

# Positron Annihilation Lifetime Study of Vapor Sorption in Polypropylene and Polytetrafluoroethylene

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## SYNOPSIS

Positron annihilation lifetime (PAL) spectra were measured for two different kinds of polymers: polypropylene (PP) and polytetrafluoroethylene (PTFE), during sorption of vapors of the following molecules: *n*-hexane, cyclohexane, benzene, methyl methacrylate, acrylic acid, and water. The behavior of *ortho*-positronium (*o*-Ps) annihilation parameters: lifetime,  $\tau_3$ , and intensity,  $I_3$ , can be explained by considering different sorption mechanisms in rubbery and glassy polymers. The mean size of the intermolecular-space holes and the relative free-volume fraction of PP and PTFE were estimated before and during the sorption process from the *o*-Ps parameters obtained. Sorption of *n*-hexane, cyclohexane, and benzene in both polymers affect the *o*-Ps component in a systematic way, for PP  $\tau_3$  and  $I_3$  tend to decrease, while in PTFE,  $\tau_3$  stay almost constant and  $I_3$  diminishes. These effects are interpreted in relation to the different states of the polymers studied: rubbery for PP and glassy for PTFE. In case of methyl methacrylate molecules, the behavior of *o*-Ps parameters was more complicated. For acrylic acid and water, their associated polarity provokes a diminution in  $I_3$ , which is explained from the viewpoint of the spur model of positronium formation. Large changes in the mean size and the fraction of free volume, as well as their constant behavior in some cases, were interpreted to be due to positive or negative interactions, respectively, between vapor molecules and PP and PTFE, which could be correlated with the solvent-interaction parameters calculated. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Due to high utilization of polymers in different applications as separation membranes, packaging materials, engineering plastics, biopolymers, etc., the study of the sorption phenomenon of gases and vapors in these materials has been of considerable interest in the recent years.<sup>1-3</sup>

The mechanisms of gas sorption and permeation in polymers has been described by several theoretical models, some of which are based on free-volume considerations.<sup>4</sup> The free-volume concept has been widely used for the interpretation of a variety of polymer properties such as glass transition, aging, and the plasticization of glassy polymers. The free volume may be defined either as the vacant space

unoccupied by the van der Waal's spheres of the polymer matrix or by some suitable integral of the potential energy evaluated as a function of the space coordinates.<sup>5</sup>

In addition to the theoretical studies, which include the methods of molecular mechanics and molecular dynamics,<sup>2</sup> there have been significant experimental effort to determine the average cavity size in a polymer matrix and the distribution of the free volume, using, mainly, the techniques of positron annihilation,<sup>6</sup> photocromic labeling,<sup>7</sup> and electrochromism.<sup>8</sup>

It has been demonstrated in several works<sup>9</sup> that application of the positron annihilation lifetime (PAL) technique makes it possible to follow the process taking place in polymers. Specifically, PAL has been applied with success to study the free-volume characteristics in these materials,<sup>10,11</sup> since PAL delivers information at a microscopic level in contrast to other methods. When a positron interacts

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with a polymeric material, it has a certain probability to form a bound state with an electron called a positronium (Ps). Once formed, *ortho*-Ps (*o*-Ps) diffuses through the material and tends to localize in sites of reduced density, such as free-volume sites. When localized, its annihilation rate is proportional to the local electron density and, by consequence, the *o*-Ps lifetime ( $\tau_3 = 1/\lambda_3$ ) provides information regarding the mean size of those localization sites. In addition, the corresponding intensity of the *o*-Ps ( $I_3$ ) is indicative of both the *o*-Ps formation probability and the density of localization sites. Thus, the unique sensitivity of PAL toward free-volume properties is due to the fact that Ps is found to be preferentially localized in the free-volume region of polymeric materials.<sup>12</sup> This has been widely confirmed in studies done on phase transitions and relaxations in several polymeric materials<sup>13</sup> as well as in studies of the vapor-sorption process on polyethylene and a kind of polyimide.<sup>14</sup>

Vapor-sorption behavior in rubbery polymers above their glass transition temperatures,  $T_g$ , follows, usually, a linear Henry's law relationship, while vapor sorption isotherms in many glassy polymers can be satisfactorily described in terms of a dual-mode sorption model.<sup>15</sup> In this case, the concentration of the penetrant is given by the sum of a Henry's law solubility contribution and a Langmuir-type adsorption term.<sup>16</sup>

In the present work, we studied the characteristics of positron annihilation during the sorption process of vapors of *n*-hexane, cyclohexane, benzene, methyl methacrylate, acrylic acid, and water into polypropylene (PP) and polytetrafluoroethylene (PTFE). PAL measurements were carried out to correlate the changes in the *o*-Ps parameters ( $\tau_3$  and  $I_3$ ) with sorption mechanisms already established for glassy and rubbery polymers, as well as to analyze how the free-volume (average size and fraction) changes during the sorption of vapor molecules, which possess different molecular volume and polarity, into the polymer matrix.

## EXPERIMENTAL

Polypropylene (PP) and polytetrafluoroethylene (PTFE) were selected for this work due to their high applicability in many fields of polymer science and technology.<sup>17</sup> At room temperature, PP is in a rubbery state ( $T_g = -18^\circ\text{C}$ ) and PTFE is in a glassy state ( $T_g = 126^\circ\text{C}$ ), which provides an interesting contrast to study the sorption mechanism similar to the comparison of polyethylene and polyimide

already reported.<sup>14</sup> PP (isotactic) pellets were supplied by General Electric Co. The pellets were melted at approximately  $176^\circ\text{C}$ , and samples of rectangular shape were cut with dimensions of  $5 \times 10 \times 2$  mm. PTFE, in the form of a sheet (thickness = 0.5 mm), was supplied by Fluorocarbon Co. and was cut to the same dimensions as was PP.

The positron source was prepared by depositing about  $25 \mu\text{Ci}$  of aqueous  $^{22}\text{NaCl}$  on a thin nickel foil of  $2.8 \text{ mg/cm}^2$  thickness and area of  $5 \times 6$  mm, which was then covered with other foil of the same size. The source was sandwiched by two identical polymer samples and placed in one arm of the glass tube employed to carry out the sorption process.<sup>18</sup> The sample was evacuated at approximately  $110^\circ\text{C}$  for 30 min and then slowly cooled down to room temperature. After cooling, the sample was kept at room temperature for 1–2 days to allow the polymer chains to become stable by aging. Liquids of *n*-hexane, cyclohexane, benzene, methyl methacrylate (MMA), acrylic acid (AA), and water, each separately, were put into another arm of the glass tube and were evacuated by the freeze-thaw method.

