

## Nanoporosity of polymer sorbents and membrane materials as seen by PALS and low temperature gas sorption

V.P. Shantarovich<sup>1,\*</sup>, V.G. Bekeshev<sup>1</sup>, I.B. Kevdina<sup>1</sup>, Yu.P. Yampolskii<sup>2</sup>, M.V. Bermeshev<sup>2</sup>,  
and N.A. Belov<sup>2</sup>

<sup>1</sup>*Semenov Institute of Chemical Physics RAS, Kosygin st.4, 119991 Moscow, Russia*

<sup>2</sup>*Topchiev Institute of Petrochemical Synthesis RAS, Leninskii Prosp. 29, 119991 Moscow, Russia*

\* email: shant@center.chph.ras.ru

Positron annihilation lifetime spectroscopy (PALS) is a recognized method for the studies of nanoporosity (size distributions of nanopores) in solids. However, until recently [1], no attempts were made to estimate the concentration limits of sensitivity of this method to elementary free volumes (EFV). The reason was that no alternative methods applied to the same problem were discussed together. Meanwhile, the studies of nanoporosity are extremely important for creation of novel polymer membrane materials and sorbents with the unique permeation, selectivity and specific surface. They are used in solving the problems of ecology, chemistry and medicine. One of the most popular methods which are an obvious alternative or addition to PALS is the low temperature gas sorption (LTGS). In this report we consider results of several investigations of polymer membrane materials and sorbents where the both PALS and LTGS are applied to the same objects. All nanoporous polymers are ranked in Table 1 according to the pore size (micropore or nanopore) and condition of the material (ready made membrane or powder). The last specificity, condition, springs up because the process of membrane casting is able to change an accessible free surface, to slow down an adsorption rate compared to those of the natural free volume structure of the given membrane material. Therefore, we have to distinguish the two kinds of the objects. Sometimes, this may be important for LTGS but not essential for PALS or vice versa. Thus, Table 1 shows which of the two methods is adequate for investigation of the chosen materials.

Table 1. Adequacy of PALS and LTGS methods for the studies of nanoporous polymer materials

Pore size State of material	Micropore <2 nm	Mesopore 2-50 nm
Powder	<b>PALS,</b> <b>LTGS</b> ( <i>HK,SF</i> )	<b>LTGS</b> ( <i>BJH</i> )
Membrane	<b>PALS</b>	<b>LTGS</b> ( <i>BJH</i> ), <i>Sc-CO<sub>2</sub></i>

*HK(SF)* and *BJH* in brackets indicate Horwath-Kawazoe (Saito-Foley) and Barrett-Joyner-Halenda methods used [1-3] to analyze low-temperature gas (N<sub>2</sub>) sorption-desorption (LTGS) curves. Inscription *Sc-CO<sub>2</sub>* for membrane mesopores (4) means LTGS experiments on mesopores in polymers swelled by CO<sub>2</sub> in super-critical state (7.38 Mpa, 31.1 °C). Possibility to apply each of the two methods for EFV studies is determined by different conditions. For the PALS, the crucial point is concentration of the positronium trapping centers (10<sup>18</sup>-10<sup>20</sup> g<sup>-1</sup>)

which has to be enough to localize *ortho*-positronium atom before annihilation. For LTGS, materials have to be only in the powder state. Thus, both methods supplement each other. Table 1 indicates that *in powders* (1) *micropores* are seen both by PALS and LTGS methods, while *mesopores* (3) are seen only by LTGS. *Micropores in readymade membranes* (2) are only for PALS measurements, since sorption process in membrane is relatively slow and dependent on membrane thickness. The only case, when mesopores are seen in membrane (4), and particularly by LTGS, is the special case of nanopores, produced by material swelling using *sc*-CO<sub>2</sub>.

In our studies, incremental volumes of pores of the given size (cm<sup>3</sup>g<sup>-1</sup>nm<sup>-1</sup> units) were measured using low temperature (77K) gas (N<sub>2</sub>) sorption-desorption isotherms, obtained with High Vacuum System ASAP-2020 MP Micromeritics (USA) in the interval of relative pressures  $P/P_0$  10<sup>-3</sup>-0.99, where P<sub>0</sub> stands for the pressure of saturated vapor of adsorbate at the temperature of measurement. The isotherms had patterns typical for microporous or mesoporous materials (hysteresis). In the PALS measurements we used spectrometer EG&G ORTEC USA with time resolution (FWHM) 300 ps and <sup>44</sup>Ti positron source.

## 1. Micropore powders and membranes

The first group of nanoporous materials Table1 (1) is formed by polymer powders (used for membrane preparation), silicon-containing tricyclonanes, perfluorinated polymers, or rigid polymers having a ladder structure and spiro-centers, formed by single C-C bonds (PIM-1, polymers of intrinsic microporosity) [4].

