POSITRON INSIGHT INTO EVOLUTION OF PORE VOLUME AND PENETRATION OF POLYMER NETWORK BY N-HEPTANE MOLECULES IN MESOPOROUS XAD4

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SUPPLEMENTARY INFORMATION

APPENDIX 1

The microstructure of the pure XAD4 polymer was investigated with the use of a scanning electron microscope (FEI Quanta 3D FEG), working at 5 and 30 kV. The representative micrographs of the pure XAD4 are shown in the Fig. 1.
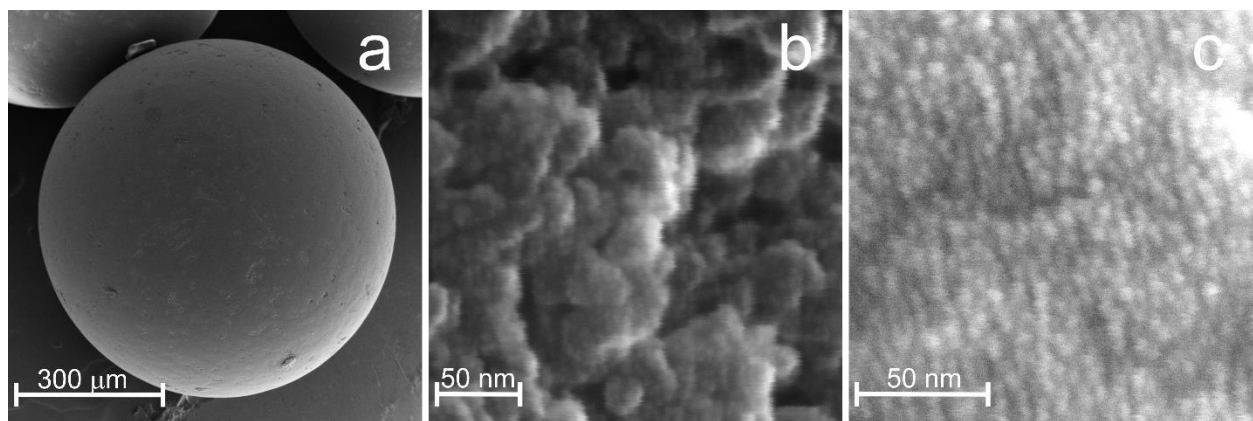

Fig.1. SEM micrographs of the pure XAD4 polymer

The presented micrograph in Fig.1a confirms that XAD4 is in the form of spherically shaped particles. SEM micrographs at higher magnification (Fig. 1b, c) reveal the complex character of the interior of XAD4 beads. They clearly show that the polymer network is composed of ca. 4.6 ± 0.5 nm nuclei.(Fig. 1c). These nuclei aggregate and create larger structures, i.e. microspheres, which are irregular in shape (Fig.1b). Such a complex structure of the macroporous polymer networks has already been thoroughly discussed.[1]

The parameters characterizing the porosity (i.e. the specific surface area, S_{BET}, the total pore volume, V_p, and the pore size, D_{avg}) of XAD4 were determined by measurements of nitrogen adsorption-desorption at 77 K, using a volumetric adsorption analyzer ASAP 2420 V2.09 (Micromeritics, USA). S_{BET} of the pure XAD4 was calculated using the BET equation at p/p_0 ~0.05 to 0.25 relative pressures. V_p was determined from single point adsorption at $p/p_0 = 0.99$. The pore size distribution (PSD) was determined from both the adsorption and desorption branch of the nitrogen isotherms using the BJH procedure. The measured LN_2 adsorption and desorption isotherms as well as the respective PSDs are presented in Fig. 2.

