Macromolecules **2002,** *35,* 9723−9729

Positron Annihilation Study of Hyper-Cross-Linked Polystyrene Networks

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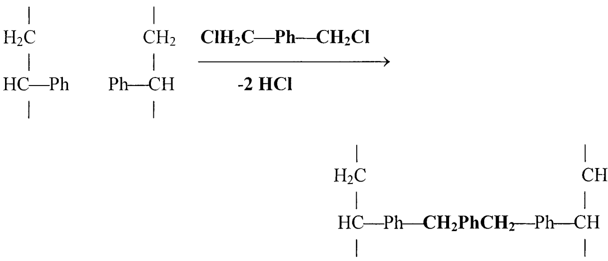
Received April 19, 2002; Revised Manuscript Received June 25, 2002

ABSTRACT: Hyper-cross-linked polystyrene sorbents with various degree of cross-linking ranging from 25% to over 100% were studied using positron annihilation lifetime (PAL) spectroscopy. Long-lived components of the lifetime distribution of positron annihilation, orthopositronium (o-Ps) lifetimes, give information on the effective size of elementary free volumes (unoccupied spaces), responsible for the properties of sorbents. Experiments were carried out in a vacuum, in air and also in oxygen and nitrogen. Narrow size distribution of elementary free volumes having radius of about 1.5 nm and concentration estimated as $\sim 10^{19}$ cm^{-3}, were found in the samples with cross-linking higher than 40%. Some of the hyper-cross-linked samples gave positronium lifetime $\tau_5 > 50$ ns, which is among the highest values ever measured for organic polymer compounds. Positronium quenching (shortening of o-Ps lifetime) due to Ps exchange interaction with oxygen, dissolved in sorbents, gave information about the character of distribution of elementary free volumes in polymers.

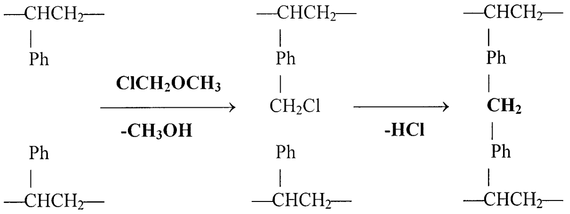
1. Introduction

Hyper-cross-linked polystyrene networks represent a new class of polymeric materials. They have been obtained by introducing a large number of rigid bridges between strongly solvated polystyrene chains. Various bifunctional compounds can been used as cross-agents, e.g., *p*-xylylene dichloride (XD) and monochlorodimethyl ether (MCDE). These agents interact with polystyrene according to the Friedel−Crafts reaction. In the first case



$$\begin{array}{ccc} | & & | \\ H_2C & & CH_2 \\ | & & | \\ HC{-}Ph & & Ph{-}CH \\ | & & | \end{array} \xrightarrow[-2\,HCl]{ClH_2C{-}Ph{-}CH_2Cl} \begin{array}{ccc} | & & | \\ H_2C & & CH_2 \\ | & & | \\ HC{-}Ph & {-}\mathbf{CH_2PhCH_2}{-} & Ph{-}CH \\ | & & | \end{array} \qquad (1)$$

and in the second case



$$\begin{array}{c} {-}CHCH_2{-} \\ | \\ Ph \\ \\ Ph \\ | \\ {-}CHCH_2{-} \end{array} \xrightarrow[-CH_3OH]{ClCH_2OCH_3} \begin{array}{c} {-}CHCH_2{-} \\ | \\ Ph \\ | \\ CH_2Cl \\ Ph \\ | \\ {-}CHCH_2{-} \end{array} \xrightarrow[-HCl]{} \begin{array}{c} {-}CHCH_2{-} \\ | \\ Ph \\ | \\ \mathbf{CH_2} \\ | \\ Ph \\ | \\ {-}CHCH_2{-} \end{array} \qquad (2)$$

Here −Ph and −Ph- denote phenyl and phenylene rings, respectively.

