

Gas Sorption in Poly(butylene terephthalate). I. Influence of Gas Molecules

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SYNOPSIS

The sorption of CO₂ and the noble gases Ne and Ar in semicrystalline glassy poly(butylene terephthalate) (PBTP) films was measured by the gravimetric method with a recording microbalance at 298 K. The sorption of CO₂ was found to be significantly higher than that of Ne and Ar. This is attributed to a specific interaction between CO₂ and PBTP. The sorption isotherm for CO₂ was analyzed by the dual-mode sorption model, while the sorption behaviors for Ne and Ar did not follow this model. Their sorption isotherms can be described by the sorption model developed here for the noble gases in PBTP. A critical adsorption pressure p^* that is dependent mainly on the relative size of the frozen microvoids and the noble gas atoms is defined in this model. The Langmuir adsorption for describing the sorption in this gas/polymer system in addition to Henry's solubility happens just above this p^* , whereas only Henry's solubility takes place below p^* . © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Gas sorption behavior in rubbery polymers above their glass transition temperature T_g follows usually a linear Henry's law relationship, i.e., the equilibrium gas concentration C being proportional to the gas pressure p . In general, gas sorption isotherms in many glassy polymers can be satisfactorily described in terms of the dual-mode sorption model.¹⁻¹² The concentration C is given by the sum of a Henry's law solubility contribution ($C_D = k_D p$) and a Langmuir-type adsorption term ($C_H = C'_H b p / (1 + b p)$) [eq. (1)]:

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

The interpretation of the physical significance of this model as well as the parameters k_D , C'_H , and b have been presented elsewhere.^{13,14}

Poly(butylene terephthalate) (PBTP) is a poly-

ester that is rapidly gaining importance as an engineering thermoplastic due to its attractive mechanical properties, rapid crystallization rate, and good moldability.¹⁵ This gives rise to the need for studying the structure and properties of this material. The sorption of CO₂ in PBTP has been studied with the gravimetric equilibrium sorption method in the temperature range of 298–338 K.¹³ It was found that the CO₂ sorption isotherms can be described by the dual-mode sorption model in the temperature range of 298–328 K. At temperatures higher than 20 K above the glass transition temperature T_g , no Langmuir adsorption takes place because the mobility of the noncrystalline chain segments—even some degrees above T_g —is still restrained through the crystals, so that the frozen microvoids remain existent for a considerable time above T_g . This is in accordance with the concept of the “rigid amorphous phase” for phenyl-ring polymers.¹⁶ The sorption behavior of other gases in PBTP was also studied.¹⁴ The results indicated that for parameter correlation more than just the Lennard–Jones potential parameter must also be taken into account. The size exclusion of gases in small-diameter microvoids was proposed.

This paper reports the sorption behavior of dif-

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ferent gases in PBTP. Their sorption mechanisms are discussed in detail.

EXPERIMENTAL

Materials

The as-received PBTP films used in the sorption experiments were free of additive commercial products. Platilon KF was supplied by Atochem Deutschland, Bonn, Germany. This transparent film had a thickness of 0.15 mm. The density of the sample was determined by the density gradient column method using an aqueous calcium nitrate solution and factory-calibrated-density glass beads at 296 K. The density of this film was 1.284 g/cm³. According to the literature concerning the density of amorphous (1.256 g/cm³)¹⁷ and that of crystalline (1.396 g/cm³) (α -modification)¹⁸ PBTP, the calculated mass related crystallinity X_{cw}^D was 21.7%. The crystallinity X_{cw}^T of 30.2% was calculated on the basis of the heat of fusion of 144.6 J/g for the pure crystals.¹⁹ A melting temperature of 498 K was also obtained by differential thermal analysis using a Mettler TA 2000 thermoanalytic device in the temperature region between 223 and 533 K. The scanning rate was 10 K/min. The sample weights were 7–10 mg; 14.5 mg of Al₂O₃ was used as reference. At a heating rate of 2 K/min and 1 Hz, the glass transition occurring at 319 K was determined by a dynamic torsional pendulum device—the Zwick Torsiomatic 5203. The wide-angle X-ray diffraction photograph was taken by a Seifert Iso-Debyelex 2002 device using filtered CuK α radiation. The X-ray result indicated that the crystals in this sample were unoriented.²⁰ From the investigation of the Fourier transform infrared spectra measured by a Perkin-Elmer 1710 infrared spectrometer, it was found that the major part of the crystals existed in the so-called α -modification, while only a small part of the crystals was present in the β -modification.²⁰ This was also found in the melt-quenched PBTP sample.²¹ The birefringence of the sample ($\Delta n = 1.45 \times 10^{-3}$) was measured by a polarizing microscope, a Leitz Ortholux II Pol-Mk, equipped with a tilting compensator. This analysis supported by the X-ray results and the dynamic mechanical properties indicated that there existed a few slightly oriented chain segments in the noncrystalline regions of the PBTP sample.²⁰