The parameters characterizing the porosity of XAD4 obtained from the LN_2 adsorption experiment are as follows: $S_{BET} = 898$ m^2/g, $V_p = 1.27$ cm^3/g and $D_{avg} = 4V_p/S_{BET} = 5.7$ nm.
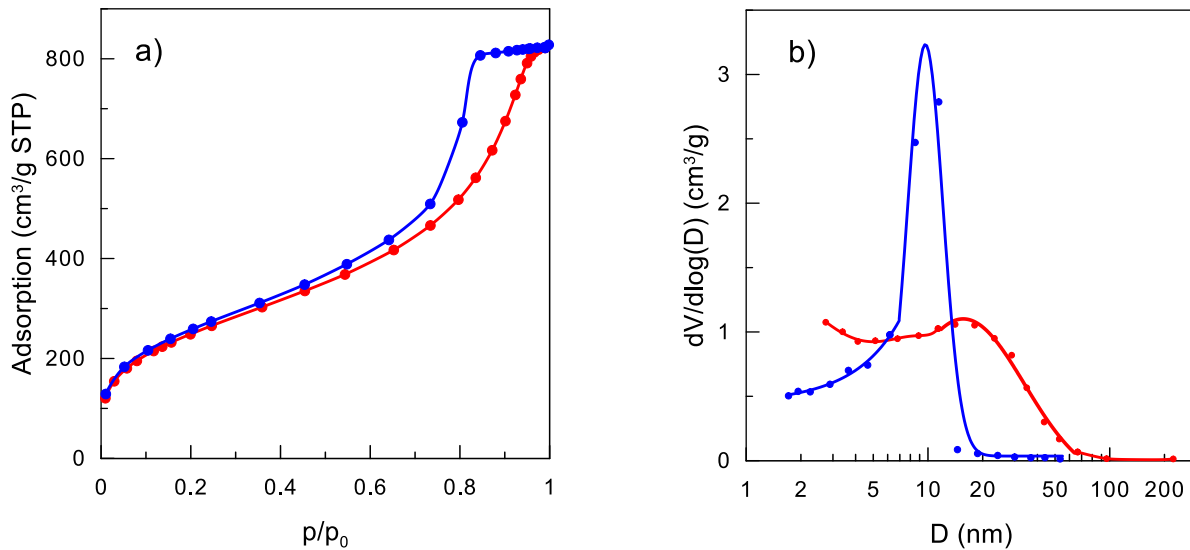
Fig.2. LN$_2$ adsorption (red) and desorption (blue) isotherms at standard temperature and pressure of the pure polymer XAD4 (a) and pore size distributions determined by applying the BJH method to the isotherms (b)

APPENDIX 2

The MELT analysis is the best-known method to determine the most probable number of components in a spectrum. However, a great number of free parameters (e.g. a grid consisting of 3000 lifetime values was used in the case of the presented results) requires minimization of the contribution of statistical dispersion (i.e. to collect the spectra with a possibly large number of counts). If this condition is not fulfilled, the shape of the lifetime distribution, returned by this routine, is a subject to a considerable spread (Fig.3).
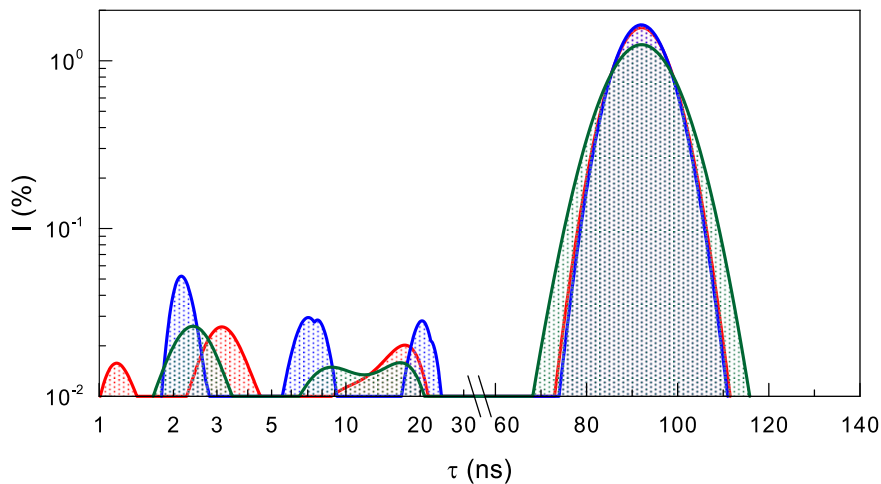