Cross-linking of polystyrene chains in solution results in the formation of an expanded highly swollen one-phase gel.[1] One distinguishing feature of the gel, as well as the material in dry state, is an extremely low density of chain packing. It is not surprising. Rigid bridges fix the spacious conformation of initial polymeric coils, keep chains at a certain distance, and prevent them from approaching one another when solvent is removed from the swollen gel. Therefore, a very large free volume characterizes dry hyper-cross-linked networks. It is so large that, from a macroscopic viewpoint, it can be considered as a substantial porosity. Indeed, the apparent inner surface area of one-phase hyper-cross-linked materials achieves 1000−1800 m^2 g^{-1}, and the pore volume amounts to 0.3−0.5 cm^3 g^{-1}. Because of this, hyper-cross-linked polystyrenes are excellent sorbents which sorption capacity exceeds significantly that of conventional porous polymeric adsorbing materials. Many methods used for the evaluation of network structure show that the dimension of "pores" (that is the space between polymeric chains) is small. However, all indirect methods give ambiguous results.

Positron annihilation lifetime (PAL) spectroscopy is one of the most direct probe methods of measuring elementary free volume (EFV) in polymers. Possibilities of this method became evident when Brandt advanced his "free volume" model.[2,3] A great number of publications (some of them are mentioned in refs 4−8) were devoted to elucidation of relations between three following groups of data: annihilation characteristics, size and number of elementary free volumes, and permeability of polymers. According to refs 2 and 3, positronium (Ps), a bound atomic system consisting of electron (e-) and positron (e+), tends to be localized or trapped before annihilation in elementary free volumes or, in other words, in domains with reduced electron density. This is due to the repulsive exchange interaction

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10.1021/ma020615b CCC: $22.00

Table 1. Effect of Cross-Linking in Polystyrene Copolymer (Vacuum)

link, %	sample	I_3, %	I_4,%	I_5,%	$\sum_i I_i$	τ_3,ns	τ_4,ns	τ_5,ns	ρ, g/cm^3	S, m^2/g
0.3	CPS(0.3)	37.31 ± 0.09			37.31	2.071 ± 0.004			1.05	0
25	CPS(0.3)-25E	31.17 ± 0.08	1.66 ± 0.06		32.83	2.276 ± 0.009	11.625 ± 0.485		1.06	0
43	CPS(0.3)-43E	11.60 ± 0.46	14.66 ± 0.61	5.73 ± 0.08	31.99	1.489 ± 0.079	3.806 ± 0.094	23.487 ± 0.391	0.88	80
66	CPS(0.3)-66E	7.54 ± 0.17	9.20 ± 0.21	13.09 ± 0.07	29.83	1.594 ± 0.064	5.492 ± 0.133	38.283 ± 0.336	0.77	750
100	CPS(0.3)-100E	6.76 ± 0.24	7.67 ± 0.10	14.99 ± 0.06	29.42	1.225 ± 0.050	5.579 ± 0.111	39.489 ± 0.279	0.76	1000

between the electron of positronium and electrons of surrounding molecules. Accordingly, so-called *pick-off* annihilation characteristics of long-lived orthopositronium (o-Ps) (lifetimes $\tau_{3,4,5}$ and corresponding intensities $I_{3,4,5}$) are dependent on concentration, size, and distribution of EFV in the material. In the present study, we used PAL spectroscopy to determine EFV in hyper-cross-linked polymers based on both linear polystyrene and styrene-0.3% divinylbenzene copolymer.

2. Experimental Section

2.1. Samples. Two types of hyper-cross-linked polystyrene materials were studied. The first type of networks was obtained[9] by cross-linking linear (L) polystyrene (PS) with a molecular weight of ca. 300 000, dissolved in ethylene dichloride, with 0.5 and 0.75 mol of *p*-xylylene dichloride (X) per 1 mol of styrene repeating unit. Then 2 mol of stannic tetrachloride per 1 mol of X was taken as catalyst. The concentration of LPS in the solution of all components was 0.125 g L^{-1}. After the starting solution was heated for 10 h at 80 °C, the gel obtained was crushed, washed rigorously with acetone, diluted hydrochloric acid, and water, and dried in an oven at 100 °C.

The second type of network was prepared on the basis of beaded styrene−0.3% divinylbenzene (DVB) copolymer CPS(0.3). This copolymer was provided by Purolite International Ltd. (U.K.) and used without additional purification. The copolymer, swollen to maximum with ethylene dichloride (about 0.120 g of polymer per 1 mL of diluent) was cross-linked with 0.2, 0.3, 0.4, 0.5, and 0.75 mol of monochlorodimethyl ether (E) per 1 mol of styrene in the presence of 1 mol of stannic tetrachloride per 1 mol of E. The reaction was carried out at 80 °C for 10 h. Cross-linked beads were washed as described above and dried under the same conditions.

