When some elementary free volumes in polymers are not seen by positron annihilation experiments

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Abstract Size distributions of elementary free volumes have been studied in mesoporous micro-heterogeneous polymer sorbents. Positron annihilation lifetime spectroscopy (PALS), low temperature gas adsorption (BET) and thermo-stimulated luminescence (TSL) measurements are employed as complementary instruments for the study. It is shown that small admixtures of rubbers are very effective for variations of the pore size distribution. While BET technique was very informative for measurements of mesopores (2-50 nm), positron annihilation was sensitive to micropores (<2 nm), but not for mesopores. The last specificity is explained by the limited positronium diffusion length in a polymer and also by inhomogeneous distribution of mesopores in heterogeneous systems. TSL measurements gave information on sizes of rubber inclusions in compositions.

1. Introduction:
Positron annihilation lifetime spectroscopy PALS is used traditionally for the studies of free volumes in polymers [1-4]. We continue this direction on examples of membrane materials and sorbents. The specific feature of this study is the including modified materials. They are modified in a way to obtain some new unique properties, for example, the specific distribution of elementary free volumes for sorbents. It was shown previously that, for membranes, preparation of nanocompositions consisting of polymers and highly dispersed non-organic admixtures (mixed membrane matrices MMM) [5-7] is very promising. Another way infers saturation of polymers with gases in supercritical state with the further heating [8]. In this study we follow the first way and apply this approach to sorbents.

Another special feature of this study is a combination of the three supplementary experimental methods: PALS, thermostimulated luminescence (TSL) and low temperature gas adsorption (BET) [3, 9]. The effect of TSL is emission of light by a substance, irradiated preliminary at low temperature, on heating. As it was stressed recently, PALS and TSL methods are generally interconnected by the same radiation-chemical nature of the processes (spur process) [10-17]. At low temperatures, intensity of positronium formation [10-13] and integral intensity of the TSL [14, 15] are dependent on the storage of the spur electrons (weakly bound electrons) and influenced by bleaching. This is another proof of the spur mechanism of the positronium formation [16, 17]. Papers [18-21] demonstrated effectiveness of PAL-TSL combination for the free volume studies in some new membrane materials and sorbents.
It came out that local rigidity (stiffness) of a polymer structure [21, 22] (estimated in the TSL experiments as intensity $\alpha$ of high temperature component of TSL curve [18]) correlates well with the effective sizes of the free volumes holes (FVHs) and, correspondingly, with $o$-positronium annihilation lifetimes. Fine correlation was found between the pore size, parameter $\alpha$ and oxygen permeation $P(O_2)$ for a number of polymeric and composition materials [3, 6, 22]. The obtained results confirmed the idea [23-25] of interconnection between the permeation, free volume and local rigidity (local tensions, steric hindrances) in a polymer matrix. These results make it possible to conclude sometimes about membrane and sorbent properties (permeation, specific surface) even without corresponding measurements, only on the basis of PAL and/or TSL data [18-20]. However, for PAL studies of composition materials, there is a peculiarity, which we would like to discuss on example of sorbents made of mesoporous polydivinylbenzene.

2. Experimental:

2.1 Measurements

Specific surface measurements, where incremental volumes of pores of the given size ($[cm^3 \cdot g^{-1} \cdot nm^{-1}]$ units, Fig.1) were measured using the data on low temperature gas (N$_2$) sorption. We used High vacuum system ASAP-2020 MP Micromeritics (USA) [3, 9] in the interval of relative pressures from $10^{-6}$ to 0.99. Adsorption-desorption isotherms obtained had a pattern typical for mesoporous adsorbents with a hysteresis loop. Size distributions of FVHs (see Fig.1, for example) are found from BJH (Barrett-Joyner-Halenda) analysis.

In the PALS measurements we used spectrometer EG&G ORTEC (USA) with time resolution (FWHM of the $^{60}$Co prompt coincidence curve) 300 ps, $^{44}$Ti radioactive source and integral statistic more than $10^6$ coincidence events for each measurement. We applied well known PATFIT program for separating the pick-off $o$-Ps components $\tau_3, I_3$ and $\tau_4, I_4$.