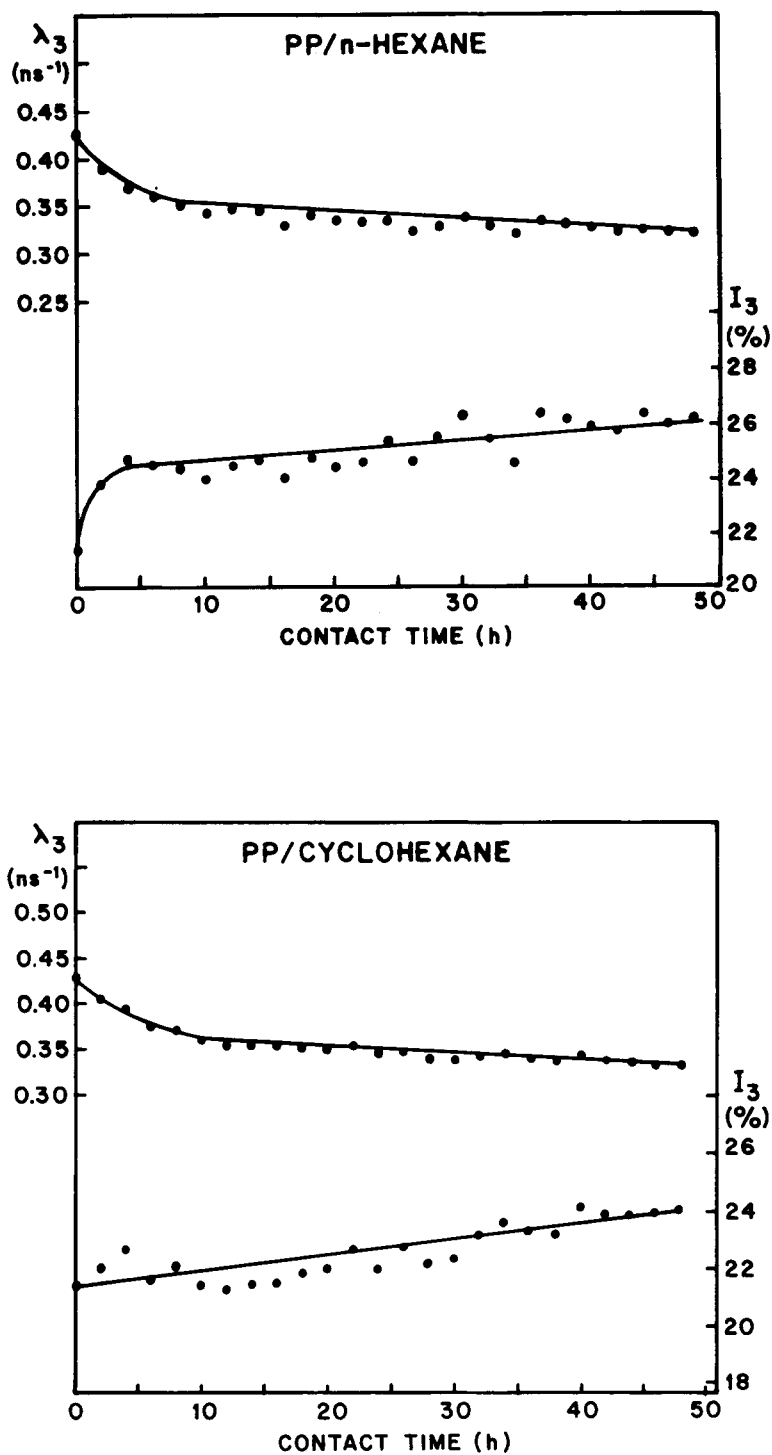
The lifetime measurements were made with a standard fast-fast coincidence system based on plastic scintillators, RCA photomultipliers, and EG&G Ortec electronics. The PAL spectrum was obtained for the polymer sample several times, before starting the vapor sorption, and then the stopcock connecting the two arms of the glass device was opened to let the vapor start contact with the sample. The PAL measurements were performed continuously and the data were recorded every 2 h. The positron lifetimes and intensities were analyzed using the program PATFIT<sup>19</sup> for each set of data.

## RESULTS AND DISCUSSION

### Polypropylene

The values of the annihilation rate ( $\lambda_3 = 1/\tau_3$ ) and intensity ( $I_3$ ) of each vapor sorbed into PP are shown in Figures 1–3 as a function of the contact time. When a vapor is sorbed into a rubbery polymer, the process takes place through a dissolution in accord with Henry's law. In this sorption mechanism, the molecules dissolved in the polymer can expand the intermolecular space between polymer chains. As a consequence, the polymer becomes more susceptible to the plasticization phenomenon.<sup>20</sup>