Thus, two samples based on linear polystyrene, LPS-100X and LPS-150X, and five samples based on styrene−DVB copolymer, CPS(0.3)-25E, CPS(0.3)-43E, CPS(0.3)-66E, CPS(0.3)-100E, and CPS(0.3)-150E, were studied. (Deformation and relaxation properties of same samples CPS(0.3)-43E, -66E, -100E, and -150E have been studied by thermomechanical methods[10]). Besides this, one sample, LPS-150XT, that was preheated at 190 °C for 1 h and sample CPS(0.3), the pattern-beaded material for all post-cross-linked polymers, were also studied. In symbols used here, numbers 25−150 stand for the degree of cross-linking. It was formally calculated as a molar portion of bridges (see scheme above) in the total number of structural network elements, i.e., bridges and unbridged styrene units. When employing 0.5 mol of cross-agent, the formal cross-linking degree is 100%. It implies that theoretically such network consists of bridges only. However, the cross-linking density is significantly higher than 100% when the initial polymer is cross-linked with 0.75 mol of bifunctional agent. In this case, we express the degree of cross-linking as the number of bridges per 100 initial styrene units. Consequently, the value 150 for this network implies that one-half of initial phenyls are simultaneously involved into formation of two bridges and the latter incorporate trisubstituted benzene rings.

2.2. Measurements. PAL measurements were performed using conventional ORTEC “fast-fast” annihilation lifetime spectrometer with resolution (full width at half-maximum fwhm of the prompt coincidence curve) about 350 ps. Since we were mostly interested in *pick-off* annihilation of o-Ps (lifetimes, which are normally longer than 1 ns), our demands for resolution power were not very high. At the same time, integral statistics in every curve was higher than 4 × 10^6 counts. Furthermore, technical advantage of this investigation was the essentially extended time interval for measurements of the PAL spectra (4096 channels instead of the normally used 1024 channels), providing that the width of one channel was about the same (40 ps/ch) as in traditional measurements. This feature helped to measure long-lived and short-lived components of the PAL spectra with the same high sensitivity. We were interested to reveal the complex character of the distribution of elementary free volumes in hyper-cross-linked polystyrene networks and to estimate the average effective size for components of the size distribution of EFV. Therefore, experimental PAL distributions were described in terms of finite number (up to five, with τ_1 fixed) of lifetime components (a version of the known PATFIT program). In this version, resolution function of the set up was one of the fitting parameters along with lifetimes and intensities. Since some unusually long lifetimes were expected in the measured samples, the background was not a fitting parameter but was determined as average value of counts in 200 channels on the left side of the peak. About 2% of annihilation in the source material (Kapton) was neglected. Vacuum pumping was controlled and carried out at room temperature. To check stability of the results, not less than 10 measurements were normally performed for each sample and average numbers were calculated (see Tables 1 and 3−5). Typical results on the number and size of elementary free volumes in one of the hyper-cross-linked samples CPS(0.3)-66E are given in Table 2.

Table 2. Three Groups of Elementary Free Volumes EFV Sensed by Positronium in Hyper-Cross-Linked Polystyrene CPS(0.3)-66E[a]

group	1	2	3
concentration, 10^{19} cm^{-3}	7.3	4.5	2.3−3.0
effective radius, Å	2−3	5	14

[a] Estimations of the number (see eqs 13 and 14) and size (eq 9) of EFV are obtained from positron annihilation data and from some additional information.

The apparent inner surface area was determined by thermal desorption of argon using the single point version and Brunauer−Emmet−Teller (BET) theory for calculations.

The apparent density of beaded polymers was determined by measuring the diameter and weight of about 100 beads. Mercury densitometry was used to measure the apparent density of irregular-shaped particles.

