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Nanoporosity of Polymer Sorbents and Membrane Materials as Seen by PALS and Low Temperature Gas Sorption

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The limits of application of positron annihilation lifetime spectroscopy and low temperature gas sorption for studying nanoporosity of polymer sorbents and membrane materials are discussed relying on the results previously obtained by the authors. For the two methods, limitations are determined by different factors: the dispersion of the material is essential for low temperature gas sorption, while concentration of nanopores of given size is important for positron annihilation lifetime spectroscopy. The both methods came out to be a useful addition to each other in the studies of micropores and mesopores.

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1. Introduction

Positron annihilation lifetime spectroscopy (PALS) is a recognized method for the studies of nanoporosity (size distributions of nanopores) in solids. However, until recently [1, 2], 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. In paper [1] we compared results of PALS and thermostimulated luminescence (TSL). One of the most popular methods, which are 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 I 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 I shows which of the two methods is adequate for investigation of the chosen materials. HK(SF) and BJH in brackets indicate Horwath–Kawazoe (Saito–Foley) and Barrett–Joyner–Halenda methods used [2–4] to analyze low-temperature gas (N_2) sorption-desorption (LTGS) curves. Inscription *Sc*-CO_2 for membrane mesopores (4) means LTGS experiments on mesopores in polymers swelled by CO_2 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 ($10^{18}-10^{20}$ g^{-1}) 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 I indicates that *in powders* (1) *micropores* are seen both by PALS and LTGS methods, while *mesopores* (3) are seen only by LTGS. *Micropores in ready-made 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_2.

TABLE I

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	**(1)** PALS, LTGS *(HK,SF)*	**(3)** LTGS *(BJH)*
membrane	**(2)** PALS	**(4)** LTGS *(BJH)*, *Sc*-CO_2

In our studies, incremental volumes of pores of the given size (cm^3 g^{-1} nm^{-1} units) were measured using low temperature (77 K) gas (N_2) sorption-desorption isotherms, obtained with Vacuum System ASAP-2020

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MP Micromeritics and NOVA Series 1200e Quantachrome (USA) in the intervals of relative pressures P/P_0 $10^{-6} \div 0.99$ and $10^{-4} \div 0.98$, respectively. Parameter P_0 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 ^{44}Ti positron source.

2. Micropore powders and membranes

The first group of nanoporous materials in Table I (1) is formed by polymer powders (used for membrane preparation), silicon-containing tricyclonanens, perfluorinated polymers, or rigid polymers having a ladder structure and spiro-centers, formed by single C–C bonds (PIM-1, polymers of intrinsic microporosity) [5].

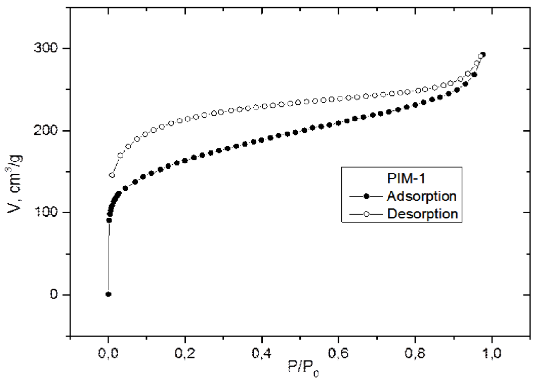

Fig. 1. Nitrogen adsorption (filled symbols) — desorption isotherms at 77 K for PIM-1.

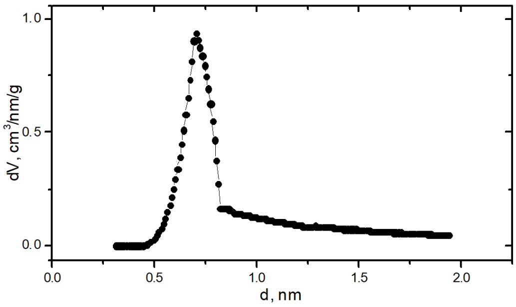

Fig. 2. Apparent pore size distribution derived from N_2 adsorption (HK) method.