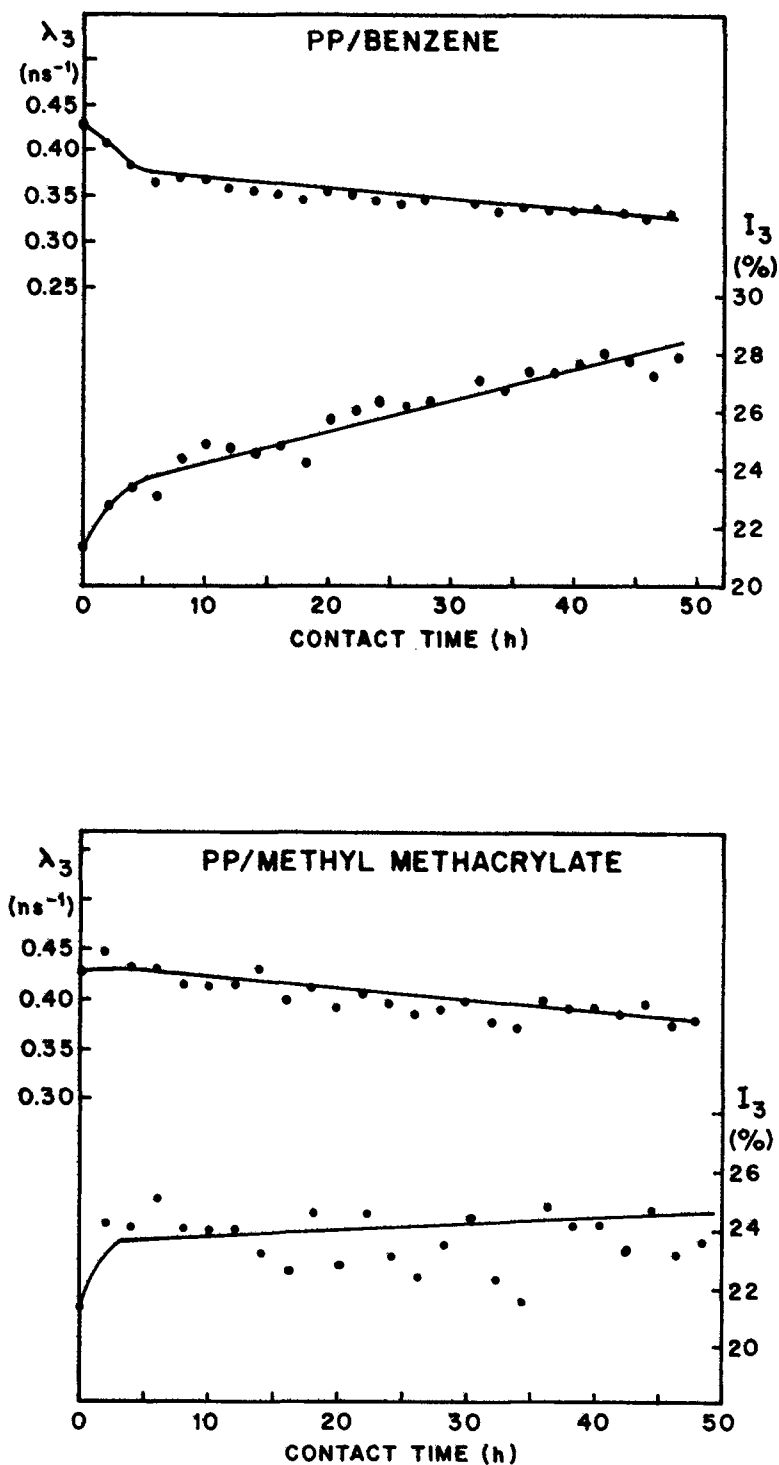
It is well recognized that the plasticization in a polymer provokes an expansion in the free-volume fraction. Thus, the equilibrium in the free-



**Figure 1** *o*-Ps parameters,  $\lambda_3$  and  $I_3$ , in PP as a function of the contact time with the vapor of *n*-hexane and *c*-hexane, respectively.

volume element distribution tends to a larger size and number and, as a consequence, the *o*-Ps can localize into larger microvacancies and to live longer. This involves a diminution in  $\lambda_3$ , as can be observed in Figures 1 and 2. This same behav-

ior was obtained in our study of vapor sorption in low-density polyethylene.<sup>14</sup> In addition, since PP becomes soft by the plasticization effect, it is thought that the surface tension of the material becomes small enough to allow the repulsive



**Figure 2** *o*-Ps parameters,  $\lambda_3$  and  $I_3$ , in PP as a function of the contact time with the vapor of benzene and MMA, respectively.

forces between the Ps and the surrounding polymer chains to form a "bubble" around the *o*-Ps atom.<sup>21</sup> The "bubble" formation can also increase the *o*-Ps lifetime.

Table I shows the values of  $\tau_3$  and of the mean size of the free volume ( $V_H$ ) as a function of the contact time between PP and the different studied substances. The mean size of the intermolecular

space holes in PP was calculated using the following equations<sup>22</sup>:

$$\tau_3 = 1/2 [1 - R/R_0 + (1/2\pi)\sin(2\pi R/R_0)]^{-1} \quad (1)$$

$$R = (3V_H/4\pi)^{1/3} \quad (2)$$

$$R_0 = R + 0.166 \quad (3)$$

where the intermolecular-space holes are assumed to be a sphere with a radius  $R$  and an electron layer of thickness  $\Delta R = 0.166$  nm. For  $n$ -hexane, cyclohexane, benzene, and MMA,  $V_H$  values tend to increase as the contact time is augmented. This behavior of the free volume is in accord with the previous explanation related to the effects that occur into the PP matrix during the sorption of vapor molecules.

When AA and water vapors were put into contact with PP, a different behavior in the  $o$ -Ps lifetime was obtained, as can be seen in Figure 3. The  $o$ -Ps lifetime remains almost constant throughout the experiment in both kinds of vapor. A plausible explanation for these results is related to the hydrophobic nature that PP has and, of course, with the solvent interactions between the polymer and the penetrant molecules. A poor solvent interaction of PP with AA and water bring, as a consequence, a poor sorption of these molecules by the polymer, which results in small variations in the polymer microstructure, as is reflected by the  $o$ -Ps lifetimes obtained.

The gradual increase of  $I_3$  in PP due to vapor sorption of  $n$ -hexane and cyclohexane and of benzene and MMA (Figs. 1 and 2, respectively) should be correlated with the plasticization effect by which the mean size of free volume increases. Following their formation,  $o$ -Ps atoms tend to localize in regions of reduced density such as areas of free volume in amorphous polymers. In this situation,  $I_3$  corresponds to both the  $o$ -Ps formation probability and the density of the intermolecular-space holes (localization sites). The plasticization due to vapor sorption promotes segmental motions of polymer chains, and this might create new localization sites resulting in an enhanced  $o$ -Ps formation. Under this situation, the free-volume fraction and  $o$ -Ps intensity are indirectly correlated through the number of trapping sites. According to Wang et al.<sup>12</sup> the free-volume fraction may roughly be calculated from the  $o$ -Ps lifetime and intensity using the following expression:

$$f = V_H C_f \quad (4)$$

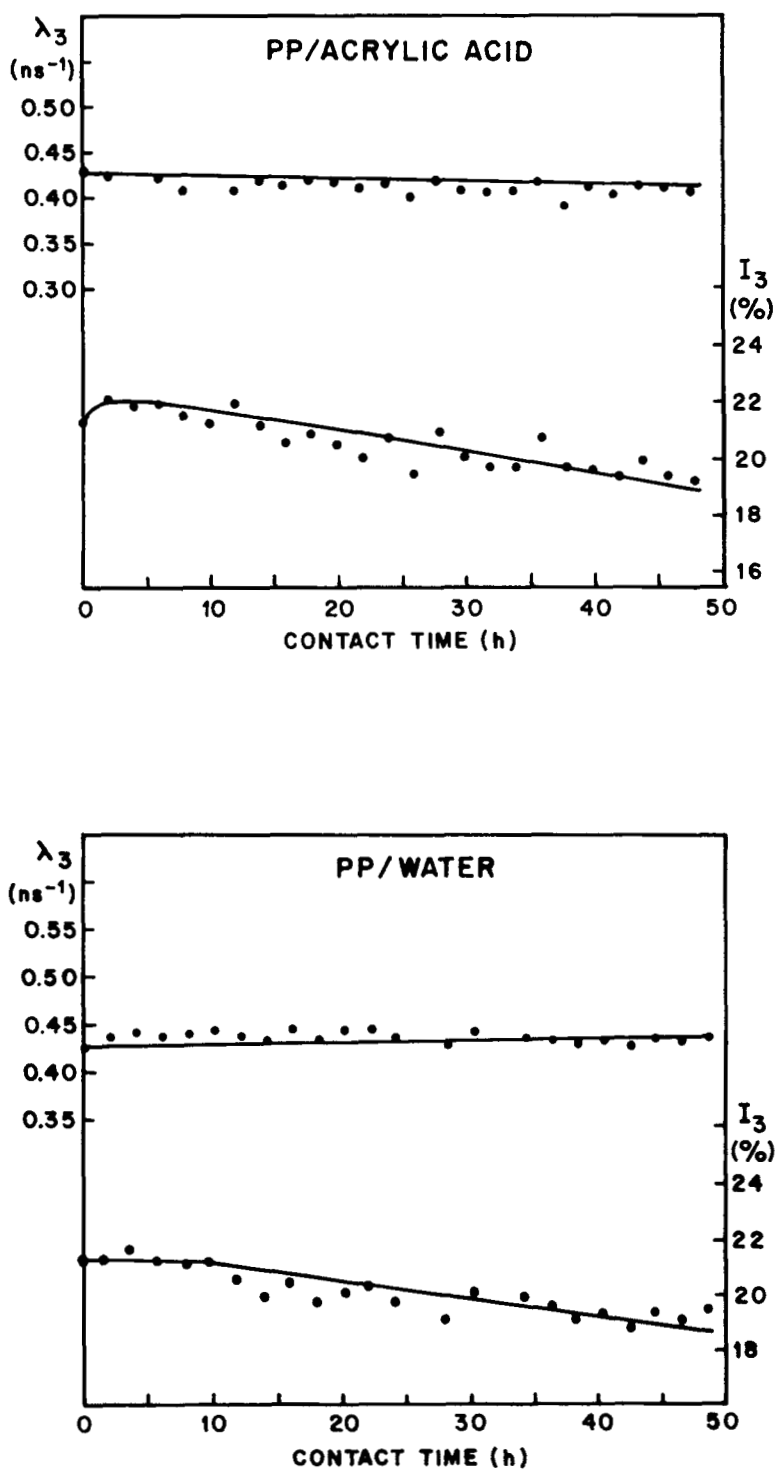
where  $V_H$  is the volume of an individual, spherical free-volume cavity calculated from the  $o$ -Ps lifetime ( $\tau_3$ ) [eq. (1)] and  $C_f$  is the concentration of these cavities in the material under study. Assuming that  $C_f$  is proportional to  $I_3$ , and that there are no cavities when  $I_3 = 0$ , then

$$f = V_H \cdot I_3 \quad (5)$$

Some studies<sup>6</sup> have shown that the product  $\tau_3 \cdot I_3$  can be considered as a rough measure of the free-volume fraction in polymers and it is estimated that the advantage of this empirical relation is that it does not depend on any suppositions that might be included in models describing a behavior of positrons in complex media.<sup>8</sup>

Table II contains  $I_3$  values obtained and  $f$  values calculated for PP during sorption of the different vapors. It is necessary to clarify that the  $f$  values reported here are just a rough measure of the free-volume fraction, since it has been considered that PP can expand its free volume ( $V_H$ ) in accord with a "bubble" formation model and, in such a case, the  $o$ -Ps lifetime would become larger than the intrinsic free-volume size. As can be seen (Table II),  $f$  tends to increase with  $n$ -hexane, cyclohexane, benzene, and MMA, having a more marked effect with  $n$ -hexane and benzene, which is in accordance with the solvent interaction parameter that these vapors present in respect to PP. This point will be presented later in this article.

Regarding the behavior shown by  $I_3$  during the sorption of AA and water in PP (Fig. 3), this is opposite to that presented by the other vapors, especially at higher contact times (after 10 h). At the first stage of sorption,  $I_3$  remains constant, but at higher contact times, it starts to decrease. It is well known that  $o$ -Ps formation in these polar mediums becomes smaller in going from solid to liquid,<sup>23</sup> and this is explained considering a solvation of  $o$ -Ps precursors by clusters of polar molecules. The diminishing of  $I_3$  can be explained in a similar way, since, when a certain quantity of vapor molecules (AA or water) are present in the polymer, these can accumulate and form clusters. The fact that  $I_3$  stays constant at the beginning of the sorption process might indicate that a certain concentration of molecules is necessary to promote cluster formation and to inhibit the  $o$ -Ps formation. In addition, some conditions related to the thickness of the polymer samples must be considered since they can influence the results. The diffusion constant for a molecule into a polymer matrix is assumed to be approximately  $1 \times 10^{-8}$  cm<sup>2</sup>/s,<sup>24</sup> which can be smaller for the situation



**Figure 3** *o*-Ps parameters,  $\lambda_3$  and  $I_3$ , in PP as a function of the contact time with the vapor of AA and water, respectively.

of a poor solvent interaction like water in PP or some vapors in PTFE. It is known that positrons stop and annihilate to a sample depth of more than 0.2 mm; then, it seems necessary to consider these

conditions and correlate them with the fact that after 10 h of contact time more changes in the *o*-Ps parameters were registered. This explanation is in accordance with the above-mentioned re-