The gases used in this study, CO₂, Ne, and Ar, had a purity of 99.99%. They were obtained from Messer-Griesheim, Düsseldorf, Germany, and were used as received.

Sorption Measurements

The sorption isotherms for the gas/PBTP systems were obtained by the gravimetric sorption apparatus that consists mainly of a Sartorius model 4436 electromicrobalance, encapsulated in a stainless-steel chamber, which permits the application of pressures up to 100 bar. Details about this device have been reported previously.^{13,14}

The gas sorption measurements were carried out at 298 K in a pressure range of 1–22 bar. As the measuring pressures between 1 and 22 bar were not large enough to draw an high-pressure asymptote, we used a nonlinear least-square analysis to determine the sorption parameters according eqs. (1), (4), and (5).

RESULTS AND DISCUSSION

CO₂ Sorption

The sorption isotherms at 298 K for CO₂, Ne, and Ar in as-received PBTP films are presented in Figure 1. At this temperature, the PBTP samples are in the glassy state. The sorption isotherm for CO₂ shows the nonlinear character well known for glassy polymers, so that it can be described well by the dual-mode sorption model [eq. (1)]. The high-pressure asymptote of eq. (1), i.e.,

$$C = k_D p + C_H \quad (2)$$

calculated using these parameters is shown in Figure 2. It indicates that the application of this analysis on the experimental data measured in the investi-

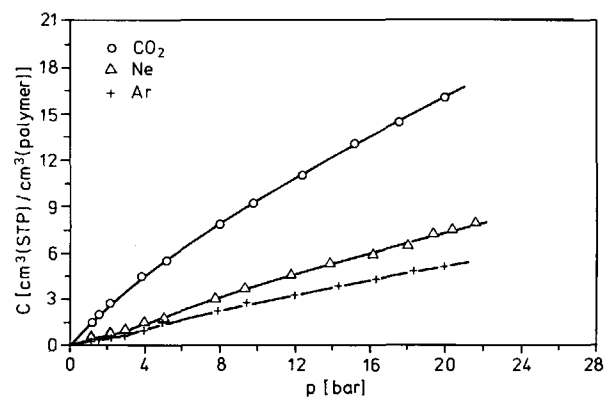


Figure 1 Sorption isotherms for CO₂, Ne, and Ar in the as-received PBTP film at 298 K. The solid lines were calculated from eq. (1) using parameters given in Table I.

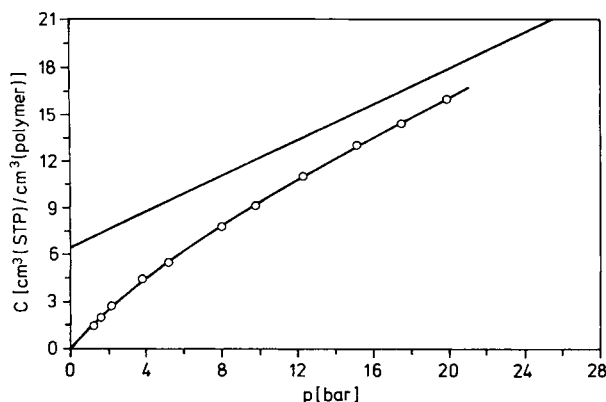


Figure 2 Sorption isotherm for CO₂ in the as-received PBTP film at 298 K. The solid lines were calculated from eq. (1) using parameters given in Table I. The straight line is the high-pressure asymptote of the solid curve.

gated pressure range is better than the previously used graphical method.¹² The obtained sorption parameters are given in Table I. The solid curve for CO₂ in Figure 1 was computed by eq. (1) using the parameters given in Table I and it is evident that they describe well the experimental data.

