

Sorption of Propane in Poly(ethyl Methacrylate) Near T_g

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Synopsis

The sorption of propane in poly(ethyl methacrylate) was investigated above and below the polymer T_g and the dual-mode sorption model parameters were evaluated. The Langmuir capacity decreased as the temperature was raised to T_g and the apparent Henry's law constant exhibited a discontinuity at T_g . The enthalpy of microvoid filling ΔH_H is more exothermic than the enthalpy of dissolution at $T < T_g$ by about 8 kJ/mol.

INTRODUCTION

The thermodynamic and transient state properties of systems composed of gases and vapors in polymers impact the utilization of polymer membranes and films in barrier coatings and packages and in gas and vapor separations. This paper describes the sorption of propane by poly(ethyl methacrylate) (PEMA) in the region of the polymer T_g in terms of the dual-mode sorption model.

The dual-mode sorption model assigns the equilibrium penetrant concentration C to two distinguishable components; a Henry's law component concentration C_D and Langmuir component concentration C_H .¹⁻⁵ The model expresses the dependence of C on the penetrant pressure p in a three-parameter equation

$$C = C_D + C_H = k_D p + C'_H b p / (1 + b p) \quad (1)$$

where k_D is the Henry's law constant, C'_H the Langmuir capacity, and b the Langmuir affinity factor. The Langmuir component is generally ascribed to penetrant located in microvoids or low-density regions frozen into glassy amorphous polymers at temperatures below T_g and the Henry's law component to the penetrant in the glassy polymer matrix. At low pressure or small b , eq. (1) reduces to

$$C = k^* p \quad (2)$$

with k^* , the apparent Henry's law constant given by

$$k^* = k_D + C'_H b \quad (3)$$

C_H is eliminated as the system passes from glassy states to the rubbery state. Two phenomena have been suggested to account for its elimination; a decrease in C'_H as T approaches T_g ⁶ and the condition that C'_H is constant below

T_g becoming $C'_H b = k_D$ at $T > T_g$, which implies^{7,8}

$$k^* = 2k_D \quad (4)$$

for $T > T_g$.

The parameters k_D and b are related to the temperature by⁹

$$k_D = k_{D0} \exp(-\Delta H_D/RT) \quad (5)$$

and

$$b = b_0 \exp(-\Delta H_H/RT) \quad (6)$$

where ΔH_D is the enthalpy of dissolution and ΔH_H the enthalpy of microvoid filling. The isosteric heat of sorption in the limit $C \rightarrow 0$, $\Delta H_s(C = 0)$, is given by

$$\Delta H_s(C = 0) = -R[\partial \ln(k_D + C'_H b)/\partial(1/T)](C = 0) \quad (7)$$

The enthalpy of transfer of the penetrant from the polymer matrix to the microvoids, ΔH^* , is defined by

$$\Delta H^* = \Delta H_H - \Delta H_D \quad (8)$$

EXPERIMENTAL

Atactic PEMA, obtained from Polyscience, Inc., as a primary standard, had an M_w of 350,000 with $M_w/M_n = 2.2$. The T_g was 65°C, determined by differential scanning calorimetry using a heating rate of 20°C/min, and tacticity was confirmed by NMR.

Thin films, $18 \pm 3 \mu\text{m}$ in thickness, were prepared by casting from dilute chloroform solutions on clean mercury. The solvent was removed under vacuum at 35–45°C for at least 4 days before placing the polymer in the sorption apparatus where it was subsequently further exposed to vacuum for at least 3 days before beginning the sorption experiments. The films were not exposed to temperatures greater than 45°C prior to initiating the sorption studies, nor were they preconditioned by exposure to high penetrant pressures. The solvent was reagent grade stored over molecular sieves.

A low pressure, finite volume, sorption apparatus previously described was used at pressures up to 60 cm Hg.¹⁰ The vapor used in the sorption experiments was propane obtained from Matheson with a purity of 99.98%. After introduction into the apparatus it was distilled bulb-to-bulb at least three times before use.

