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Chlorinated PTMSP membranes: permeability, free volume and physical properties

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Abstract

Permeability and positron annihilation measurements were carried out on PTMSP membranes, in the pristine structure, as well as in the modified polymer after chlorination. It is found that permeability decreases in the chlorinated films; this can be correlated to the microscopic free volume decrease as probed by positronium. Effect of ageing was also investigated. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Free volume; Permeability; Positron annihilation

1. Introduction

Poly[(1-trimethylsilyl)-1-propine] (PTMSP) is a well-known polymer, characterized nowadays [1] by the highest permeability to gases: e.g. 3.4×10^{-7} for nitrogen and 6.1×10^{-7} for oxygen, expressed by ($\mathrm{cm^3\,(STP)\,cm/s\,cmHg\,cm^2}$), at room temperature. Permeability decrease has always been observed, both when chemical modifications are done [2–5] on the polymer, and when physical ageing is induced [6]. The main purpose of this communication is the study of the relationships between the chemically modified structure after chlorination (PTMSPCL) and its free volume and permeability variations, in comparison to the PTMSP analogous properties. Positron annihilation lifetime spectroscopy was used as an experimental technique, as in a previous investigation of PTMSP [6]; indeed, this relatively simple tool can probe the properties of the free volume holes in a non-destructive way [7]. Since both PTMSP and PTMSPCL are glassy polymers, transport properties [1] are a function of pressure as predicted by the dual sorption theory. Therefore, we also made permeability isothermal measurements on the chlorinated membranes at different pressures.

2. Experimental

2.1. Materials

PTMSP was prepared according to Masuda et al. [8]; the membranes were obtained from 3% polymer solution in tetrachloroethylene [9]. The chlorinated membranes were obtained by immersion in chlorine water in the conditions already indicated [9].

2.2. D.S.C. measurements

Thermal analysis was performed on a Mettler 3000 DSC instrument, under nitrogen atmosphere, with a scanning rate of 10°C/min, in a temperature range −150–400°C. The sample mass was 11 mg.

2.3. Permeability measurements

Permeability was measured by a gas flow method under pressure; Fig. 1 shows the apparatus prepared in our laboratory. The permeating gas flows to the lower part of the cell: its pressure is ruled by valve 1. Pressure fluctuations are controlled with the uncertainty of 0.3 mmHg by a 10 l capacity auxiliary tank (E). Pressure is measured by a sensor (A) MKS Baratron 222B (resolution 2.5 mm Hg). The permeated gas flow is measured by a capillary flowmeter (C) operating at atmospheric pressure.

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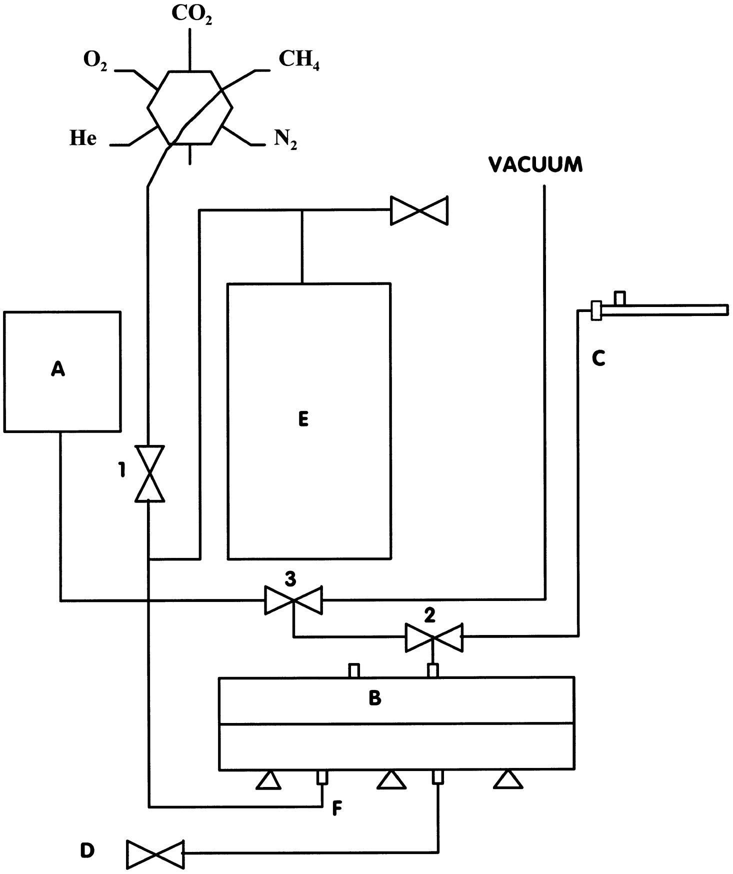

Fig. 1. Permeability measurements apparatus. (A) Manometers; (B) permeation cell; (C) fluxometer; (D) valve; (E) auxiliary tank; (F) gas entrance; 1,2,3, valves.