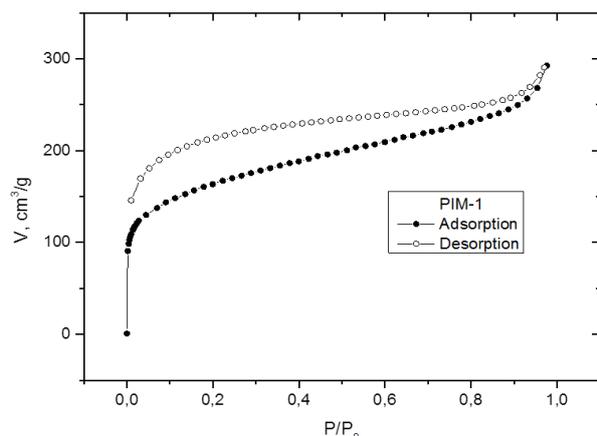


Fig.1 Nitrogen adsorption (filled symbols)-desorption isotherms at 77K for PIM-1.

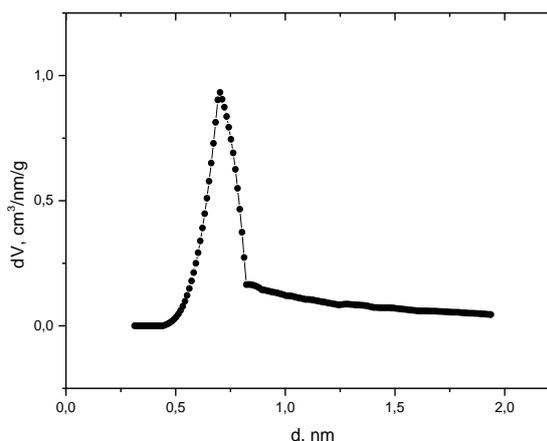


Fig.2 Apparent pore size distribution derived from N<sub>2</sub> adsorption (*HK*) method.

Figs 1, 2 (this study) demonstrate, for example, results of LTGS measurements (together with *HK* calculations) of size distribution of micropores in powder PIM-1.

Remarkably, the most probable micropore size  $\approx 0.8$  nm, according to LTGS (*HK, SF*), Fig.2, corresponds to the results of PALS measurements ( $\tau_4 = 6-7$  ns, depending on the sample history) [5] both for powder Table 1 (1) and membrane Table 1 (2). This infers similarity of the internal structure of powder grains and membrane, though direct LTGS measurement on membrane turned out to be impossible. Therefore, PALS measurements are correct for the both micropore powders and membranes.

## 2. Mesopore powders

Further on, the case of “mesopore powder” Table 1 (3) we consider on example of polymer sorbents, mesoporous heterogeneous copolymers of divinylbenzene (MD) with

rubbers, such as polyisoprene (MD/PI), polyisobutylene (MD/PIB), polybutadiene (MD/PB) (Figs.3,4) [6]. The sorption-desorption isotherms with hysteresis loops (Fig.3) have the pattern characteristic of mesoporous samples. The results of processing of the sorption data (*BJH* analysis) showed that the mesopore width distribution extends to the region  $1.7 < D < 50$  nm with maximum 27.5 nm (Fig.4, Table 2), while the most long-lived positronium component ( $\tau_4 = 66.58 \pm 4.19$  ns) corresponds only to 3.58 nm, which is much smaller.

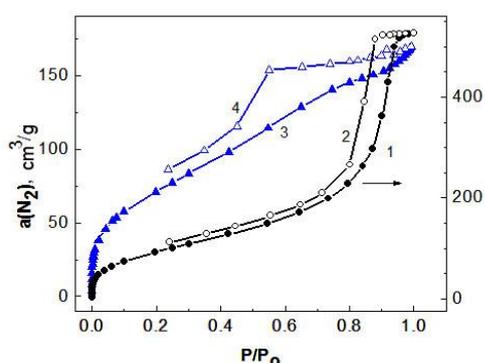


Fig.3 Adsorption (1,3) and desorption (2,4) MD/PI and MD/PIB samples [6].

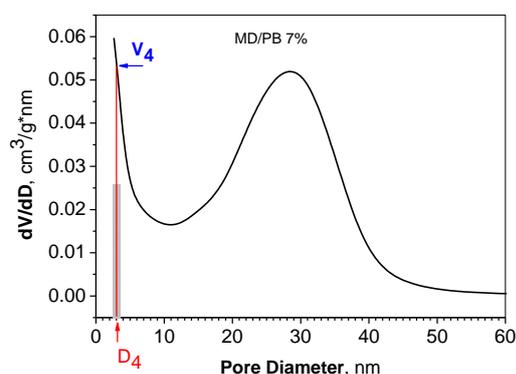


Fig.4 Mesopore width distribution obtained by for *BJH* method from LTGS data shown in Fig.3 [6].

Table 2 Divinylbenzene-based polymeric sorbents. The most probable mesopore width according to four components positron annihilation lifetime analysis  $D_4^{PAL}$  and from LTGS results (Barrett-Joyner-Halenda analysis)  $D_{av}^{BJH}$ . The last column shows specific surface of the studied compounds [6].