Fig.3 Histograms of o-Ps lifetimes obtained by MELT for three different positron annihilation lifetime spectra, which were collected sequentially one after the other for XAD4 at p/p$_0$ = 0. The spectra consisted of 1.6×10^7 counts (i.e. the typical number of counts in the spectra analyzed by LT, which is half of the typical number of counts collected for MELT analyses)

APPENDIX 3

Each routine used for the data analysis (i.e. LT and MELT) is based on a quite different method. They both result in an approximation of the real lifetime distribution subjected to a different aberration. Therefore, it is expected that their results may differ significantly. Indeed, the difference between the discrete components from LT and the continuous distribution from MELT in the range of short-lived components is considerable (Fig.4). However, the parameters of the longest-lived component, where the distribution of lifetimes was assumed in both methods, are much more similar for both methods of analysis. The distribution obtained from LT is broader than the one from MELT, but its width at the half of the maximum is greater only by ca. 10%.
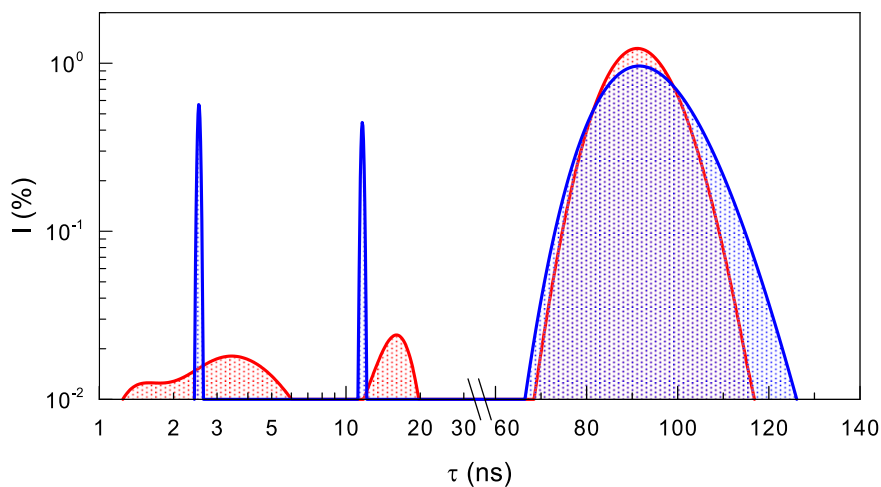
Fig.4 Histograms of o-Ps lifetimes obtained by MELT (red line) and LT (blue line) for the same positron annihilation lifetime spectrum measured for XAD4 at $p/p_0 = 0$. The spectrum consisted of 3.3×10^7 counts. The narrow peaks at 2.5 ns and 12 ns in LT results symbolize discrete components, which should be represented by δ functions.

APPENDIX 4

Although the experimental setup was not designed for the measurement of the amount of *n*-heptane introduced to the sample, it is possible to estimate it from the flow through the dosing valve and the vapor pressures on both sides of the valve.[2] An additional measurement of the flows and times required for a stepwise change in the *n*-heptane pressure over the sample was performed to estimate the mass of adsorbed alkane. The flow through the valve was kept possibly constant to avoid any distortion caused by possibly inaccurate valve calibration or vapor condensation inside it. The number of various pressures was reduced in comparison to the PALS measurement to minimize the influence of possible instabilities. Additionally, the temperature was constantly monitored and, even though its fluctuations were below 1 K, appropriate corrections were applied. The mass of *n*-heptane relative to the mass of the sample was calculated. The results were corrected for the mass of *n*-heptane introduced to the measurement chamber without any sample.