2.4. Positron measurements

The positron apparatus has been described elsewhere already [6]; the resolution was about 230 ps. Spectra extended over 2048 channels; the conversion was 50 ps/ch. The activity of the positron source (^{22}Na embedded between two 1.08 mg cm^{-2} Kapton foils) was 0.3 MBq. The sample-source assembly was inserted — in the usual sandwich configuration — into a glass container, connected to a vacuum system. All the measurements were performed at room temperature and at a pressure less than 5×10^{-5} mbar. Each spectrum contained about 7×10^{6} counts. Deconvolutions were carried out through the computer code *LT* [10], with a suitable correction for the positrons annihilated in the Kapton.

3. Results and discussion

The examined PTMSPCL had an intrinsic viscosity of $\eta = 0.83$ dl/g in toluene at 30°C, while the pristine PTMSP had intrinsic viscosity of $\eta = 2.25$ dl/g : this shows that during chlorination a chain breaking takes place.

Fig. 2 shows the D.S.C. behaviour of both the pristine and the chlorinated polymers. An exothermic decomposition of the chlorinated polymer begins at 200°C and is completed at 365°C, 100 degrees below the pristine PTMSP decomposition temperature. This shows that chlorination gives some destabilisation to the PTMSP structure. Chlorination probably induces some structure flexibility too, which could be ascribed both to the increased number of the chain ends due to the chain breaking and to the loss of the bulky $-Si(CH_3)_3$ groups (see later), which reduce the main chain rigidity. These observations agree with the density increase of about 10%, on passing from 0.833 to 0.919 g/cm^3, showing a tighter packing of macromolecular chains after chlorination.

The elemental and X-ray microanalysis have shown a mean chlorine content in PTMSPCL of 6%, and have shown the existence of a distribution of Si and Cl inside the membrane: chlorine concentration increases from the middle of the membrane section to the edges. A corresponding decrease of Si concentration suggests that chlorine insertion in the chain is accompanied by silicon displacement, in agreement with the reaction mechanism which foresees the Cl insertion on the propine carbon connected to $Si(CH_3)_3$, which is eliminated [9].

Permeability values related to O_2 and N_2 of PTMSPCL are shown in Fig. 3. As far as PTMSPCL is concerned, O_2 permeability versus pressure slowly decreases until an