TREATMENT OF DATA

A simple equation of state containing the second virial coefficient was used to convert the pressure of propane to moles at the low pressures employed in the sorption.¹¹

For $T > T_g$, k^* in eq. (3) was evaluated using a linear regression on the dependence of C on p . For $T < T_g$, the dual-mode sorption model parameters,

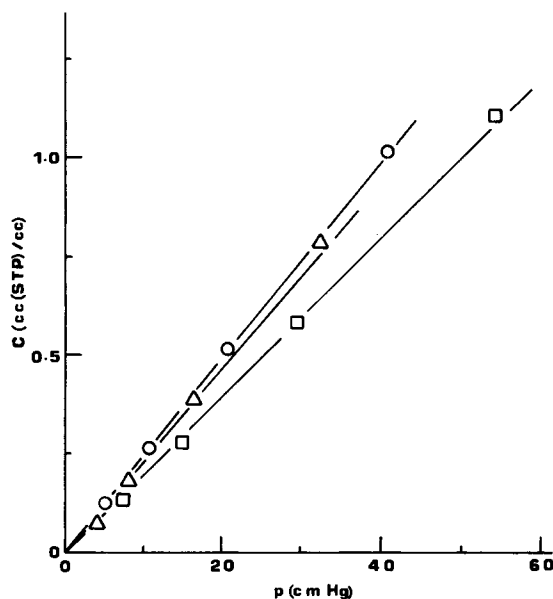


Fig. 1. Sorption isotherms at temperatures above T_g : (○) 342 K; (△) 348 K; (□) 353 K.

k_D , C'_H , and b , were determined using a nonlinear regression procedure.¹⁰ The van't Hoff type dependences of k_D and b on temperature were used to constrain the entire data set obtained below T_g in the calculation of the parameters. Standard deviations were also determined.

The values of ΔH_D , ΔH_H , $\Delta H_{S(C=0)}$ were calculated from graphs of $\ln k_D$, $\ln b$, $\ln(k_D + C'_H b)$ vs. $1/T$ and ΔH^* was calculated from eq. (8).

RESULTS AND DISCUSSION

The linear sorption isotherms shown in Figure 1 were obtained above T_g . The apparent Henry's law constants are listed in Table I. At temperatures well below T_g the isotherms were concave toward the pressure axis as shown in Figure 2. The dual-mode sorption model parameters obtained for these isotherms are given in Table II. The decline in C'_H as the temperature approached T_g is shown to be linear in Figure 3. The sorption isotherm determined at 60°C, about 5°C below T_g , was linear and its slope was within

TABLE I
Apparent Henry's Law Constants for the Linear Isotherms

T (K)	$10^2 k_D^a$ ($\text{cm}^3 \text{ STP}/\text{cm}^3 \text{ cm Hg}$)
333	2.10(±3%)
333 ^a	2.06(±3%)
342	2.44(±6%)
348	2.27(±7%)
353	1.96(±9%)

^a Indicates the sorption trial after annealing.

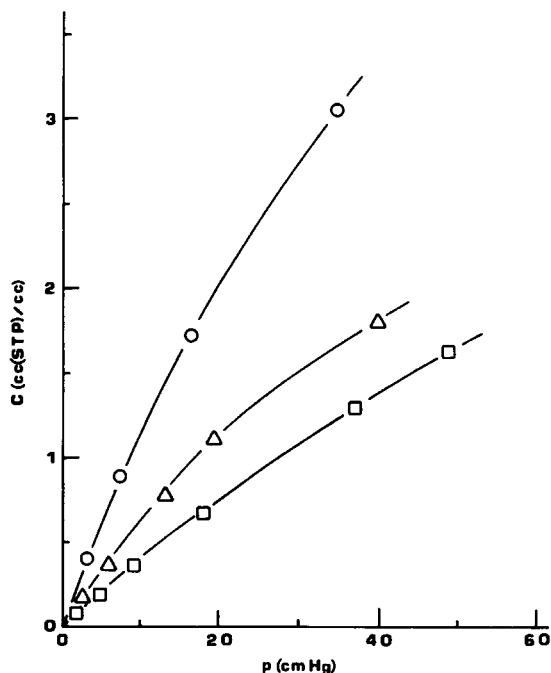


Fig. 2. Sorption isotherms at temperatures below T_g : (O) 288 K; (Δ) 303 K; (\square) 318 K.

experimental error of that obtained for the second isotherm determined after lengthy annealing in vacuum at 60°C. These results indicate that C'_H declines to zero near the T_g of PEMA under the conditions of sorption experiments. This behavior of C'_H is consistent with the result obtained by Koros et al.¹² for CO₂ in PEMA.

