion and equilibrium sorption of various gases in polycarbonate, interpreting the results with the dual sorption model. Paul et al.[8,9] used the polymer for an extensive study of sorption and permeation measurements on glassy polymers. Barrie et al.[10] obtained dual sorption parameters and their temperature dependence for the propane-polycarbonate system. Edin and Chen[11] determined the apparent diffusion coefficient $\overline{D}$ and penetrant solubility at low pressure for propane and other hydrocarbons in polycarbonate. Chen[12] also investigated the effect of sub-T_g annealing on $\overline{D}$.

Prolonged annealing of an amorphous, glassy polymer at temperatures a few degrees below T_g increases the polymer density[13] and reduces the equilibrium sorption of penetrant as demonstrated, for example, in the CO_2–polycarbonate system.[14,15] This decrease is attributed to the decrease in C'_H.[14–16] The sub-T_g annealing of extruded polycarbonate also slightly reduced $\overline{D}$ at low pressure for propane and methane.[12]

EXPERIMENTAL

The finite-volume sorption procedure was used to determine the sorption equilibrium and kinetics properties.[17] A single-pressure transducer was used in the apparatus, necessitating a linear extrapolation of pressure versus $t^{1/2}$ to determine the initial pressure p_0. Average membrane thickness was determined from mass-density-area measurements and with a micrometer caliper. The differential scanning calorimeter (DSC) determinations were obtained with a du Pont 990 thermal analyzer with the DSC/DTA cell base module. X-ray diffraction for crystallinity detection was accomplished with a Norelco instrument.

The bisphenol-A polycarbonate, Lexan, supplied by the General Electric Company had number-average and weight-average molecular weights of 12,500 and 35,300, respectively. Films were cast on mercury at about 34–36°C from 5 to 10% solutions in methylene chloride to produce clear films. Thicknesses were in the $(2.8 \text{ to } 3.2) \times 10^{-4}$ cm range. Rapid solvent evaporation near its boiling point was required to produce tough, clear, amorphous films. No melting was detected by DSC and the x-ray diffraction results were consistent with an amorphous structure. Slow solvent removal produced brittle, opaque, crystalline films. Melting was detected by DSC and crystallinity by x-ray diffraction. The films were degassed in vacuum at 40–80°C for several days before measurements were attempted. Sorption experiments were run using membranes as prepared and after annealing in vacuum at 130–135°C.

The polymer was used as received without further purification. The propane used as penetrant was 99.5% pure and was subjected to freeze-pump-thaw cycles after being introduced into the sorption apparatus.

Journal of Applied Polymer Science, Vol. 25, 2109–2113 (1980)

0021-8995/80/0025-2109$01.00

TABLE I
Thermal Treatment of Films

Sample	Thermal treatment
PC-1	3 days in vacuum at 40–50°C
PC-A1	Treatment of PC-1 plus 49 hr at 135°C in vacuum
PC-A2	Treatment of PC-A1 plus 51 hr at 135°C in vacuum
PC-10	3 days in vacuum at 80°C
PC-A10	Treatment of PC-10 plus 72 hr at 135°C in vacuum.

The thermal treatments of the films are summarized in Table I. The T_g's for these films were in the range 148–155°C.

Sorption–desorption measurements were carried out on PC-1, PC-A1, and PC-A2 at 50°C to determine the dependence of C on p and provide data for calculating the dual sorption parameters. Similar measurements were made on PC-10 and PC-A10, over a temperature range with fewer experiments at each temperature, and the dual parameters were determined at only a few temperatures.

SORPTION BEHAVIOR

The equilibrium sorption data for PC-1, PC-A1, and PC-A2 were analyzed using the dual sorption isotherm, eq. (1), rearranged to

$$p/C_H = 1/C'_H b + p/C'_H \tag{2}$$

where $C_H = C - k_D p$. Values of k_D were selected arbitrarily and C'_H and b determined from the slope and intercept of p/C_H vs. p. The reported values of C'_H and b are those obtained for k_D producing the maximum coefficient of determination in a linear least-squares regression. The results are provided in Table II. The C'_H parameter for PC-A1 was evaluated using the values of k_D and b determined for PC-1 and PC-A2 obtained by the regression method because the maximum in the coefficient of determination in this case was too broad to provide meaningful values of the parameters. The expected consistency of k_D and b in PC-1 and PC-A2 is outstanding, warranting the forced parameter values for PC-A1.