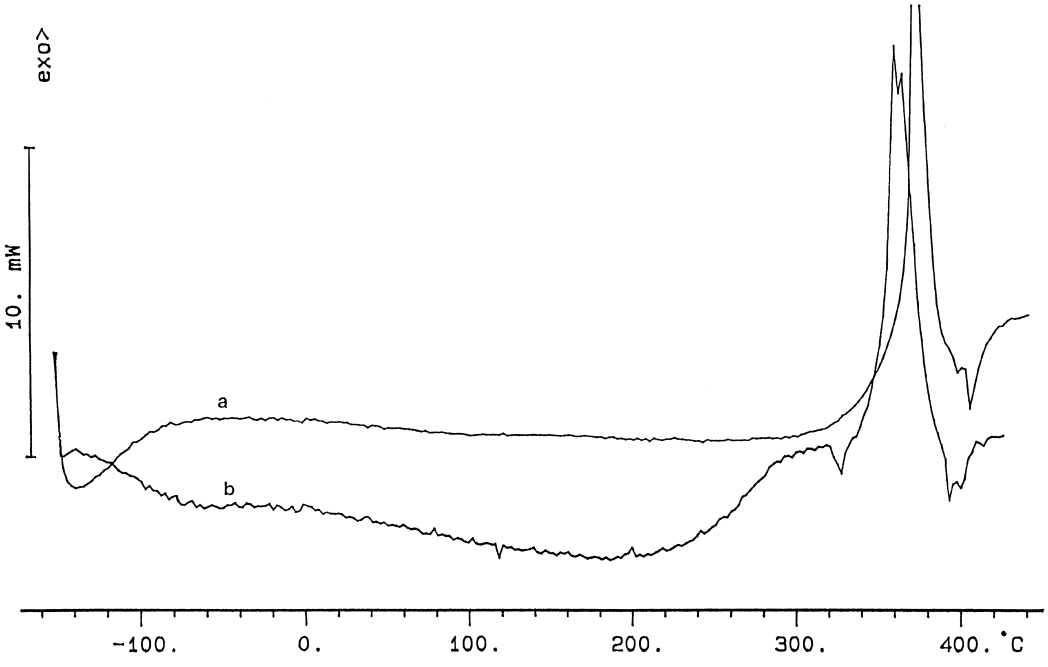

Fig. 2. D.S.C. analysis of pristine PTMSP (plot a) and of chlorinated PTMSP (plot b).

asymptote is reached, while N_2 permeability appears practically constant. Correspondingly, selectivity follows the oxygen behaviour versus pressure. Permeability is lower of about one order of magnitude in comparison with the pristine PTMSP permeability, which was 9.2×10^{-7} (cm^3 (STP) cm/s cmHg cm^2) for O_2 and 6.7×10^{-7} for N_2 (at 0.5 absolute MPa). According to our measurements selectivity (O_2/N_2) is of the order of 2.

Annihilation time spectra were analysed in four components; the results are shown in Table 1. The shortest component can be at least partially attributed to *para*-Ps decay, although other decay processes (e.g. positron annihilated from regions with higher electron density) can contribute. The second component's lifetime, τ_2, can be ascribed to decays of the positrons not forming bound states, but annihilated in the free spaces. The other two components

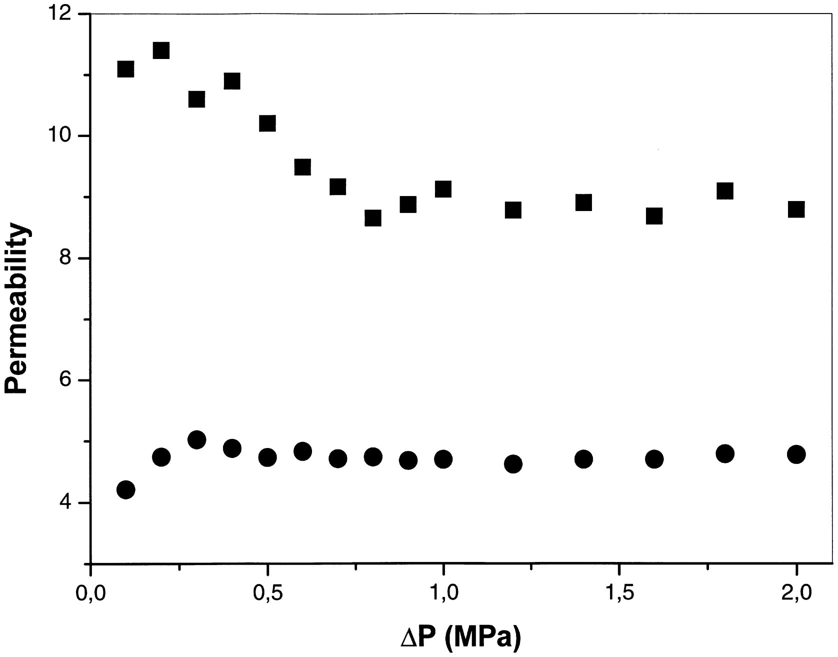

Fig. 3. Oxygen (squares) and nitrogen (circles) permeability (cm^3 (STP) cm)/(cm^2 s cmHg) versus *trans*-membrane pressure difference ΔP (MPa) in PTMSPCL.