Figures 1 and 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) [6] both for powder Table I (1) and membrane Table I (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.

3. Mesopore powders

Further on, the case of "mesopore powder" Table I (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, Table II) [7, 8]. 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 $D \leq 50$ nm with position of maximum D_{av}^{BJH} [nm], shown in Fig. 4, Table II. For example, D_{av}^{BJH} for MD/PB is 27.5 nm, while the most long-lived positronium component ($\tau_4 = 66.58 \pm 4.19$ ns) corresponds, according to the Tao–Eldrup model [9], only to $D_4^{PAL} = 3.58$ nm. Situation is not improved essentially in the case if nonspherical shape of elementary free volume (rectangular tubal pore [10]) is used. Corresponding values of D_4^{PAL} are shown in Table II in brackets. Thus, it is obvious that PALS method is not effective in detecting mesopores in powder polymer sorbent, since $D_4^{PAL} \ll D_{av}^{BJH}$.

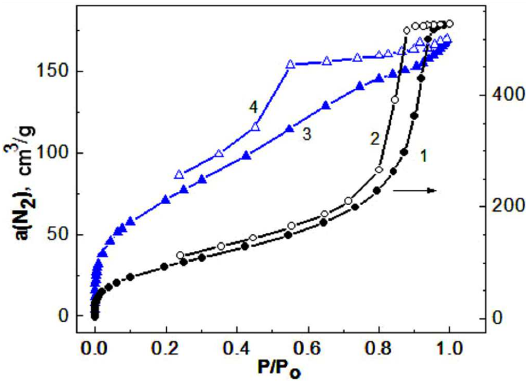

Fig. 3. Adsorption (1,3) and desorption (2,4) for MD/PI and MD/PIB samples [7].

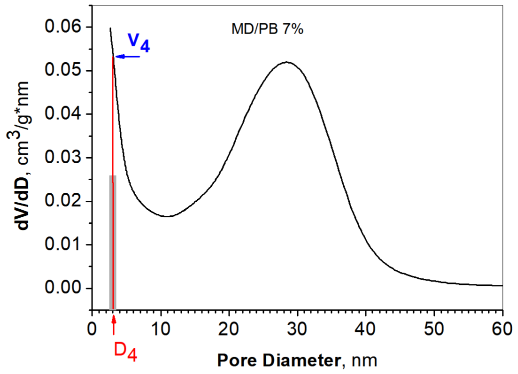

Fig. 4. Mesopore width distribution obtained by BJH method from LTGS data shown in Fig. 3 [7].

TABLE II

Divinylbenzene-based polymeric sorbents. The most probable mesopore width according to four components positron annihilation lifetime analysis D_4^{PAL} and from LTGS results (the Barrett–Joyner–Halenda analysis) D_{av}^{BJH}. The last column shows specific surface of the studied compounds [7, 8].

Polymer	τ_3 [ns]; I_3 [%]	τ_4 [ns]; I_4 [%]	D_4^{PAL} [nm]	D_{av}^{BJH} [nm]	S_{mes}^{BJH} [m^2/g]
XAD-4	1.93±0.02 23.73±0.39	50.37±1.41 16.3±0.20	3.0 (3.95)	15.20 [11]	900 [11]
MPD	2.10±0.02 26.19±0.39	46.61±1.13 11.5±0.11	2.86 (3.68)	20.48	700
MD/PI	1.91±0.02 30.55±0.44	64.19±3.92 9.53±0.29	3.50 (5.17)	17.63	400
MD/PIB	2.19±0.02 33.80±0.30	45.81±1.32 9.58±0.11	2.84 (3.63)	7.76	270
MD/PB	1.92±0.01 32.95±0.35	66.58±4.19 6.28±0.21	3.58 (5.43)	27.50	310

Interestingly, areas of PALS and LTGS application partly overlap (see area $\tau_4 \rightarrow D_4$, V_4 in Fig. 4). This fact can be used for estimation of *o*-Ps mobility before localization: $d^{\mathrm{Ps}} = L^2/6\tau$, where $L = N_4^{-3}$ stands for non-localized Ps diffusion length, and τ is accepted to be 0.3 ns (free positron annihilation lifetime). For MPD, for example, effective diffusion coefficient $d^{\mathrm{Ps}} = 3 \times 10^{-4}$ cm^2/s, which is close to data, published in [12].