Figure 4 is a graph of $\ln k^*$ vs. $1/T$ for $T > T_g$ and $\ln k_D$ vs. $1/T$ for $T < T_g$. The value of k_D obtained from the linear isotherm at 60°C is a linear extension of the values of k_D calculated using eq. (1) for the other isotherms below T_g . However, it is less than the value of k^* obtained at 69°C, about 4°C above T_g . A distinct discontinuity in the curve occurs near T_g . Such a discontinuity has been observed in other systems.⁸⁻¹⁰ The magnitude of the discontinuity, approximately 0.3, is less than the value predicted by Pace and Datyner.^{7,8}

The sorption enthalpies obtained for $T < T_g$ are listed in Table III. Figure 5 shows plots of the appropriate parameters vs. T^{-1} . The enthalpy of micro-

TABLE II
Dual-Mode Sorption Model Parameters

T (K)	$10^2 k_D$ (cm ³ STP/ cm ³ cm Hg)	C'_H (cm ³ STP/cm ³)	$10^2 b$ (cm Hg) ⁻¹	$10^2 S_L$ (cm ³ STP/ cm ³ cm Hg)	$10^2 C'_H b$ (cm ³ STP/ cm ³ cm Hg)
288	3.02(±7%)	4.83(±10%)	2.10(±11%)	13.2(±10%)	10.1(±6%)
303	2.73(±10%)	3.10(±14%)	1.20(±17%)	6.45(±12%)	3.72(±8%)
318	2.24(±9%)	1.77(±15%)	1.05(±19%)	4.10(±13%)	1.86(±6%)

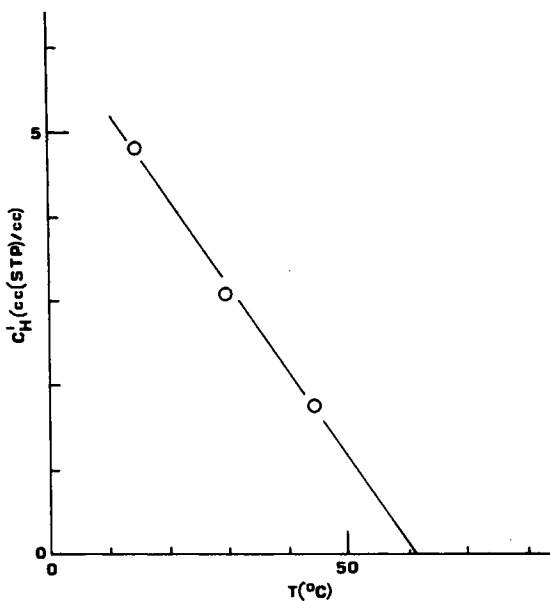


Fig. 3. Langmuir capacity vs. temperature.