Table 1
Annihilation time spectra in PTMSP and in PTMSPCL as a function of physical ageing. In the table the radius R_3 of channel-like holes, the average volume V_4 and width ΔV_4 of the hole volume distribution for the larger holes in PTMSP and in PTMSPCL are also shown

Sample	τ_1 (ns)	I_1 (%)	τ_2 (ns)	I_2 (%)	τ_3 (ns)	I_3 (%)	τ_4 (ns)	I_4 (%)	σ_4 (ns)	R_3 (nm)	V_4 (nm^3)	ΔV_4 (nm^3)
PTMSPCL, native	0.19(2)	14(2)	0.43(1)	66(2)	2.8(3)	2.5(3)	10.8(4)	17.7(5)	2.4(3)	0.27(2)	1.2(1)	0.4(1)
PTMSPCL, 1 month	0.17(2)	11(2)	0.46(1)	68(2)	3.2(4)	4.1(4)	11.4(4)	16.6(5)	2.1(3)	0.30(2)	1.4(1)	0.3(1)
PTMSPCL, 2 months	0.17(2)	11(2)	0.44(1)	67(2)	2.2(2)	4.3(4)	10.9(4)	17.0(5)	2.8(4)	0.23(2)	1.2(1)	0.4(1)
PTMSPCL, 10 months	0.14(2)	7(2)	0.41(1)	70(2)	1.9(2)	5.2(5)	10.6(4)	17.0(5)	2.9(4)	0.21(2)	1.2(1)	0.4(1)
PTMSP, native	0.18(2)	16(3)	0.42(1)	48(2)	4.7(4)	5.3(5)	12.1(4)	30.5(6)	3.4(4)	0.37(2)	1.4(1)	0.5(1)
PTMSP, 2 months	0.17(2)	15(3)	0.41(1)	57(2)	3.2(3)	5.0(5)	11.4(4)	25.3(5)	3.2(4)	0.30(2)	1.3(1)	0.5(1)

have much longer lifetimes and are unambiguously attributed to *o*-Ps decays. Similar results were already found in PTMSP membranes [11]. Lifetime τ_3, and intensity I_3 of the third component in PTMSPCL show an opposite trend with physical ageing: the first decreases, the second increases. On the other hand, parameters of the longest component (i.e. τ_4 and I_4) are quite constant. In PTMSP it is found that τ_3 and I_4 notably decrease with ageing, while I_3 and τ_4 decrease very little.

A correlation exists between *o*-Ps lifetime τ and size of the nanoholes forming the free volume. According to the usual model [12], the following relationship between τ (ns) and radius of the hole (in spherical approximation) R (Å) is obtained:

$$\tau^{-1} = 2\left[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(2\pi\frac{R}{R_0}\right)\right] \qquad (1)$$

where $\delta R = R_0 - R = 1.66$ Å [13]. Eq. (1) should be considered only as a rough approximation, since real cavities are irregularly shaped. The presence of two distinct *o*-Ps components can be interpreted, in the simplest way, in terms of two distinct kinds of free volume holes: larger cages (corresponding to τ_4) connected with channel-like holes (related to τ_3); the polymer chains are kept aside by bulky trimethylsilylpropine groups [6].

The longest lifetime τ_4 is comparable in PTMSPCL and PTMSP, which means similar average volumes V_4 for the larger cavities. On the other hand, τ_3 is significantly smaller in the chlorinated membrane and involves smaller radii R_3 for the cylindrical holes, which decrease with time in both the polymers. The lifetime τ_3 of the native PTMSPCL (2.8 ns) is similar to that in the aged PTMSP polymer (3.2 ns). These data can be compared to the permeability in PTMSPCL, which is much lower than that in the native PTMSP, but similar to permeability in the aged PTMSP [6]. This membrane shows a decrease of the initial permeability of more than a decade. Chlorination appears to be responsible for permeability reduction because it eliminates bulky $-\mathrm{Si(CH_3)_3}$ groups and reduces molecular weight allowing a tighter packing of the chains; this gives origin to a structure with radii R_3 smaller than in the original PTMSP. Therefore, permeability decrease in PTMSPCL seems to be attributable mainly to the lower dimension of R_3 with respect to native PTMSP; the largest holes are probably not much responsible for the permeability reduction, according to the suggested model [6] of a series coupling among smaller (R_3) and larger (R_4) holes, of which the smaller ones are critical for gas transport. Radii R_3 of channel-like holes and volumes V_4 of larger holes are compared in Table 1 for the membranes of the two polymers. Volumes were calculated from Eq. (1), in spherical approximation; on the other hand, radii R_3 were estimated by means of an equation similar to Eq. (1), but using a cylindrical approximation [15].