APPENDIX 5

The Δ parameter has a significant impact on the results calculated by the ETE model. The difference between pore sizes obtained using Δ differing by 10% (i.e. Δ = 0.15 nm and 0.166 nm characteristic for porous polymer walls and *n*-heptane, respectively) is ca. 25% (Fig.5). It should be expected that Δ takes intermediate values for pore walls, which are not completely covered by *n*-heptane. The simplest assumption is that it changes linearly between 0.15 nm and 0.166 nm until a single monolayer is formed on the pore surface at ca. $p/p_0 = 0.51$. This pressure was estimated from the expected reduction of the empty pore volume when the monolayer with thickness of ca. 0.56 nm is present on pore walls (the Langmuir adsorption model, the pore size distribution of XAD4 and spherical shape of pores were assumed). The pore sizes calculated using gradually incrementing Δ lay between the pressure dependences for Δ = 0.15 nm and 0.166 nm of the average pore size. It is worth noticing that the dependence for varying Δ and its further part, when Δ is stabilized at 0.166 nm, lie almost perfectly on the straight line. This seems to be a coincidence, because the presented example of monolayer formation is not suitable to describe *n*-heptane adsorption in XAD4. However, it cannot be excluded that Δ changes in a similar way as in the presented simplified example.
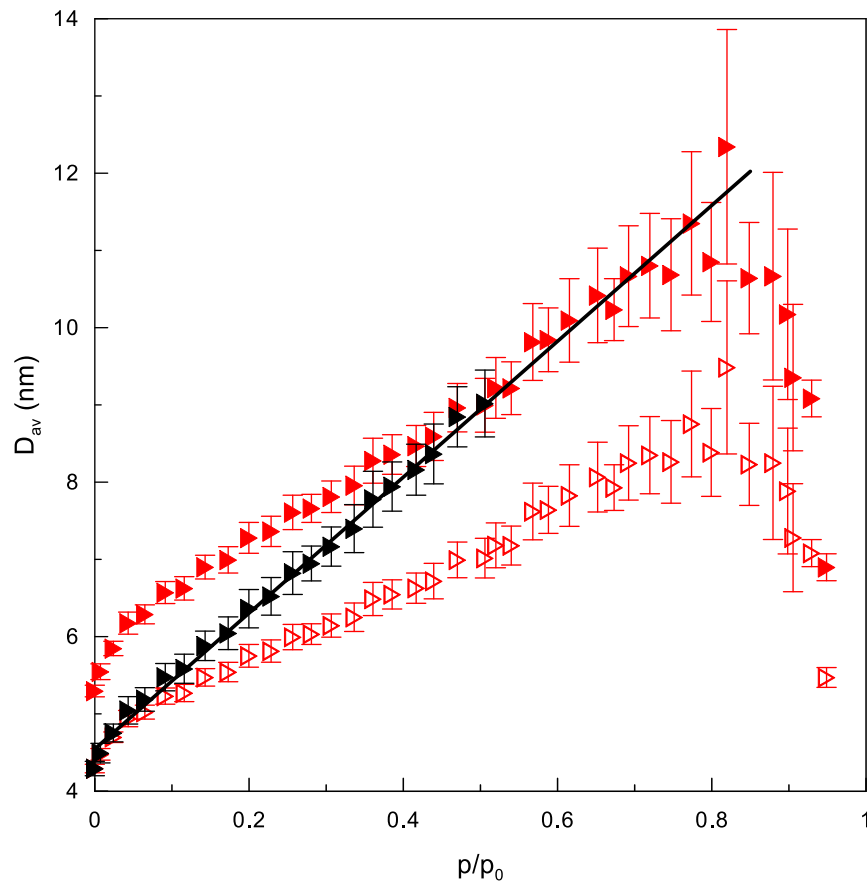
Fig.5 Evolution of the average mesopore size (D_{av}) during adsorption calculated from τ_5 using the ETE model assuming Δ = 0.15 nm (red open symbols), Δ = 0.166 nm (red close symbols), and Δ gradually incrementing with pressure from 0.15 nm to 0.166 nm (black symbols).