**Table I** *o*-Ps Lifetime and Free-Volume Mean Size Values Determined Before and After Vapor Sorption in PP

Contact Time (h)	<i>n</i> -Hexane		<i>c</i> -Hexane		Benzene		MMA	
	$\tau_3$ (ns)	$V_H$ (nm <sup>3</sup> )	$\tau_3$ (ns)	$V_H$ (nm <sup>3</sup> )	$\tau_3$ (ns)	$V_H$ (nm <sup>3</sup> )	$\tau_3$ (ns)	$V_H$ (nm <sup>3</sup> )
0	2.362	0.133	2.341	0.131	2.371	0.134	2.345	0.131
6	3.067	0.209	2.659	0.164	2.731	0.172	2.314	0.128
12	2.873	0.187	2.801	0.179	2.764	0.175	2.403	0.137
18	2.923	0.193	2.824	0.182	2.857	0.185	2.415	0.138
24	2.976	0.199	2.873	0.187	2.864	0.186	2.500	0.147
30	2.949	0.196	2.923	0.193	2.885	0.188	2.481	0.145
36	2.985	0.200	2.898	0.190	2.916	0.192	2.475	0.144
42	3.076	0.210	2.907	0.191	2.899	0.190	2.551	0.152
48	3.086	0.211	2.949	0.196	2.954	0.197	2.590	0.156

quired elapsed time for cluster formation inside the polymer.

### Polytetrafluoroethylene

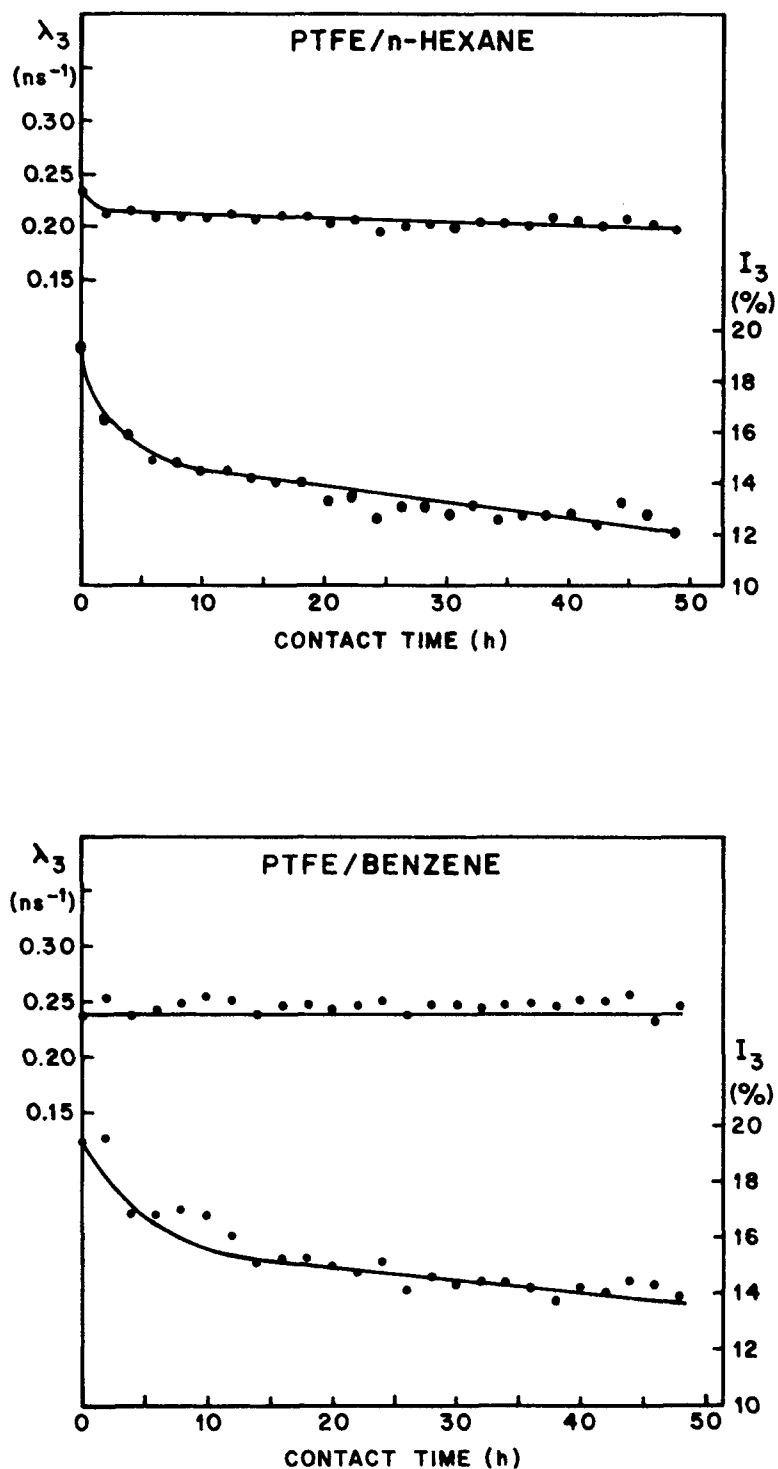
As was mentioned in the Introduction, in glassy polymers, vapor sorption is governed by a dual mechanism, which involves both the Henry-type and the Langmuir-type sorptions. However, in glassy polymers, like PTFE, the plasticization proceeds slowly because the relaxation times are long. Then, only the effects of filling the microvacancies of the polymer by vapor molecules (the Langmuir-type sorption) are observed at early contact times of the sorption. In this situation,  $\lambda_3$  should increase while  $I_3$  tends to decrease. In Figures 4–6, it is shown that  $\lambda_3$  was constant along the sorption of the different vapors used. This might be explained by considering, as is well known, that PTFE is a very inert polymer

toward many chemical substances; thus, it is difficult for this polymer to be swelled by the penetrating vapor molecules. If the polymer cannot be swelled, it is very difficult for the mean size of *o*-Ps to increase since there is no plasticization effect which could contribute to that phenomenon, as in PP. Apparently, there is not a noticeable effect of diminution in the mean size of free volume, and, of course, of reduction of the *o*-Ps lifetime, by the filling of some microvacancies in PTFE by vapor molecules.  $V_H$  values were calculated using eqs. (1)–(3) and considering  $\tau_3$  values obtained for all the vapors during their sorption in PTFE; these results are presented in Table III, where it can be observed that  $V_H$  values calculated for PTFE along with the contact time with the vapors have a minimum variation with respect to  $V_H$  values calculated for PTFE alone (contact time = 0).