We used TSL-4 (Russia) device for measurements of integral (on the wave length of light) yield of TSL on heating in the temperature range 80-370 K. Scanning time was 30 min. The intensities of high temperature components of the curves $\alpha$ were calculated as described earlier [18, 19] and were taken as measure of local rigidity of the studied matrices.

2.2. Materials

The objects for investigation were prepared on the basis of mesoporous polydivinylbenzene (MPD), where additional porosity is created by some porogen solvents during polymerization of divinylbenzene. The commercial analogous system is called XAD-4 (Table 1). For modification, small amounts (7 vol. %) of linear polymers (rubbers with linear structure and not very high molecular weight) were added to the reaction mixture on the stage of polymerization of divinylbenzene. The resulting systems are supposed to be microheterogeneous and known as mesoporous nanocompositions. Changing the kind of the rubber (polybutadiene PB, polyisoprene PI, polyisobutylene PIB) and conditions of polymerization, polymers with different size distributions of free volumes holes (FVH) had been prepared.

3. Results and discussion:

Results of PALS, low temperature gas (N$_2$) adsorption BET (treated according to BJH [9]), and TSL data are shown in Figures 1, 2 and in Tables 1, 2. It is seen that densities of the samples (\(\rho\)) are very low ($\approx 0.5$ g cm$^{-3}$) and fraction of the free volume is turned out to be about 50%. At the same time, the longest $o$-Ps lifetime and corresponding intensity are smaller than those for the cross-linked polystyrenes CPS [3] which have about the same specific surface ($\approx 1000$ m$^2$ g$^{-1}$). However, densities of polystyrenes CPS are essentially higher ($\approx 0.7$ g cm$^{-3}$). This is an evidence that the studied samples are mesoporous, but not microporous, and the Ps atom is not able to localize in the largest, the most distant free volumes. Actually, in table 1, average diameters of EFV $D_{av, BJH}$ are essentially different
from those determined from the longest $\omega$-Ps lifetime $\tau_4$ (46-67 ns correspond to $D_4=2.9-3.6$ nm). The curve in figure 1 shows size distribution of incremental volumes ($[cm^3 \ g^{-1} \ nm^{-1}]$ units) of pores with diameter $D$ from the intervals $\Delta D=1$ ns. It seems reasonable to suppose that the free volumes with $D_{4}^{\text{PAL}}$ from the interval 1 ns are those forming the longest lived component $I_4$. In this case, $N_I=6V_4^{\text{BJH}}/\pi D_4^3$. For MPD, for example, this gives $0.6\times10^{19}$ $g^{-1}$, and this is obviously the lowest concentration of EFV accessible for Ps in this polymer.

Table 1. Polydivinylbenzene-based polymeric sorbents. Positron annihilation data, BJH (Barrett-Joyner-Halenda) adsorption results and parameter $\alpha$ from the TSL curves. The figures in bold present data that are most frequently referred to in the discussion.

| Sorbent | $\tau_4$, ns | $I_4$, % | $\tau_4$, ns | $I_4+I_5$, % | $D_3^{\text{PAL}}$, nm | $D_3^{\text{BJH}}$, nm | $S_{\text{nmes}}^{\text{BJH}}$, $m^2 \ g^{-1}$ | $\alpha\times10^4$ |
|---------|--------------|----------|--------------|---------------|-------------------|--------------------|-------------------|-------------|
| XAD-4   | 1.93±0.02    | 50.37±1.41| 40.26        | 900           |
| MPD     | 2.10±0.02    | 46.61±1.13| 37.69        | 2.86          |
| MD/PI   | 1.91±0.02    | 64.19±3.92| 40.08        | 3.50          |
| MD/PIB  | 2.19±0.02    | 45.81±1.32| 43.38        | 2.84          |
| MD/PB   | 1.92±0.01    | 66.58±4.19| 39.23        | 3.58          |

*Corresponding numbers $D_{4}^{\text{PAL}}$ for all the substances are about 0.6 nm.