APPENDIX 6

The lognormal shape of the lifetime distribution assumed a priori in LT causes that the results are not reliable if the real distribution differs greatly from the lognormal one. This can be a reason why the increase in the concentration of large pores is observed for the LT results (i.e. the whole lognormal distribution would shift towards large pores if the real distribution has a very long, but low tail from the side of large pores). There is no such issue in MELT analyses, where no assumption is made to the shape of the distribution. A tail or, optionally, a low peak on the long-lived side of the peak related to mesopores should be visible in MELT results. However, the comparison of the results of both methods does not exhibit significant deviation between them (Fig.6). Thus, the MELT results confirm the lognormal shape of the long-lived component. The spectrum used in these analyses was obtained by summation of the spectra from the pressure range 0.47-0.51.
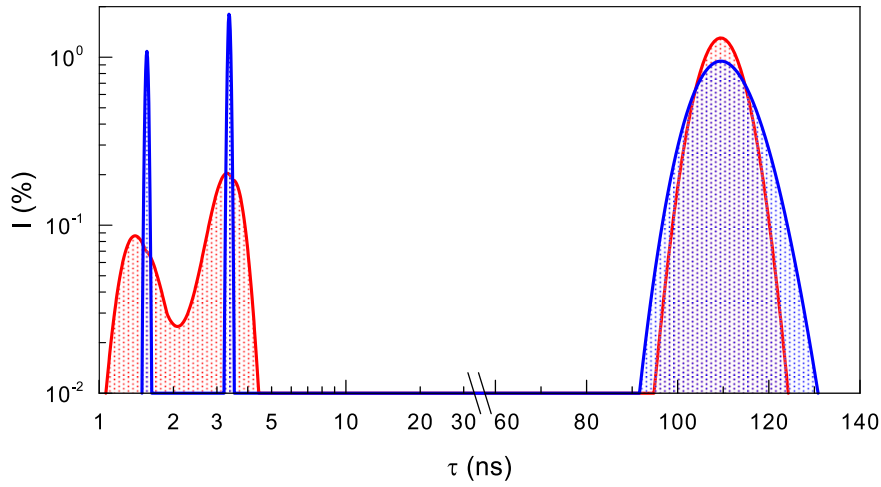
Fig.6 Histograms of o-Ps lifetimes obtained by MELT (red line) and LT (blue line) for the same positron annihilation lifetime spectrum for XAD4 with partially adsorbed *n*-heptane (p/p_0 = 0.47-0.51).

Another cause of the false broadening of the mesopore-related component can be a deficiency of LT, which may not distinguish a long-lived component from the background properly. Such an effect would be more pronounced for the low-intensity components. The series of spectra with known parameters were simulated and analyzed to verify whether they can be a cause of the broadening observed in the studied case. The simulated spectra have the same number of components, similar lifetimes, intensities, and dispersion as the measured ones. They differ only in intensities, which are transferred from I_5 to I_4 by 5% from one spectrum to another. The LT analyses show that the broadening of the long-lived component is not large. Moreover, it is systematically observed only if $I_5 < 15\%$ (Table 1).

Table 1 Parameters of the long-lived component obtained by the LT for the simulated spectra, where τ_5 = 110 ns, σ_5 = 15 ns, and I_5 was changed from 30% to 5%.

I_5	ΔI_5	τ_5	$\Delta\tau_5$	σ_5	$\Delta\sigma_5$
30.0	0.5	109.7	0.7	15.1	3.8
25.0	0.5	109.7	0.7	14.7	4.4
20.0	0.4	110.2	0.8	16.5	4.3
15.0	0.3	109.7	0.9	14.7	5.2
10.0	0.2	109.9	1.0	17.1	5.6
5.0	0.3	110.1	1.4	16.8	7.4