Hole dimensions are distributed around average values, and a distribution of *o*-Ps lifetimes should be expected. Correspondingly, we analysed the annihilation time spectra assuming that the longest component displayed a distribution of lifetimes. Its significant parameters are the average lifetime τ_4 and the width σ_4, which are shown in Table 1. Through a transformation from the lifetime distribution into hole volumes distribution [14] we obtain the results shown in Fig. 4, where the hole volumes distribution function for PTMSP is compared to those for PTMSPCL at two different ages. The width of the holes distribution in the chlorinated samples slightly increases with ageing, whereas the average volume is almost constant; the width is larger in the PTMSP membrane, as well as the average volume. However, the differences among the distributions are rather small, on the whole. The statistics of our data allowed us to consider only the longest component in terms of a distribution of lifetimes. Concerning the intensities of the *o*-Ps components, which is often related to the holes number [7], I_4 decreases with ageing in PTMSP, whilst it remains almost constant in PTMSPCL. On the other hand, I_3 is unaffected by ageing in PTMSP and increases with ageing time in PTMSPCL. If we accept a correlation between *o*-Ps intensity and holes density, we conclude that the number of larger holes reduces with time in PTMSP and remains quite constant in PTMSPCL, whilst channel-like holes density increases in PTMSPCL, being constant in PTMSP. The decrease of the larger holes density in PTMSP involves a reduction of the free volume, since the average volume of the holes remains constant; this interpretation is supported by measurements of the density, which increases with time [6]. We point out that a direct comparison between the *o*-Ps intensities in the two different materials is not significant, as far as the holes density is concerned. The strong decrease of the

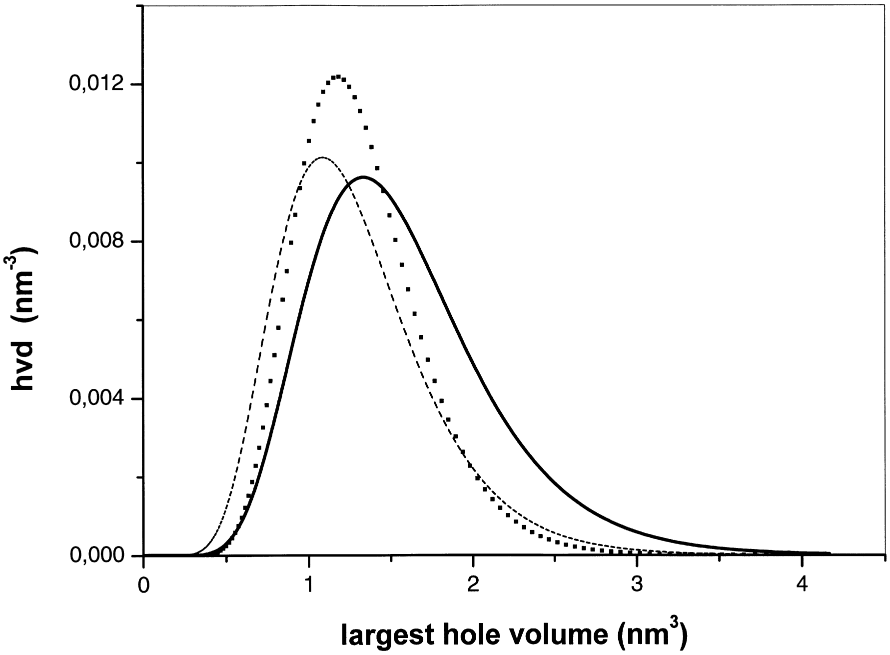

Fig. 4. Hole volume distribution (hvd) for the largest cavities in native PTMSP (continuous), and in PTMSPCL: native (dashed) and 10 months aged (dotted).

total *o*-Ps intensity in PTMSPCL with respect to that in PTMSP is reasonable, by taking into account that chlorine inhibits Ps formation. Anyway, the higher density in PTMSPCL with respect to PTMSP can be taken as an index of a lower fraction of holes.

4. Conclusions

In this work a comparison between two different silylpropine membranes was carried out, centred on the concept of free volume. The chlorinated native membrane is denser than native PTMSP and its permeability is about one order of magnitude lower. Such macroscopic features correspond to a microscopic description of the free volume, as given experimentally by the positron annihilation lifetime spectroscopy. We found that the results are compatible with the existence of two kinds of holes; the larger ones are similar in the two structures, although their volume distribution is broader in PTMSP. Smaller holes probably play an important role in the transport properties: the reduction with the physical ageing of their average diameter reasonably involves a strong decrease in the permeability in PTMSP, and the lower permeability in the chlorinated membrane with respect to native PTMSP is probably due to the smaller dimensions of the channel-like holes radii.

Acknowledgements

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