

# Positron Annihilation Lifetime Studies of Gas Sorption and Desorption in Polyethylene and Poly[1-(trimethylsilyl)-1-propyne]

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Received 11 February 2000; accepted 14 June 2000

**ABSTRACT:** The variation of free-volume parameters (lifetime, intensity, and distribution) after sorption and desorption of CO<sub>2</sub> and CH<sub>4</sub> gases in the glassy polymer poly[1-(trimethylsilyl)-1-propyne] (PTMSP) and in the rubbery high-density polyethylene (HDPE) and low-density polyethylene (LDPE) were determined by the PAL technique. Size distributions deduced from PAL measurements reveal the presence of large free-volume holes in PTMSP with an average size of 0.725 nm<sup>3</sup> and intensity of 22% in addition to a free-volume hole size of 0.197 nm<sup>3</sup> with an intensity of 11%. In polyethylene free-volume hole sizes of 0.107 and 0.153 nm<sup>3</sup> with intensities of 21% and 25% could be deduced for HDPE and LDPE, respectively. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 970–974, 2001

**Key words:** poly[1-(trimethylsilyl)-1-propyne]; polyethylene; gas sorption and desorption; positron annihilation; lifetime distribution

## INTRODUCTION

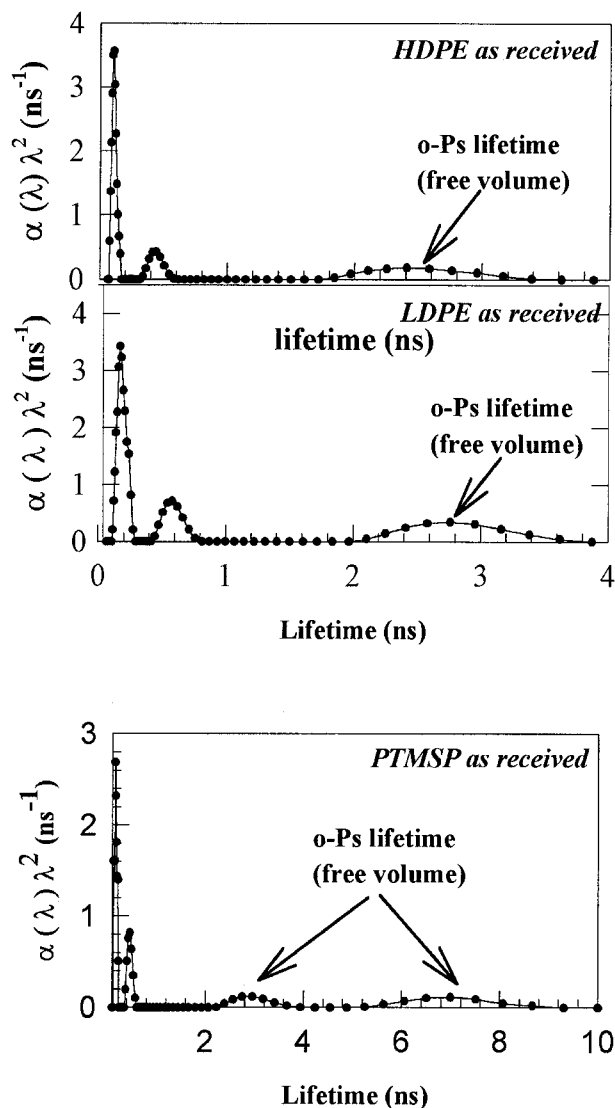
The understanding of the origin behind the variation of the permeability of gases in various polymers has become of utmost importance because of the wide range of applications of these polymers as protective coatings, as food packaging, and as gas separation membranes. Therefore, the application of new techniques will yield new insights into the mechanism of the transport of gases in both rubbery and glassy polymers.