APPENDIX 7

The MATLAB script *showPSDs.m* was developed to allow calculation of the pore size distributions and the parameters related to them (D_{av}, V, V_s, V_l etc.) for all data obtained from the LT analyses. The results are displayed as graphs (Fig.7) and written to XLS files. The script allows choosing values of D_0 different from 5.3 nm to verify the impact of this parameter on the pressure dependences of V_s and V_l.
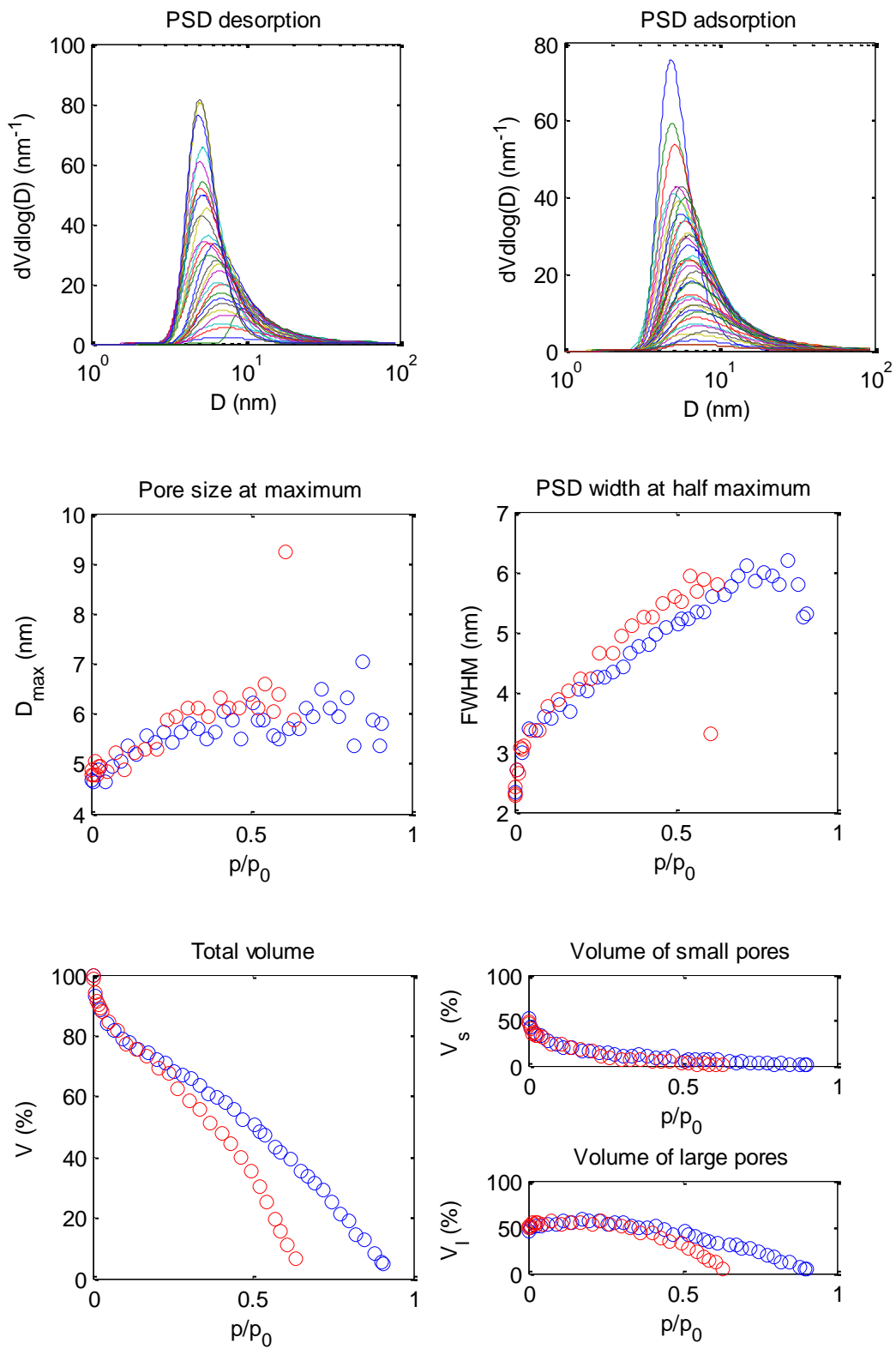
Fig.7 Example graphs generated by the MATLAB script *showPSDs.m*.