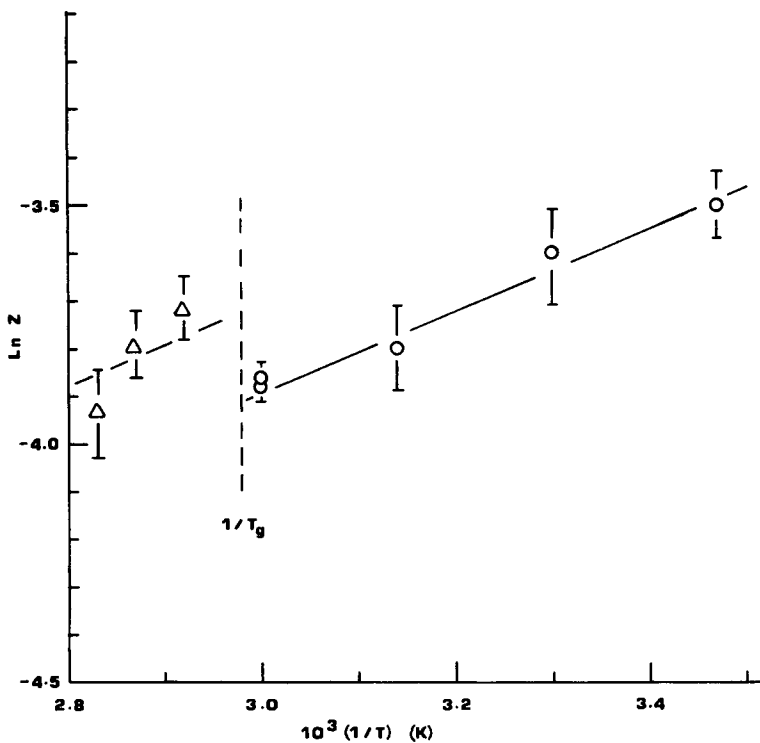
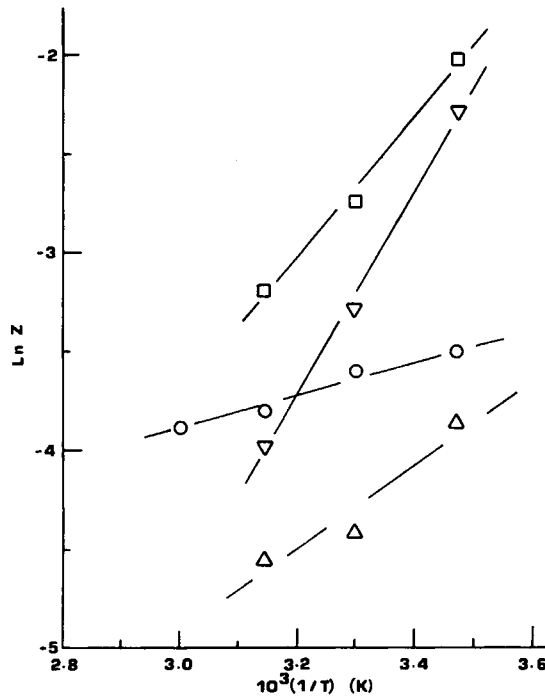


Fig. 4. $\ln Z$ vs. T^{-1} for temperatures above and below T_g : (Δ) $Z = k^*$; (\circ) $Z = k_D$.

TABLE III
 Enthalpies of Sorption

Property	Enthalpy (ks/mol)
ΔH_D	-6.7
ΔH_H	-14.4
$\Delta H_b(C = 0)$	-29.4
ΔH^*	-7.7


 Fig. 5. $\ln Z$ vs. T^{-1} : (O) $Z = k_D$; (Δ) $Z = b$; (∇) $Z = C_H^* b$; (\square) $Z = k_D + C_H^* b$.

void-filling ΔH_H is more exothermic than the enthalpy of dissolution ΔH_D . The enthalpy for transforming propane from the polymer matrix to the microvoids ΔH^* is -7.7 kJ/mol. Koros et al.¹² obtained $\Delta H_D = -11$ kJ/mol and $\Delta H_b = 8.3$ kJ/mol for the sorption of CO_2 in glassy PEMA. The positive ΔH_b was attributed to residual traces of casting solvent. Barrie et al.⁹ found ΔH^* to be zero and -17 kJ/mol for the sorption of propane in two samples of polystyrene, and -10 kJ/mol in polycarbonate. Casur and Smith¹³ obtained $\Delta H^* = 12.6$ kJ/mol for the sorption of propane in ethyl cellulose calculated by eq. (8) and a value of -19.6 kJ/mol using the slope of $\ln(C_H^* b)$ vs. $1/T$ as the apparent enthalpy of microvoid filling. The significantly negative value of ΔH^* for the sorption of propane in PEMA is consistent with a greater attraction of the propane by the microvoids compared to the polymer matrix.

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Received June 19, 1986

Accepted August 29, 1986