By the application of the positron annihilation lifetime technique (PAL) to polymers, a correlation has been found between the diffusion coeffi-

cients of gases and the free-volume hole size deduced from PAL measurements<sup>1,2</sup> and permeation.<sup>3</sup> In the present work the PAL technique, which has been proven as a unique probe for the characterization of free-volume properties of polymers,<sup>4</sup> was applied to monitor the variation of free-volume properties after gas sorption and desorption in PTMSP, HDPE, and LDPE. The PTMSP glassy polymer is known<sup>5</sup> to have gas diffusion and permeability coefficients larger by almost 2 orders of magnitude compared to those obtained in rubbery polymers such as HDPE and LDPE. This has been attributed to the large free-volume holes arising from its structure, which consists of stiff and very loose packing of backbone chains separated by bulky trimethylsilyl side groups CH<sub>3</sub>—C=C—Si(CH<sub>3</sub>)<sub>3</sub>. These groups will hinder intrasegmental rotation and prevent chain packing.

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*Journal of Applied Polymer Science*, Vol. 80, 970–974 (2001)  
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**Figure 1** Lifetime distributions of HDPE, LDPE and PTMSP samples as received. The distribution lifetime was obtained by using the Laplace inversion program CONTIN.

Moreover, PTMSP is characterized by the instability of its properties<sup>6</sup> after prolonged storage in the ambient atmosphere at room temperature. After aging of PTMSP, the third and fourth lifetime components were found to decrease. This has been explained by the intensive interchain interactions leading to an increase in chain packing and to a decrease in the gas diffusion and permeability coefficients as well as a growth of its density. It is therefore of interest to investigate the variations in the properties of free-volume holes after CO<sub>2</sub> and CH<sub>4</sub> sorption and desorption in PTMSP, HDPE and LDPE.

## EXPERIMENTAL

Fresh samples of polyethylene (PE), were purchased from B. V. VinkKunststoffen Company, Holland. The density and the thickness of HDPE samples were 0.964 g/cm<sup>3</sup> and 3 mm, respectively. The density and the thickness of LDPE samples were 0.910 g/cm<sup>3</sup> and 2 mm, respectively. The fresh samples were first heated in vacuum (10<sup>-3</sup> mbar) in a water bath for 1 h and then cooled down to room temperature. They were then filled with gas while heating at 100°C at a pressure of 10 bar and then left for 24 h under vacuum to cool to room temperature. Desorption of the gas was also performed at 100°C. The PTMSP samples were prepared at the University of Twente, Holland. The density of the PTMSP sample was 0.82 g/cm<sup>3</sup>. The sample films were stacked to a thickness of 1.5 mm to minimize the surface effect. PTMSP samples were exposed to gas at 1 bar at room temperature in order to achieve the same amount of soluble gas as in the polyethylene samples. This was found to be approximately 2 × 10<sup>19</sup> molecules/cm<sup>3</sup>.

The positron lifetime measurements were performed at room temperature by using a conventional fast-fast coincidence system with a time resolution of 250 ps (FWHM). The 50 μCi <sup>22</sup>Na positron source, held between 7-μm-thick kapton foils, was sandwiched between two identical pieces of the sample. PAL spectra were accumulated to total counts of 10<sup>6</sup> and 10<sup>7</sup>. The spectra were analyzed into three or four lifetime components using the PATFIT<sup>7</sup> program with the constraint τ<sub>1</sub> = 0.125 ns. The free-volume size distributions were deduced using the CONTIN computer code.<sup>8</sup> Tungsten was used as a reference sample.

## RESULTS AND DISCUSSION

The PAL spectra of PE samples were analyzed into three lifetime components. In PTMSP a

**Table I** Some Properties<sup>9</sup> of PE and PTMSP

	HDPE	LDPE	PTMSP
S cm <sup>3</sup> (STP)/ cm <sup>3</sup> · cmHg	0.24	0.24	0.106
D cm <sup>2</sup> /s	5.8 × 10 <sup>-7</sup>	5.8 × 10 <sup>-7</sup>	2.17 × 10 <sup>-5</sup>
P cm <sup>3</sup> (STP)/s cm · cm Hg	3.5 × 10 <sup>-9</sup>	3.5 × 10 <sup>-9</sup>	28 × 10 <sup>-7</sup>