The dual sorption parameter values listed in Table II reported by Barrie et al.[10] were obtained for a polycarbonate film cast on glass from methylene chloride and degassed for several days at 50–70°C; a preparation similar to that used in this work. It was not annealed. A nonlinear regression analysis of data obtained from accurate infinite-bath sorption experiments was used. Considering the separate casting, the differences in experimental procedure and analysis, the lack of data at high pressures, and the limitations of the finite-bath procedure of this work, the agreement between the results appears satisfactory.

Koros et al.[9] determined dual sorption parameters for other gases in polycarbonate at 35°C and

TABLE II
Dual Sorption Parameters for the Propane-Polycarbonate Systems

Film	T (°C)	$10^2 k_D$ $\left(\frac{\text{cm}^3\text{(STP)}}{\text{cm}^3\ \text{cm Hg}}\right)$	C'_H $\left(\frac{\text{cm}^3\text{(STP)}}{\text{cm}^3}\right)$	b $\left(\frac{1}{\text{cm Hg}}\right)$	K $\frac{C'_H b}{k_D}$
		Unannealed films			
PC-1	50.0	4.5	0.72	0.23	3.7
PC-10	48.7	3.0	1.5	0.08	4.0
(ref. 10)	50.1	4.1	0.95	0.20	4.6
		Annealed films			
PC-A1	50.0	4.5[a]	0.53	0.22[a]	2.6
PC-A2	50.0	4.5	0.48	0.22	2.4

[a] Values obtained for PC-1 and PC-A2 are used for PC-A1.

TABLE III

Diffusion Coefficients for Propane/Polycarbonate at 50.0°C

Film	Run	p_i [a] (cm Hg)	p_f [a] (cm Hg)	c_i $\left(\frac{\text{cm}^3\text{(STP)}}{\text{cm}^3}\right)$	c_f $\left(\frac{\text{cm}^3\text{(STP)}}{\text{cm}^3}\right)$	$10^{10}\bar{D}$ $\left(\frac{\text{cm}^2}{\text{sec}}\right)$	$10^{10}D_D$ $\left(\frac{\text{cm}^2}{\text{sec}}\right)$
PC-1	IA	0	13.35	0	1.31	1.07	1.32
	IB	13.35	1.93	1.31	0.31	0.52	1.58
	IIA	0	4.03	0	0.52	0.58	1.22
	IIIA	0	12.38	0	1.18	0.77	1.14
PC-A1	IVA	0	12.74	0	0.89	1.41	2.08
	IVB	12.74	2.38	0.89	0.11	0.55	1.93
	VA	0	4.45	0	0.43	0.99	1.84
	VIA	0	12.77	0	1.01	0.76	1.96
	VIB	12.77	2.36	1.01	0.24	0.62	2.29
PC-A2	VIIA	0	3.72	0	0.38	0.86	1.50
	VIIB	3.72	0.91	0.38	0.10	0.60	1.73
	VIIIA	0	6.34	0	0.60	0.70	1.93
	VIIIB	6.34	1.33	0.60	0.17	0.62	2.17
	IXA	0	9.95	0	0.77	0.94	1.92
	IXB	9.95	1.81	0.77	0.15	0.74	2.23
	XA	0	12.90	0	0.94	0.79	2.17
	XB	12.90	2.35	0.94	0.19	0.63	2.24

[a] Initial and final variables indicated by i and f.

TABLE IV
Limiting Diffusion Coefficient $\bar{D}(C = 0)$ and Activation Energies

Film	T (°C)	$10^{11}\bar{D}(C = 0)$ (cm^{3}sec^{-1})	$E_{\bar{D}}$ (kJ mole^{-1})
PC-10	38.7	3.5	47
	48.7	5.0	
	62.3	12.6	
	62.6	12.3	
	73.2	19.5	
	76.1	24.0	
PC-A10	38.8	5.1	51
	46.5	7.9	
	60.6	20.0	
	73.3	34.7	

correlated their values with the Leonard–Jones potential well depth. Extrapolation of their data to predict values for propane gives $k_D \cong 0.03$ cm^3 (STP) cm^{-3} (cm Hg)$^{-1}$, $C'_H \cong 30$ cm^3 (STP) cm^{-3} (cm Hg)$^{-1}$, $b \cong 0.006$ (cm Hg)$^{-1}$, and $K \cong 6$. Although k_D and K agree reasonably well with the extrapolated values, C'_H and b differ significantly.

The decrease in C brought about by sub-T_g annealing with the accompanying decrease in C'_H is qualitatively consistent with previous determinations of this effect.[12,15–17] The ratio of C'_H in an annealed film to its value in the unannealed film permits a comparison with studies using other penetrants. Values of 0.74 and 0.67 were obtained for the propane–polycarbonate system annealed at 135°C for 49 and 100 hr, respectively. Chan and Paul[15] annealed polycarbonate at 125°C and used CO_2 as the penetrant in a high-pressure apparatus. The observed ratios for that system at 49 and 100 hr were 0.76 and 0.73.