3. Results and Discussion

3.1. Formation of Localized Ps. Analytical dependence of the long-lived component intensities on the number of elementary free volumes is important for interpretation of the results. Fraction of positrons, which *formed* o-Ps and *is observed* as long-lived component in the PAL spectrum, is dependent not only on the number of EFV (possibility of localization) but also on the density of electrons in positron spur (possibility of Ps formation). Positrons produce spur electrons during their slowing down. The validity of the spur model of Ps formation in polymers was strongly confirmed recently by experiments on additional Ps formation in irradiated polymers at low temperatures.[11,12] The model infers that in the case of lack of the spur electrons, no Ps will be formed, though the number of EFV is very high. In addition, precursors of the trapped o-Ps can be either nonlocalized o-Ps, or nonlocalized e^+, which forms Ps on the spur electron inside or in close vicinity to EFV. This situation can be described by a simple system of kinetic eqs (eq 3) where the relation between positronium trapping rate ν_i^{t} and annihilation rate of nonlocalized positronium $\lambda_{\mathrm{f}}^{\mathrm{Ps}}$ (which is probably about the same as the free positron annihilation rate[6] λ_{f}^{+}, i.e. $\lambda_{\mathrm{f}}^{\mathrm{Ps}} = \lambda_{\mathrm{f}}^{+} \equiv \lambda_{\mathrm{f}}$) determines the choice of the precursor for localized o-Ps:

$$\mathrm{d}P_{\mathrm{f}}^{+}/\mathrm{d}t = = -(\lambda_{\mathrm{f}}^{+} + \nu_{\mathrm{form}})P_{\mathrm{f}}^{+}, \quad P_{\mathrm{f}}^{+}(0) = 1$$

$$\mathrm{d}P_{\mathrm{f}}^{\mathrm{Ps}}/\mathrm{d}t = ({}^{3}/_{4})\nu_{\mathrm{form}}P_{\mathrm{f}}^{+} - (\lambda_{\mathrm{f}} + \sum_i \nu_i^{\mathrm{t}})P_{\mathrm{f}}^{\mathrm{Ps}}, \quad P_{\mathrm{f}}^{\mathrm{Ps}}(0) = 0 \tag{3}$$

$$\mathrm{d}P_{\mathrm{t}i}^{\mathrm{Ps}} = \nu_i^{\mathrm{t}}P_{\mathrm{f}}^{\mathrm{Ps}} - \gamma_i P_{\mathrm{t}i}^{\mathrm{Ps}}, \quad P_{\mathrm{t}i}^{\mathrm{Ps}}(0) = 0$$

with summing up over the numbers of the long-lived components ($i = 3, 4$, etc.) and also with P_{f}^{+}, $P_{\mathrm{f}}^{\mathrm{Ps}}$ and $P_{\mathrm{t}i}^{\mathrm{Ps}}$ standing for the probabilities to find free positron, nonlocalized positronium, and trapped positronium correspondingly; $\gamma_i = 1/\tau_i$ is the rate of annihilation in the void. Here and below, for the convenience of discussion we assign the same label i for the lifetime component and for the type of the void in a sample. Transitions between the EFV of different type are neglected. A factor of 3/4 is observed because we consider behavior of the triplet positronium.

The intensity of the long-lived orthopositronium component

$$I_i = ({}^{3}/_{4})\{\nu_{\mathrm{form}}/(\lambda_{\mathrm{f}} - \gamma_i + \nu_{\mathrm{form}})\}[\nu_i^{\mathrm{t}}/(\lambda_{\mathrm{f}} - \gamma_i + \sum_i \nu_i^{\mathrm{t}})] \tag{4}$$

Trapping rate

$$\nu_i^{\mathrm{t}} = 4\pi D^{\mathrm{Ps}}\mathrm{R}_i N_i, \tag{5}$$

where D^{Ps} means the diffusion coefficient of nonlocalized Ps, R_i is the radius for interaction, which we take to be equal to the EFV effective radius, and N_i is the number of trapping centers of a given type.

The relation $\nu_i^{\mathrm{t}} \leq \lambda_{\mathrm{f}}$ infers nonlocalized o-Ps as a precursor of localized Ps, when intensities of the long-lived positronium components I_i are dependent on concentrations of the corresponding EFV (eq 4).

The case of

$$\nu_i^{\mathrm{t}} \gg \lambda_{\mathrm{f}}, \quad \nu_{\mathrm{form}} \gg \gamma_i \tag{6}$$

corresponds to

$$I_i = (3Q/4)\nu_i^{\mathrm{t}}/\sum_i \nu_i^{\mathrm{t}} = (3Q/4)R_i N_i/\sum_i R_i N_i, \tag{7}$$

where $Q = \nu_{\mathrm{form}}/(\lambda_{\mathrm{f}} + \nu_{\mathrm{form}})$ is the fraction of positrons forming positronium in a sample.