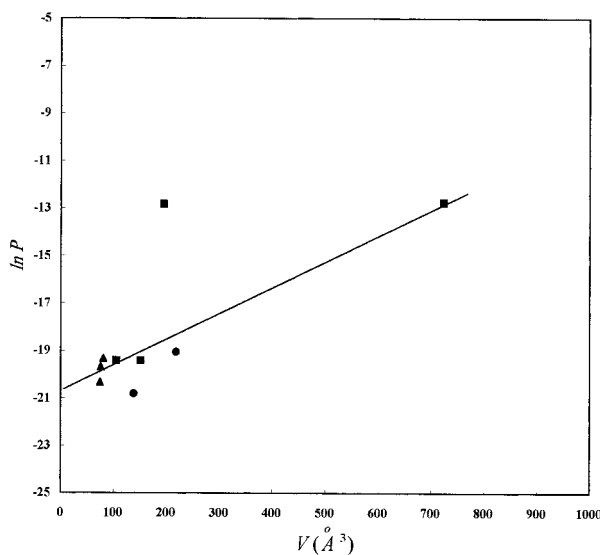
**Table II O-Ps Lifetime Components of HDPE, LDPE and PTMSP as Received Samples as Well as After CO<sub>2</sub> Sorption and Desorption**

	HDPE			LDPE			PTMSP		
	As Received	Sorption	Desorption	As Received	Sorption	Desorption	As Received	Sorption	Desorption
$\tau_3$ ns	2.252 ± 0.02	2.762 ± 0.01	2.450 ± 0.01	2.581 ± 0.02	3.180 ± 0.02	2.756 ± 0.01	2.961 ± 0.01	2.388 ± 0.02	3.180 ± 0.01
$I_3$ %	21 ± 0.2	27 ± 0.11	21 ± 0.1	25 ± 0.2	29 ± 0.11	26 ± 0.1	11 ± 0.1	6 ± 0.15	12 ± 0.1
$\tau_4$ ns							6.990 ± 0.02	6.058 ± 0.01	7.510 ± 0.01
$I_4$ %							22 ± 0.2	18 ± 0.18	23 ± 0.19

fourth component of 7 ns was observed. Figure 1 shows the positron annihilation rate distributions  $\lambda^2 \alpha(\lambda)$  for the as-received samples. The average free-volume sizes ( $V$ ) in HDPE, LDPE, and PTMSP for the as-received samples as well as after gas sorption and desorption were calculated according to the equations<sup>4</sup> for the lifetime  $\tau_3$  or  $\tau_4$  and the intensity  $I_3$  or  $I_4$  of o-Ps in a spherical hole of radius ( $R$ ) such that

$$\tau_{3or4} = 1/2[1 - R/R_0 + (1/2)\pi \sin 2\pi R/R_0]^{-1}$$

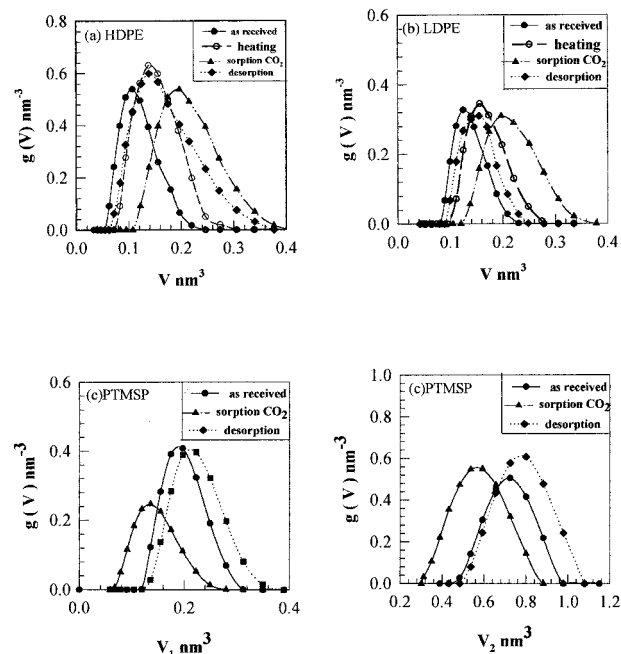
with  $R_0 = R + \Delta R$  and  $\Delta R = 0.165$  nm, and  $V = 4/3 \pi R^3$ . For CO<sub>2</sub>, as an example, gas transport coefficients<sup>5,9</sup> are listed in Table I. In Table II are listed the positron parameters in the as-received samples of HDPE, LDPE, and PTMSP as well as the corresponding parameters after sorption and desorption of CO<sub>2</sub>. In Figure 2 the permeability