Polymer	$\tau_3$ , ns; $I_3$ , %	$\tau_4$ , ns; $I_4$ , %	$D_4^{PAL}$ , nm	$D_{av}^{BJH}$ , nm	$S_{mes}^{BJH}$ , m <sup>2</sup> /g
XAD-4	1.93±0.02 23.73±0.39	50.37±1.41 16.3±0.20			900
MPD	2.10±0.02 26.19±0.39	46.61±1.13 11.5±0.11	2.86	20.48	700
MD/PI	1.91±0.02 30.55±0.44	64.19±3.92 9.53±0.29	3.50	17.63	400
MD/PIB	2.19±0.02 33.80±0.30	45.81±1.32 9.58±0.11	2.84	7.76	270
MD/PB	1.92±0.01 32.95±0.35	66.58±4.19 6.28±0.21	3.58	27.50	310

Thus, it is obvious that PALS method is not effective in detecting mesopores even in powders, since  $D_4^{PAL} \ll D_{av}^{BJH}$ .

### 3. Mesopores in polymer membranes

Consider now mesopores in polymer membranes (Table 1(4)). This is the most difficult case for the studies of porous polymers, since accessible external surface in membrane is much smaller than that in powders (Table 1 (3)). Correspondingly, the rate of LTGS is much lower than in powders and depends on membrane thickness, which makes experiment uncertain. On the other hand, the apparent density of mesopores is too low for positronium trapping and, correspondingly, for the pore characterization using PALS. The only exclusion, when LTGS

could be used, was found [1,7] in poly(hexafluoropropylene) PHFP, where mesopores, directly open to atmosphere, were generated by sample swelling in *sc*-CO<sub>2</sub>.(Table 3).

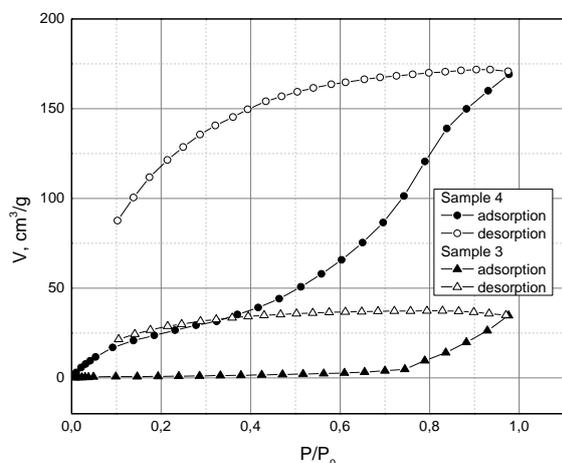


Fig.5 Sorption and desorption isotherms for annealed “nonporous” PHFP (sample 3, Table 3) and PHFP treated with *sc*-CO<sub>2</sub> (sample 4) [7].

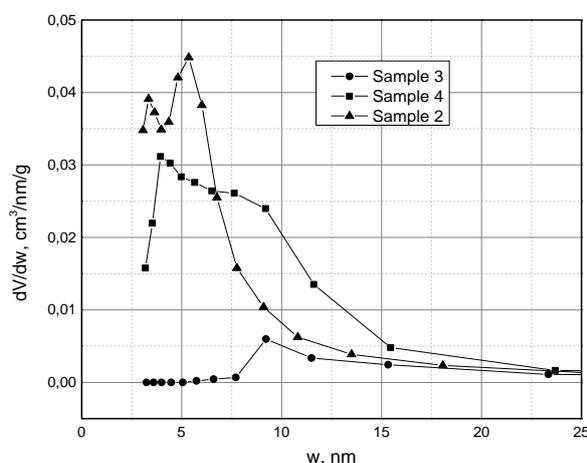


Fig. 6 Meso-pore size distribution for the annealed PHFP sample (sample 3), and two *sc*-CO<sub>2</sub> treated porous samples [7].

Table 3. Positron annihilation data for polyhexafluoropropylene samples (1) “ascast”; (2) 1+ *sc*-CO<sub>2</sub>; (3) annealed; (4) 3+ *sc*-CO<sub>2</sub>.

Sam- ple №	Sample	$\tau_4$ , ns	$I_4$ ,%	$D_4^{PAL}$ , Å
(1)	PHFP casting	$5.58 \pm 0.14$	$11.90 \pm 0.63$	10.0
(2)	PHFP casting+ <i>sc</i> -CO <sub>2</sub>	$8.13 \pm 0.14$	$12.24 \pm 0.35$	12.3
(3)	PHFP annealing	$4.48 \pm 0.07$	$14.17 \pm 0.41$	9.1
(4)	PHFP annealing + <i>sc</i> -CO <sub>2</sub>	$7.33 \pm 0.14$	$14.26 \pm 0.51$	11.7

Comparison of  $D_4^{PAL}$  from Table3 and mesopore size distribution in Fig.6 demonstrate an advantage of LTGS method in this case.

## Literature

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