Consequently

$$I_k/I_m = (R_k N_k)/(R_m N_m) \tag{8}$$

Here k and m are the labels of the voids of different characters.

It will be seen below that some of our lifetime spectra contained three long-lived o-Ps components, and the condition in (6) is fulfilled.

3.2. Effect of the Cross-Linking. The free volume model of positronium annihilation predicts localization of Ps atoms in elementary free volumes (EFV) of polymer structure. When the number of EFV is higher and the effective radius of EFV is larger, the intensity of the long-lived Ps component also becomes higher, and the o-Ps lifetime becomes longer. Normally, first two lifetimes (τ_1, intensity I_1, and τ_2, intensity I_2) in the PAL spectra of polymers are associated with short-lived para-Ps and with annihilation of e^+, which did not form Ps. In cross-linked polymers we used maximum five lifetime components. For illustration, we give here PAL spectrum for LPS-150X in a vacuum:

lifetimes	0.125	0.365	1.226	6.118	52.126
	fixed	±0.003	±0.055	±0.171	± 0.237
intensities	15.21	44.83	5.47	5.20	29.29
	±0.30	±0.23	±0.22	±0.09	±0.06

The last three lifetimes $\tau_3(I_3)$, $\tau_4(I_4)$, and $\tau_5(I_5)$ are related to o-Ps annihilation in EFV of polymer structure. We will pay main attention to these parameters of the PAL spectra. The value of the longest lifetime τ_5 is really unique. According to our knowledge, a polymer matrix with such a long lifetime of positrons was described only once for the porous resins studied by Jean et al.[13] Good variance of the fit (on the level of 1.06), together with high precision of intensities of the components, convinced us that description of the spectra in terms of five components is sufficient. For convenient comparison of the PAL spectra, we fixed the first lifetime τ_1 equal to the lifetime of para-Ps (0.125 ns). This assumption seems reasonable, since in the most cases the ratio $I_1 = (1/3)(I_3 + I_4 + I_5)$ was fulfilled. Characteristics of the last three components obtained in the analyses with fixed lifetime τ_1 are shown in the tables.

Effect of post-cross-linking strongly swollen polymers is shown in Table 1. It is seen that increase in the percent of linking gives essential development of the PAL spectra compared to that of the initial material CPS(0.3). Two new long-lived components (τ_4, I_4; τ_5, I_5) appear in CPS(0.3)-43E, CPS(0.3)-66E, and CPS(0.3)-100E in addition to the initial one (τ_3, I_3) in CSP(0.3). This effect means the emergence of new elementary volumes of larger size. Effective radius of EFV can be found from the known formula (eq 9),[14−16] corrected for the intrinsic annihilation rate λ_0^{t} of o-Ps:[5]

$$\lambda_i = \tau_i^{-1} = \lambda_0{}^{t} + 2\left[1 - \frac{R_i}{R_i + \Delta R} + \frac{1}{2\pi}\sin\frac{2\pi R_i}{R_i + \Delta R}\right], \ \mathrm{ns}^{-1} \tag{9}$$

Similar estimations could be done as well using another well-calibrated equation.[17]

Parts a−c of Figure 1 demonstrate that this correction is really needed in the samples, where long Ps lifetime becomes comparable with intrinsic o-Ps lifetime, 140 ns. Sample CPS(0.3)-25E is notable by the fact that the effect of post-cross-linking only starts to reveal itself here. Along with the main free volume elements (effective radius 2−3 Å), new elements with effective radii of 5 and 14 Å appear. Intensity of the longest component becomes higher with a further increase in cross-linking degree.