According to the suggestion of Koros et al.^{6,7} we tested whether a single Langmuir expression fits the data for the hole-filling process, i.e., the adsorption process. It can be demonstrated by plotting $1/C_H$ vs. $1/p$ to check the linearity. After rearrangement of the basic form of the Langmuir equation,

$$\frac{1}{C_H} = \frac{1}{C'_H} + \frac{1}{C'_H b p} \quad (3)$$

C_H was computed by eq. (2) using the k_D in Table I. From the data for CO₂, a linear dependence between $1/C_H$ and $1/p$ was plotted in Figure 3. The solid straight line in Figure 3 was computed using the values of C'_H and b given in Table I, which shows good agreement with the data.

Table I Sorption Parameters k_D , C'_H , and b and Critical Adsorption Pressures p^* (T = 298 K, As-received PBTP Film)

Gas	$k_D \times 10^4$ (cm ³ [STP]/ cm ³ Polymer bar)	C'_H (cm ³ [STP]/ cm ³ Polymer)	$b \times 10^4$ (bar ⁻¹)	p^* (bar)
Ne	2.94	2.42	0.86	3.3
Ar	2.15	1.10	1.72	2.8
CO ₂	5.64	6.49	1.32	—

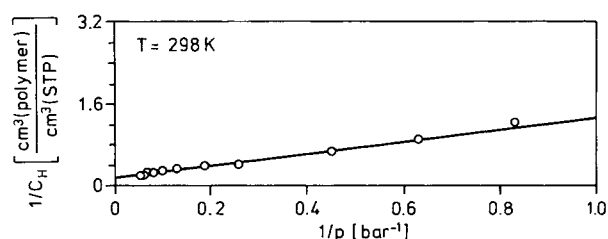


Figure 3 Test of the Langmuir equation for describing CO₂ sorption data. The solid lines were computed by eq. (3) using parameters given in Table I.

Influence of Gas Molecules

The sorption for the various gases in PBTP follow the ascending order of Ar < Ne < CO₂, although the mean molecular diameter of CO₂ is greater than the atom diameters of the noble gases, Ne and Ar (Table II). The high concentration for CO₂ relative to other gases has been reported for CO₂/poly(vinyl chloride), CO₂/poly(methyl methacrylate), and CO₂/PBTP system.^{10,14} The large CO₂ sorption may be attributed to a specific CO₂/PBTP interaction effect, which is not present for the other gases. The CO₂ molecule possesses a more linear structure, and the electronic cloud is built through the π -electrons of the both double linkages (C=O). Also, PBTP has a conjugated π -system formed through the π -electrons of the phenylene rings and the carbonyl groups. Therefore, it is not eliminatable that the main molecular axis of CO₂ is oriented along the π -systems of the terephthalate unit by polar interaction, so that a favorable CO₂ adsorption occurs on the inner surfaces of the frozen microvoids. This effect results also in high solubility of CO₂ in the noncrystalline regions of PBTP. In consequence, higher sorption parameters, C'_H , k_D , and b , were obtained (Table I).

As the sorption isotherms for Ne and Ar in PBTP did not show the typical curvature as predicted by the dual-sorption theory, the sorption parameters cannot be determined by fitting according to eq. (1). The concentration dependence as a function of pressure is first linear at the low-pressure range and obeys just the dual-sorption theory above a critical pressure. For the noble gases, it is assumed that only

Table II Diameter of Gases

Gas	CO ₂	Ne	Ar
$d \times 10^8$ (cm)	3.94	2.82	3.54

small interaction forces exist between the gas atoms and PBTP molecules. Furthermore, the size of the noble gases compared with that of the frozen microvoids is so small that they can move freely through microvoids at low pressures. The Langmuir adsorption cannot take place on the surfaces of the frozen microvoids, because the van der Waals interaction forces are too small. Just above the critical adsorption pressure p^* , the distances between the gas atoms and the inner surface of the frozen microvoids are so small that the adsorption is possible by the van der Waals interaction force. Only Henry's solubility takes place at the low pressures below the critical adsorption pressure p^* .