4. Mesopores in polymer membranes

Consider now mesopores in polymer membranes (Table I (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 I (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 [2, 3] in poly(hexafluoropropylene) PHFP, where mesopores, directly open to atmosphere, were generated by sample swelling in *Sc*-CO$_2$ (Table III, Figs. 5, 6).

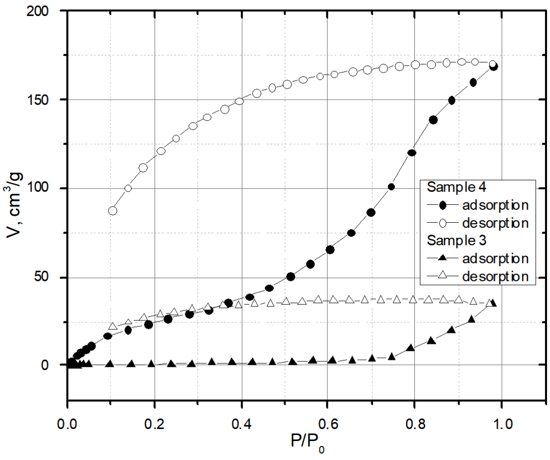

Fig. 5. Sorption and desorption isotherms for annealed "nonporous" PHFP (sample 3, Table III) and PHFP treated with *sc*-CO$_2$ (sample 4) [2, 3].

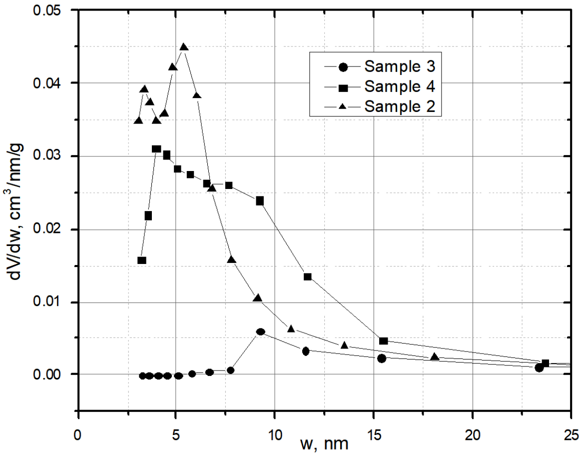

Fig. 6. Meso-pore size distribution for the annealed PHFP sample (sample 3), and two *Sc*-CO$_2$ treated porous samples [2, 3].

TABLE III

Positron annihilation data for polyhexafluoropropylene samples (1) "as-cast", (2) $1 + sc\mathrm{-CO_2}$, (3) annealed, (4) $3 + sc\mathrm{-CO_2}$ [2, 3].

No.	τ_4 [ns]	I_4 [%]	D_4^{PAL} [Å]
(1)	5.58±0.14	11.90±0.63	10.0
(2)	8.13±0.14	12.24±0.35	12.3
(3)	4.48±0.07	14.17±0.41	9.1
(4)	7.33±0.14	14.26±0.51	11.7

The data illustrate effect of PHFP swelling in sc-CO2: sorption-desorption isotherms for the annealed and CO$_2$-treated PHFP are essentially different (Fig. 5), which finally shows production of mesopores (pore width 5–10 nm) in the last sample. Meanwhile, these pores are not "visible" for PALS. Comparison of D_4^{PAL} from Table III and mesopore size distribution in Fig. 6 demonstrates an advantage of LTGS method in this case.

5. Conclusion

The attempts to study nanoporous polymers, using combination of PALS with some alternative techniques, were discussed in this paper for the case of LTGS. Results for various membrane materials and sorbents with micropore and mesopore structures were described. The combination of the two methods enabled to formulate conditions of their effective application and get additional information on the mechanisms of positron annihilation.

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