The *o*-Ps intensity,  $I_3$ , had a typical behavior for

**Table II** *o*-Ps Intensity of Formation and Free-Volume Fraction Values Determined Before and After Vapor Sorption in PP

Contact Time (h)	<i>n</i> -Hexane		<i>c</i> -Hexane		Benzene		MMA	
	$I_3$ (%)	$f$ (nm <sup>3</sup> )	$I_3$ (%)	$f$ (nm <sup>3</sup> )	$I_3$ (%)	$f$ (nm <sup>3</sup> )	$I_3$ (%)	$f$ (nm <sup>3</sup> )
0	21.34	2.83	21.32	2.79	21.34	2.85	21.31	2.79
6	24.54	5.13	21.66	3.55	23.16	3.98	25.12	3.21
12	24.54	4.58	21.32	3.81	24.87	4.35	24.12	3.30
18	24.81	4.78	21.93	3.99	24.36	4.50	24.71	3.41
24	25.48	5.07	22.14	4.14	26.47	4.92	23.28	3.42
30	26.43	5.18	23.33	4.50	27.12	5.09	24.60	3.57
36	26.55	5.31	23.57	4.48	27.57	5.29	24.06	3.46
42	25.98	5.45	24.14	4.61	28.21	5.35	23.57	3.58
48	26.37	5.56	24.35	4.77	28.16	5.55	23.94	3.73



**Figure 4** *o*-Ps parameters,  $\lambda_3$  and  $I_3$ , in PTFE as a function of the contact time with the vapor of *n*-hexane and benzene, respectively.

sorption in glassy polymers for the majority of analyzed vapors, i.e.,  $I_3$  diminished at the first stage of sorption for *n*-hexane (Fig. 4), benzene (Fig. 4), MMA (Fig. 5), and AA (Fig. 5). This behavior can

be understood by the reduction of the number of microvacancies available to form Ps being occupied by vapor molecules as the contact time increases.

However, with vapor molecules of cyclohexane



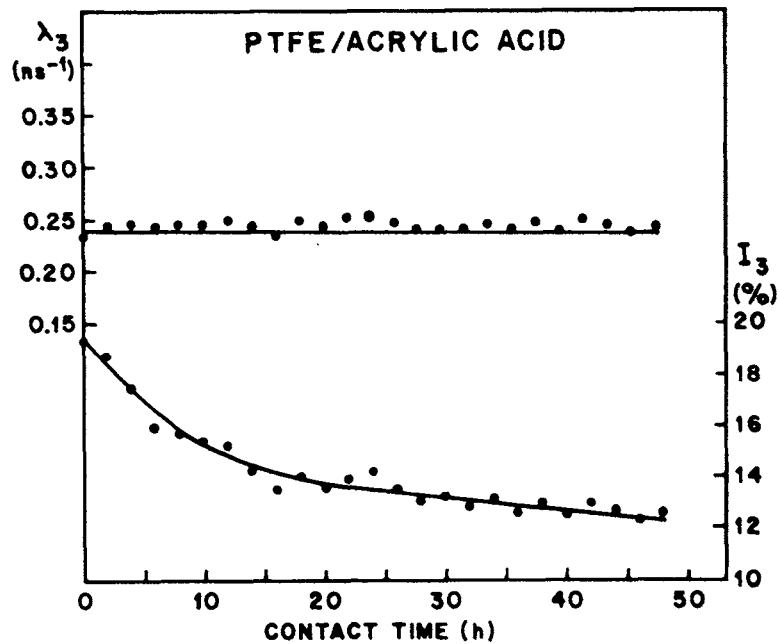
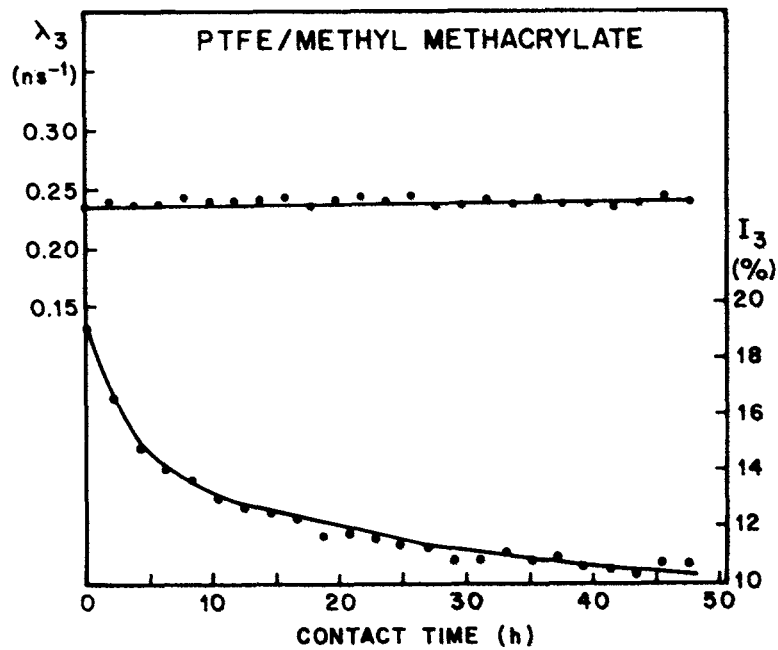
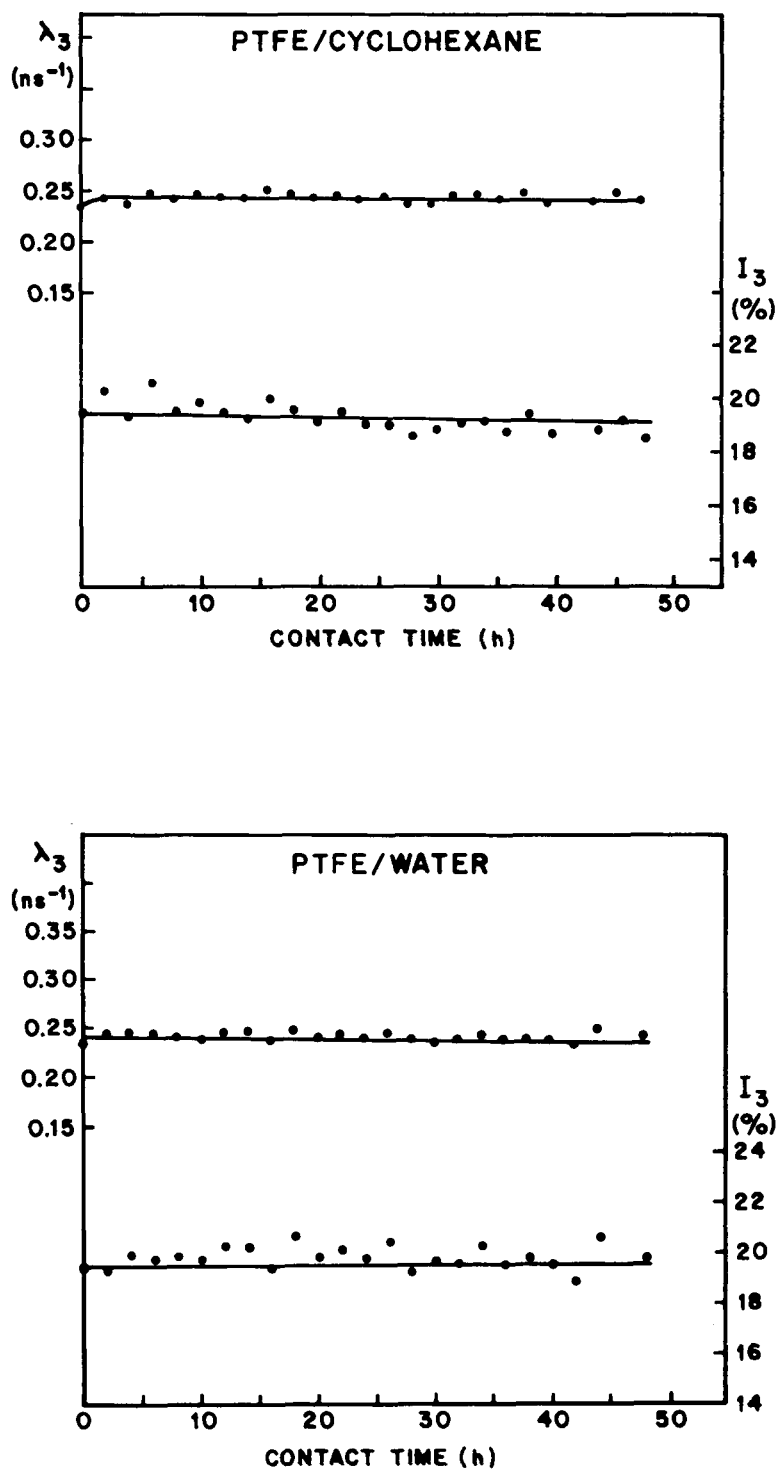