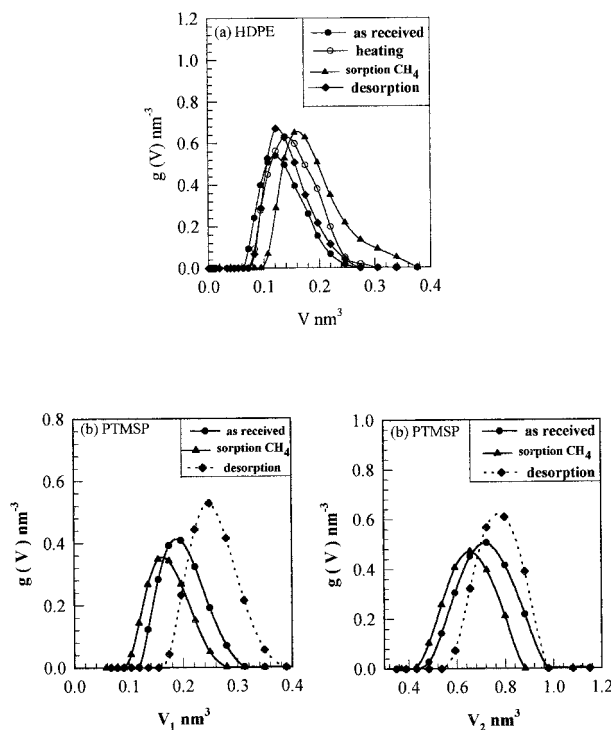
**Figure 2** CO<sub>2</sub> permeability versus mean free-volume size: (■) present work, and (●) polyimides,<sup>11</sup> (▲) PET copolyesters.<sup>3</sup> The small free-volume size in PTMSP significantly deviates from the fitting line.

coefficients ( $P$ ) of CO<sub>2</sub> gas for PTMSP, HDPE, and LDPE are represented as a function of the mean free-volume size ( $V$ ). Included also are the results obtained previously on polyimides<sup>10,11</sup> and in poly(ethylene terephthalate) (PET),<sup>3</sup> as well as in the copolyesters PEC(30)T and PEC(65)P. The data could be fitted using the empirical equation  $P = k_1 \exp(k_2 V)$  suggested by Yang et al.<sup>3</sup> The fitting parameters  $k_1$  and  $k_2$  were found to be  $1.13 \times 10^{-9}$  and 0.01, respectively. It is interesting to note that in PTMSP the small free-volume size deviates significantly from the fitting line, indicating that the large free-volume size seems to be responsible for its large gas permeability.

The size distributions,  $g(V)$ , for the as-received samples as well as after sorption and desorption of CO<sub>2</sub> and CH<sub>4</sub> were deduced by transformation



**Figure 3** The free-volume distributions in (a) HDPE, (b) LDPE and (c) PTMSP samples as received, as well as after CO<sub>2</sub> sorption and desorption.



**Figure 4** The free-volume distributions in (a) HDPE and (b) PTMSP samples as received, as well as after  $\text{CH}_4$  sorption and desorption.

of the rate distributions using the following equations<sup>8</sup>

$$f(R) = 2\Delta R[\cos 2\pi R/(R + \Delta R) - 1]\alpha(\lambda)/(R + \Delta R)^2 \text{ and } g(V) = f(R)/4\pi R^2.$$

These are represented in Figures 3 and 4, respectively.