An indubitably existing size distribution of the microvoids in the PBTP matrix is neglected for the following discussion. Therefore, an average size of microvoids will be considered to develop the following sorption model that can explain the sorption behavior of the noble gases in PBTP:

Below the critical adsorption pressure p^* ($0 < p \leq p^*$),

$$C = k_D p \quad (4)$$

and above p^* ($p > p^*$),

$$C = k_D p + \frac{C'_H b (p - p^*)}{1 + b(p - p^*)} \quad (5)$$

In this case, eq. (3) becomes

$$\frac{1}{C_H} = \frac{1}{C - k_D p} = \frac{1}{C'_H} + \frac{1}{C'_H b (p - p^*)} \quad p > p^* \quad (6)$$

The critical adsorption pressure p^* is dependent mainly on the relative size of the frozen microvoids and the noble gas atoms. At the applied temperature, pressure p^* depends not only on the structures and properties of the noble gases but also on the morphologies of polymers.

The critical adsorption pressure and the sorption parameter in eqs. (4) and (5) for Ne and Ar were determined by nonlinear least-square analysis. The results are listed in Table I. The solid curves in Figure 1 for Ne and Ar represent the calculated sorption isotherms of eqs. (4) and (5) using these parameters, which show that this model for the sorption of the noble gases in PBTP is in good agreement with the experiment.

The adequacy of the Langmuir adsorption for describing the sorption in excess of Henry's solubility above the critical adsorption pressure p^* can be

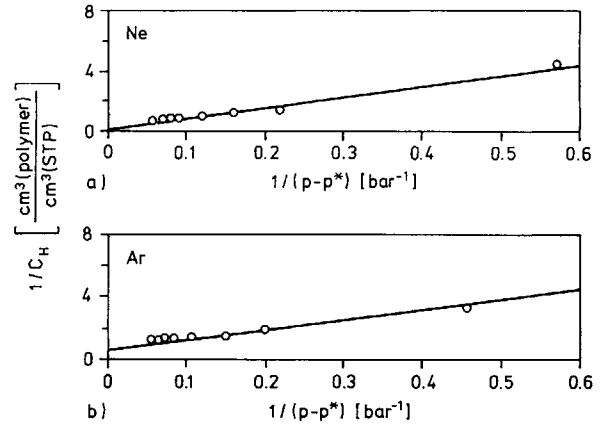


Figure 4 Test of the Langmuir equation for describing sorption data of Ne and Ar at 298 K. The solid lines were computed by eq. (6) using the parameters given in Table I.

demonstrated by plotting $1/C_H$ vs. $1/(p - p^*)$ from eq. (6). The solid lines in Figure 4 were calculated from eq. (6) using the appropriate parameters from Table I, and they describe well the data points above p^* . This proves the assumption for the Langmuir adsorption in this sorption model for the noble gases in PBTP.

From comparison with the data in Table I, it is also found that the adsorption pressure p^* for Ne is higher than that for Ar. This indicates that the smaller the size of the noble gases compared to that of the frozen microvoids in PBTP, the freer the gas molecules can move in the microvoids and the higher the p^* . The higher concentration for Ne relating to Ar in Figure 1 has to be attributed to the fact that a greater number of Ne atoms were sorbed on a site of the same size in the noncrystalline regions. Therefore, the k_D and C'_H for Ne are also greater than that for Ar.

CONCLUSIONS

The sorption for CO_2 , Ne, and Ar in the glassy semicrystalline PBTP film appears as a combination of Henry's law solubility and Langmuir adsorption in the regions of measuring pressures. The concentration of CO_2 is much higher than that of the noble gases Ne and Ar. This is attributed to a specific interaction between CO_2 and the terephthalate unit in the polymer by π -electronic effect. The sorption isotherm for CO_2 can be described by the dual-mode sorption model, while the sorption isotherms for Ne

and Ar did not to follow this model and are described well by the sorption model developed here for the noble gases in PBTP. A critical adsorption pressure p^* , which is estimated to be dependent mainly on the relative size of the frozen microvoids and the noble gas atoms, is defined in this model. The Langmuir adsorption for describing the sorption in the noble gas/PBTP system in addition to Henry's solubility takes place just above this p^* , whereas only Henry's solubility occurs below p^* .

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