Figure 5 *o*-Ps parameters,  $\lambda_3$  and  $I_3$ , in PTFE as a function of the contact time with the vapor of MMA and AA, respectively.

and water, the behavior of  $I_3$  is different from the above-mentioned, since this parameter remained constant through the sorption experiments (Fig. 6). These results can be attributed to the structure and

physical properties (solubility parameter) that these vapors have. Cyclohexane possesses one of the largest molecular volumes (0.179 nm<sup>3</sup>) of the vapors used here, which, in addition to a poor solvent interaction



**Figure 6** *o*-Ps parameters,  $\lambda_3$  and  $I_3$ , in PTFE as a function of the contact time with the vapor of *c*-hexane and water, respectively.

parameter with respect to PTFE, might be the reason that sorption could not occur in this system. By the way, the results of water sorption show that, apparently, there is not a sorption phenomenon

since both *o*-Ps annihilation parameters remain constants. PTFE possesses a hydrophobic nature, which has, as a consequence, that vapor molecules of water cannot penetrate this polymer matrix.

**Table III** *o*-Ps Lifetime and Free-Volume Mean Size Values Determined Before and After Vapor Sorption in PTFE

Contact Time (h)	<i>n</i> -Hexane		<i>c</i> -Hexane		Benzene		MMA		AA		Water	
	$\tau_3$ (ns)	$V_H$ (nm <sup>3</sup> )	$\tau_3$ (ns)	$V_H$ (nm <sup>3</sup> )	$\tau_3$ (ns)	$V_H$ (nm <sup>3</sup> )	$\tau_3$ (ns)	$V_H$ (nm <sup>3</sup> )	$\tau_3$ (ns)	$V_H$ (nm <sup>3</sup> )	$\tau_3$ (ns)	$V_H$ (nm <sup>3</sup> )
0	4.263	0.354	4.255	0.352	4.260	0.353	4.255	0.352	4.257	0.353	4.246	0.353
6	4.756	0.417	4.016	0.322	4.110	0.334	4.184	0.343	4.065	0.328	4.065	0.328
12	4.649	0.403	4.065	0.328	3.969	0.316	4.115	0.335	3.968	0.316	4.016	0.322
18	4.675	0.406	4.000	0.320	4.023	0.323	4.184	0.343	3.984	0.318	3.984	0.318
24	4.999	0.449	4.081	0.330	3.954	0.315	4.115	0.335	3.876	0.305	4.098	0.333
30	4.879	0.433	4.149	0.339	4.002	0.321	4.166	0.341	4.065	0.328	4.116	0.335
36	4.807	0.424	4.048	0.326	3.948	0.314	4.048	0.326	4.065	0.328	4.098	0.333
42	4.799	0.423	4.115	0.335	3.922	0.311	4.201	0.346	3.921	0.311	4.184	0.320
48	4.863	0.431	4.032	0.324	3.976	0.317	4.065	0.328	4.016	0.322	4.000	0.320

The variations of the free-volume fraction of PTFE during sorption of the different vapors can be observed in Table IV. For all the vapors that present sorption in PTFE,  $f$  diminishes from the initial value, which involves a filling process of microvacancies in PTFE; however, for those vapors (cyclohexane and water) which have no interaction with this polymer,  $f$  presents almost no change.

By analyzing the vapor-sorption results in PTFE, it appears that there does not exist a high sorption of vapors by this polymer. This is expected, since, in this case, no evidence exists for the behavior of *o*-Ps parameters ( $\lambda_3$  and  $I_3$ ) that can be associated with cluster formation, in comparison with that occurring in PP. In addition, the fact that  $\lambda_3$  does not exhibit an appreciable change with all the vapors also supports this assumption.

In a general way, the results obtained here are related to the effects of vapor sorption on PP and

PTFE detected by PAL and are in accordance with the different sorption mechanisms that occur in two polymers with different aggregation states.

To obtain a better understanding of the results encountered by PAL, the number of vapor molecules that can be accommodated in each free-volume cavity of PP and PTFE were calculated. Furthermore, the solvent interaction parameter was also calculated for each vapor and polymer studied here. These values are presented in Table V.