The variations in the size distributions of polyethylene samples after  $\text{CO}_2$  or  $\text{CH}_4$  sorption and desorption are quite similar: After sorption the distributions become broader and shift to larger size for HDPE as well as LDPE, that is,  $I_3$  and  $\tau_3$  are increasing. After desorption the original distributions are restored. This is in accordance with Henry-type sorption, where the plasticization effect leads to enhancement of both  $I_3$  and  $\tau_3$ . Since polymer chain segments in a rubbery state are in the thermodynamic equilibrium state, the size of free space that has been enlarged by  $\text{CO}_2$  or  $\text{CH}_4$  can return to its original size when the gases are released. This agrees with previous work on polyethylene.<sup>11–14</sup>

For PTMSP samples the size distributions after  $\text{CO}_2$  and  $\text{CH}_4$  sorption become less broad and

shift to small values, that is, both  $I_3$  and  $\tau_3$  and  $I_4$  and  $\tau_4$  are reduced. This behavior is in accordance with Langmuir-type sorption, in which dissolved gas molecules fill in free volumes, leading to a reduction in the o-Ps intensities and lifetimes. These results are in accordance with previous results<sup>6</sup> in which the behavior occurred for the small holes as well as for the large ones. Using the data in Figure 2 the deduced  $\text{CO}_2$  permeability is reduced to  $5 \times 10^{-7}$ , which agree with the value previously determined by these authors after  $\text{CO}_2$  aging using the mass spectrometric method. After desorption the distributions do not remain the same (just as other glassy polymers behave) after being exposed to gas molecules at low pressure, because in this case relaxation is expected to be slow. Instead, the distributions became broader and shift to large sizes after desorption of  $\text{CO}_2$  or  $\text{CH}_4$  gases. This behavior occurs for the small holes as well as for the large ones. Such an increase after  $\text{CO}_2$  or  $\text{CH}_4$  desorption can be understood on the basis of the known instability<sup>6</sup> of PTMSP because of its low packing density and has already been reported<sup>11</sup> about many glassy polymers. The similarity in effect of  $\text{CO}_2$  and  $\text{CH}_4$ , which have almost equal sizes ( $0.029 \text{ nm}^3$ ), suggests that the increase in o-Ps formation is related to structural changes, which seem to be size dependent.

According to the rule correlating permeability coefficients and free-volume holes, an increase in permeability could be expected after  $\text{CO}_2$  desorption by a factor of almost 2.

## CONCLUSIONS

Application of PAL measurements to study the effect of  $\text{CO}_2$  and  $\text{CH}_4$  gas sorption and desorption on free-volume properties of LDPE, HDPE, and PTMSP yielded the following conclusions:

- A correlation between  $\text{CO}_2$  permeability and the mean free-volume size ( $V$ ) can be established in accordance with the equation  $P = k_1 \exp(k_2 V)$ . The large deviation of the small free-volume size from the fitting curve indicates that the large  $\text{CO}_2$  gas permeability of PTMSP is due to its large volume.
- In HDPE and LDPE the variation of the free-volume distribution upon  $\text{CO}_2$  or  $\text{CH}_4$  sorption and desorption, follows the Henry-type sorption–desorption mechanism.

In PTMSP the variation of these distributions is in accordance with the Langmuir type, but only

in the case of gas sorption. After desorption the increase in  $V$  (although small for  $V_2$ ) has two explanations:

1. Plasticization of the free-volume holes after being filled with gases—This explanation can be ruled out because it is not expected in glassy polymers exposed to gas molecules at low pressures.
2. Initiation of structural changes by the gas molecules—Such changes can be understood on the basis of the known instability of PTMSP properties.
3. A positronium probe has been revealed as an effective probe of the sorption and desorption mechanism in polymers.

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