Attached files:

The MATLAB script:

```
showPSDs.m
```

The data required by the script:

```
tauD_cyl_T=295K_delta=0.166nm.mat
XAD4+C7_ads.xls
XAD4+C7_des.xls
```

The results calculated and saved by the script:

```
XAD4+C7H16_des_params.xls
XAD4+C7H16_ads_params.xls
XAD4+C7H16_des_dVdD.xls
XAD4+C7H16_ads_dVdD.xls
```

APPENDIX 8

The pressure dependences of I_3 and I_4 (Fig.8) as well as τ_3 and τ_4 (Fig.9) in polymer and silica differ in a qualitative way. The comparison between them allows discussing the differences in a mechanism of n-heptane interaction with pore walls.
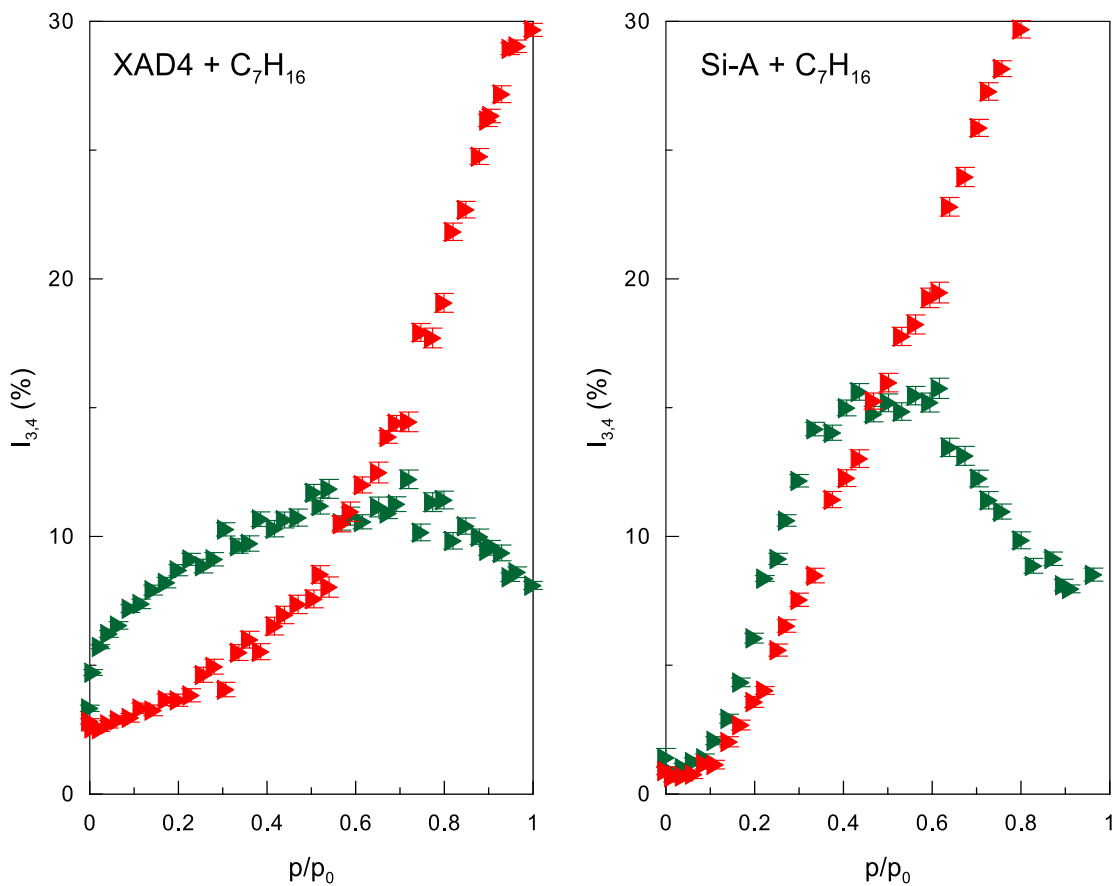

Fig.8 Intensities I_3 (green triangles) and I_4 (red triangles) of the short-lived o-Ps components in the polymer XAD4 and the silica Si-A[3] as a function of relative pressure of n-heptane during adsorption.