Using the individual free-volume cavity sizes ( $V_H$ ) in Tables I and III for PP and PTFE, respectively, at contact time zero, and the average volume per molecule of the liquids occupied at 23°C, the average number of molecules residing in a PP and PTFE free-volume cavity can be calculated.

The penetration of a vapor molecule of any substance through a polymer may depend on solvent interactions between the polymer and the penetrant,

**Table IV** *o*-Ps Intensity of Formation and Free-Volume Fraction Values Determined Before and After Vapor Sorption in PTFE

Contact Time (h)	<i>n</i> -Hexane		<i>c</i> -Hexane		Benzene		MMA		AA		Water	
	$I_3$ (%)	$f$ (nm <sup>3</sup> )	$I_3$ (%)	$f$ (nm <sup>3</sup> )	$I_3$ (%)	$f$ (nm <sup>3</sup> )	$I_3$ (%)	$f$ (nm <sup>3</sup> )	$I_3$ (%)	$f$ (nm <sup>3</sup> )	$I_3$ (%)	$f$ (nm <sup>3</sup> )
0	19.42	6.87	19.39	6.82	19.41	6.85	19.46	6.85	19.40	6.84	19.47	6.87
6	14.93	6.22	20.66	6.65	16.83	5.62	14.06	4.82	16.04	5.26	19.85	6.51
12	14.56	5.86	19.57	6.42	16.11	5.09	12.73	4.26	15.32	4.84	20.36	6.55
18	14.07	5.71	19.69	6.30	15.29	4.93	11.68	4.00	14.08	4.47	20.78	6.61
24	12.64	5.67	19.07	6.29	15.20	4.79	11.41	3.82	14.28	4.35	19.97	6.65
30	12.82	5.55	18.87	6.39	14.33	4.60	10.87	3.70	13.26	4.35	19.87	6.65
36	12.77	5.41	18.89	6.16	14.21	4.46	11.00	3.58	12.66	4.15	19.73	6.57
42	12.46	5.27	18.78	6.29	14.12	4.39	10.35	3.58	13.02	4.05	19.75	6.77
48	12.24	5.27	18.63	6.04	14.01	4.44	10.53	3.45	12.65	4.07	20.14	6.44

**Table V Free Volume and Solvent Interaction Parameter Data for the Vapor Sorption Into PP and PTFE**

Vapor	PP		PTFE	
	Molecules/ Cavity	<i>X</i>	Molecules/ Cavity	<i>X</i>
<i>n</i> -Hexane	0.65	1.14	1.75	0.59
<i>c</i> -Hexane	0.73	0.52	1.96	1.08
Benzene	0.89	0.34	2.39	1.70
MMA	0.92	0.36	2.46	1.34
AA	1.17	1.26	3.11	4.28
Water	4.43	6.55	11.81	9.45

as well as on the free volume of the former. In some situations, when the free-volume cavity sizes are unable to accommodate the penetrant molecules, the driving force of molecule sorption is the solvent interaction between the molecules and the polymer. For a polymer and a solvent to be completely miscible over the entire composition range, the Flory-Huggins theory<sup>25</sup> requires a solvent interaction parameter (*X*) value < 0.5. The solvent interaction parameter is defined by

$$X = 0.34 + (V_1/RT) (\delta_1 - \delta_2) \quad (6)$$

where  $V_1$  is the molar volume of the solvent, and  $\delta_1$  and  $\delta_2$  are the solubility parameters of the solvent and the polymer, respectively.

From the data of Table V, the quantity of molecules that the free-volume size of PP can accommodate is less than the one for *n*-hexane, cyclohexane, benzene, and MMA. However, in accord with the results of PAL, these substances can penetrate into the PP matrix, and perhaps the driving force for this is their *X* values, which are near to or less than 0.5. For sorption of AA and water in PP, it appears that the driving force is related to the number of molecules that these substances can accommodate into free-volume cavities of the polymer, because their solvent interaction parameters are not as small as is required, especially for water.

Regarding the data of the average number of molecules per cavity in PTFE and the *X* values obtained, it can be considered that the driving force is the function of both parameters, as for the PP system. *n*-Hexane and cyclohexane have a similar value of the number of molecules per cavity. However, considering the PAL results, *n*-hexane can penetrate into PTFE while cyclohexane cannot. In this situation, the only difference is that *n*-hexane has an *X*

value near to 0.5 but cyclohexane possesses an *X* value larger than 0.5. For benzene, MMA, and AA, the quantity of molecules that can be accommodated into the PTFE free-volume size is larger than that of *n*-hexane and cyclohexane, while *X* values for those substances increase; thus, it might be considered that, in this case, even when *X* values are not adequate, that the determining factor that governs the slight penetration of those molecules is the free-volume size present in PTFE. Referring to water molecules, these could be accommodated to a large extent into the PTFE free-volume cavity, but the value of *X* is very far from 0.5, which avoids the penetration of water molecules into PTFE. This was successfully detected by the PAL technique since  $\lambda_3$  and  $I_3$  remained constant during the contact time, as was already mentioned. However, this is a trial to demonstrate that in our experiments we detected the changes occurring into the polymer matrix during the sorption phenomena and not as a possible condensation of the vapors between the positron source and the polymer sample.

## CONCLUSION

Following the vapor-sorption phenomenon in polymers by the positron annihilation lifetime (PAL) technique, it has been shown that the behavior shown by *o*-Ps parameters: lifetime,  $\tau_3$ , and the intensity of formation,  $I_3$ , is governed by the kind of sorption mechanism that occurs in the polymer depending on its aggregation state: Henry's law for rubbery polymer (PP) and a dual model for glassy polymer (PTFE).

Since PAL is a unique technique to detect free-volume characteristics, such as mean size and density, in polymers, it was possible to observe the filling process of the microvoids in PTFE by those vapor molecules that were capable of penetration, and, on the other hand, it was possible to measure the enlargement of the free volume in PP due to those substances which were able to penetrate and to plasticize that polymer.

In accord with PAL results, it seems that both factors: solvent interaction parameter and free-volume cavity sizes, are playing an important role in promoting or inhibiting sorption of the analyzed vapors. In addition, it seems that in some cases they are complementary, but, in others, one of them appears as the dominant factor over the other. Further studies are necessary for a better understanding in this direction.

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