Table 2. Additional characteristics found from the PAL and BET (BJH) measurements.

| Sorbent | $V_2^{\text{BJH}}$, $cm^3 \ g^{-1}$ | $\rho$, $g \ cm^{-3}$ | $F_{vf}$, % | $V_4^{\text{BJH}}$, $cm^3 \ g^{-1} \ nm^{-1}$ | $N_I\times10^{19}$, $g^{-1}$ | $N_J\times10^{19}$, $g^{-1}$ | $S_{\text{micro}}$, $m^2 \ g^{-1}$ |
|---------|-----------------------------------|------------------------|-------------|-----------------------------------------------|-----------------------------|-------------------------------|-------------------------------|
| MPD     | 1.20                              | 0.48                   | 57          | 0.072                                         | 0.60                        | 6.51                          | 72.3                          |
| MD/PI   | 0.84                              | 0.58                   | 48          | 0.045                                         | 0.22                        | 4.10                          | 42.3                          |
| MD/PIB  | 1.29                              | 0.46                   | 59          | 0.055                                         | 0.50                        | 8.35                          | 86.8                          |
| MD/PB   | 0.24                              | 0.51                   | 12          | 0.044                                         | 0.80                        | 25.00                         | 63.7                          |

*The range of the pore diameters $D$ was from 1.7 to 300 nm.

From this, positronium diffusion coefficient can be estimated as $d^{Ps}=L^2/6\tau$, where $L = N_4^{-1/3}$ stands for non-localized Ps diffusion length and $\tau$ is accepted to be about 0.3 ns (free positron annihilation life time). For MPD, for example, this gives $d^{Ps}=3\times10^{-4}$ $cm^2/s$, which is close to data, published in [26]. The advantage of the PAL method compared to the gas sorption, is a possibility to determine concentration of the micropores $N_I$ (corresponding to $\tau_4$, $I_4$, Tables 1,2) undetectable by BET: $N_I=N_J I_I/D_4/D_3$ [24]. The results obtained correspond to mesoporous character of the studied samples [27] ($S_{\text{nmes}}^{\text{BJH}}>S_{\text{micro}}$).

Finally, we mention some of TSL results: parameters $\alpha$ in Table 1 and TSL curves for MPD, (MD/PB 7%), and curve for pure 1,4 PB taken with intensity 7% of that for MPD (Figure 2). First, the data illustrate an obvious correlation between TSL parameter $\alpha$ (local stiffness, rigidity [19]) and mesoporosity characteristics (specific surface $S_{\text{nmes}}^{\text{BJH}}$ and $D_{av}^{\text{BJH}}$ (bold numbers in Table 1)). Second, TSL for pure PB (PO), though being much more intensive than that for MD, does not reveal itself in the TSL of (MD/PB 7%); there is no peak at 170K, typical for PB, in the TSL of composition. Therefore we have to conclude: though composition materials of the given type are considered as heterogeneous, effective size of micro-heterogeneities (phase inhomogeneities ) is not higher than...
200-300 Å. In opposite case, characteristic curves of the components (positions of the characteristic peaks) would be easily seen.

![Graph](image)

**Figure 1.** Comparison of the PAL and BET data on porosity of (MD/PB 7%) sample: positron annihilation (thick vertical line, presenting the area of about 1 ns width, centered in the vicinity of $D_4$) and low temperature gas sorption (dependence of incremental free volume on the pore diameter).

![Graph](image)

**Figure 2.** Thermostimulated luminescence curves for (1)- polymer composition (MD/PB 7%), (2)- basic polymer MPD and (3)- 1,4-PB component with intensity 7% relative to the curve for the basic polymer.
4. Conclusion
Some composition materials, novel polymer sorbents, consisting of mesoporous polydivinylbenzene and different rubbers of linear structure had been characterized by different shapes of mesopore size-distributions. The sorbents are studied using positron annihilation in combination with other methods: thermostimulated luminescence and low temperature gas adsorption. Due to combination of the methods, the limiting cases, when Ps atom loses its sensitivity to presence of elementary free volumes, still seen by other methods, are found. The results had been used for estimation of mobility of the positronium atom in the studied polymers.

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