Fig.9 Lifetimes τ_3 (green triangles) and τ_4 (red triangles) of the short-lived o-Ps components in the polymer XAD4 and the silica Si-A[3] as a function of relative pressure of *n*-heptane during adsorption.
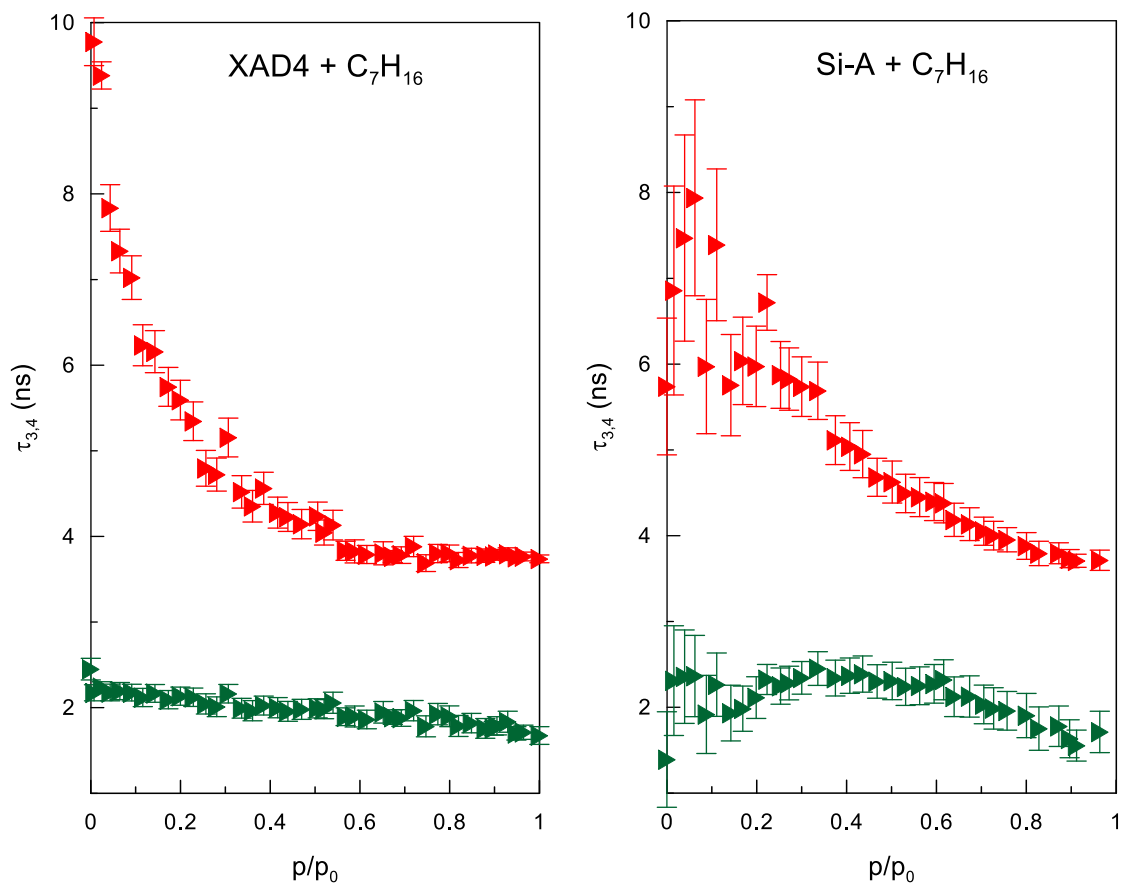
REFERENCES

1. O. Okay, *Prog. Polym. Sci.*, 2000, **25**, 711-779.

2. ISA S75.01, Flow Equations for Sizing Control Valves, Standards and Recommended Practices for Instrumentation and Control, 10th ed., Vol. 2, 1989

3. A. Kierys, R. Zaleski, M. Tydda and J. Goworek, *Adsorption*, 2013, **19**, 529-535.