The finite-volume sorption procedure, even in this apparatus restricted to low pressure and dependent on measurements with a single transducer, provides an analysis of the essential features of the sorption of a gas by a polymer glass. An equilibrium-concentration decrease resulting from annealing was observed and related to the decrease in the Langmuir capacity.

DIFFUSION

The apparent diffusion coefficient $\bar{D}$ can be simply determined from the transient portion of the finite-volume sorption experiment when $\bar{D}$ is independent of penetrant concentrations.[18] This analysis utilizes only the data at large t, where C is approaching the equilibrium concentration C_f. The value of $\bar{D}$ calculated in this manner should approximate $\bar{D}$ at C_f in both sorption and desorption experiments if $\bar{D}$ does not have a strong dependence on C. The diffusion coefficient for gases in glassy polymers is expected to be a function of C.[3] Inspection of Table III reveals a weak increase in $\bar{D}$ with increasing C_f. Barrie et al.[10] observed a somewhat greater dependence of the apparent diffusion coefficient on concentration, with $\bar{D}$ determined from initial sorption rates in an infinite-bath experiment. Extrapolation of $\bar{D}$ to $C_f = 0$ gives $\bar{D}$ $(C_f = 0) \cong 5 \times 10^{-11}$ cm^2 sec^{-1} for PC-1, PC-A1, PC-A2, and PC-10, with the value for the annealed film PC-A10 somewhat higher, $\sim 9 \times 10^{-11}$ cm^{2}sec^{-1}. These values are larger than the value D $(C = 0) = 2.1 \times 10^{-11}$ cm^{2}sec^{-1} obtained by Barrie et al.[10] at 50°C. In contrast to this constant or increase in $\bar{D}$ $(C_f = 0)$ with annealing, Chen[12] observed a smoothly decreasing function of $\bar{D}$ at low pressure when an extruded film was annealed at 120°C. The initial decrease was significant, but continued annealing from 20 to 125 hr reduced $\bar{D}$ by only 6%, a change likely too small to be determined unequivocally in the finite-bath apparatus.

Values for $\bar{D}$ $(C = 0)$ determined as a function of temperature for the unannealed film PC-10 and after annealing it at 135°C for 72 hr, PC-A10, are summarized in Table IV. The activation energies for these films are somewhat lower than those observed by the other investigators; 62 kJ mole^{-1} (ref. 10), and 68 kJ mole^{-1} (ref. 11).

Vieth and Sladek[19] provided a method for analyzing dual sorption diffusion from transient sorption measurements of a finite bath experiment. The flux per unit area J in dual sorption diffusion is

$$J = -D\frac{\partial c}{\partial x} = -D_D\frac{\partial C_D}{\partial x} - D_H\frac{\partial C_H}{\partial x} \tag{3}$$

where D_D and D_H are diffusion coefficients for the penetrant assigned to C_D and C_H, respectively. Usually both are assumed constant, and in the original method $D_H \boxed{=} 0$. The restriction of $D_H = 0$ has been removed for other methods of measurement.[4,10] In this method the relative pressure change, $\phi \equiv [p(t) - p_o]/(p_f - p_0)$, where p_0 and p_f are the initial and final pressures, are plotted against $(\theta'/D)^{1/2}$, where

$$\frac{\theta'}{D} = \frac{t}{L^2}\left(1 + \frac{C'_H b/k_D}{(1 + bp)^2}\right)^{-1} \tag{4}$$

and L is the membrane thickness. The resulting curve is compared to the generalized correlation curve ϕ vs. $(\theta')^{1/2}$ obtained numerically by Veith and Sladek[19] and $D^{-1/2}$ is the scaling factor required to superimpose the two curves. The results are included in Table III as D_D. D_D is larger in the annealed films than in the unannealed films; however, it does not increase when the annealing period is extended from 49 to 100 hr. If sub-T_g annealing reduces C_H without altering C_D one might expect D_D to be unaffected. An increase in D_D, as well as the instance in which $\overline{D}$ increased with initial annealing, was unexpected. This behavior could be the result of removal of traces of solvent retained even through the extensive pretreatment and the previous sorption experiments at lower temperature, or a thermally induced relaxation in the high-density region of this glass cast under conditions involving rapid solvent removal.

The authors are grateful to Dr. M. J. Drews for his assistance in obtaining the DSC results.

Note added in proof: A decrease in the time lag with sub-T_g annealing has recently been observed for permeation of CO_2 in polycarbonate.[20]

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Received January 24, 1980
Accepted February 12, 1980