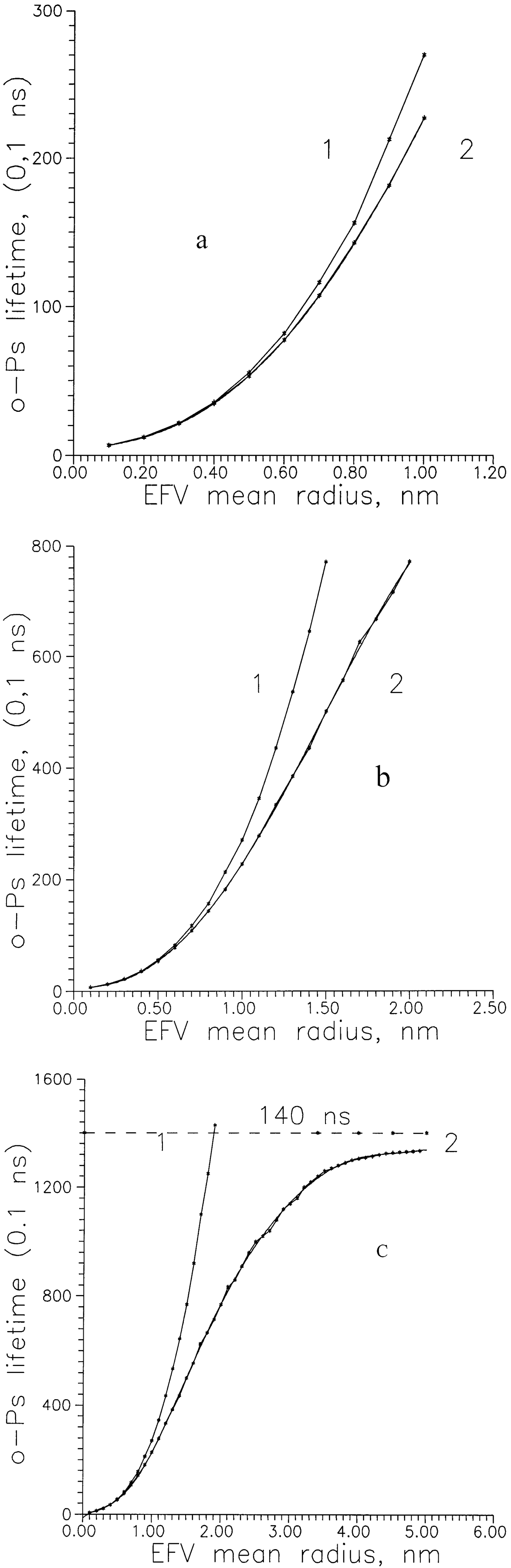

Figure 1. (a−c) Positronium lifetimes, corresponding to different effective sizes of elementary free volumes: curve 1, according to the Tao−Eldrup formula; curve 2, taking into account also the free o-Ps annihilation rate λ_0^t (see eq 9).

It is seen that, despite essential increase in the free volume in the hyper-cross-linked samples, integral intensity of long-lived components *is not increasing* and is about 30−40% for all studied samples, including LPS-150X mentioned above. It means that the amount of long-lived Ps in a system is determined primarily not by the amount and the size of elementary free volumes, as it was determined by eq 4, but mostly by the rate of Ps formation in the spur ν_{form}, by the density of electrons in the spur N_e:

$$\nu_{\text{form}} = 4\pi D_f^+ R_{\text{int}} N_e \qquad (10)$$

In this formula, D_f^+ is positron diffusion coefficient and R_{int} is an effective radius for e^+ and e^- interaction with Ps formation. All these parameters are probably the same in all linked polystyrenes studied. The number of free volumes is probably so high (already in the initial sample CPS(0.3)) that each formed Ps atom is instantly trapped ($\nu_i^t \gg \lambda_f$). The number of formed positronium atoms is determined by the limited number of electrons in the positron spur but not by the number of free volumes. Thus, in the case of the voids of one type $I_i = I_3 = 3Q/4$ (see eq 7).

However, situation is different in the case of several types of EFV. Under these circumstances, free volumes of different size are observed not because of formation and trapping of additional Ps atoms, but because the newly created larger free volumes compete with old smaller EFV for localization of Ps atoms. New lifetimes in the spectrum appear, but the integral intensity practically does not change. As it seen from eqs 7 and 8, long-lived component intensities I_i are proportional to the products R_iN_i, in this case, and the ratio of the intensities may be informative. In other words, in the case (eq 6) for a given polymer having three kinds of voids

$$I_3{:}I_4{:}I_5 = (R_3N_3){:}(R_4N_4){:}(R_5N_5) \qquad (11)$$

Using eq 9, effective radii $R_3 = 2-3$ Å, $R_4 = 5$ Å, and $R_5 = 14$ Å were determined. For CPS(0.3)-66E, for example, $I_3 = 7.5\%$, $I_4 = 9.2\%$, and $I_5 = 13.09\%$. Numbers in the ratio in (11) show that concentrations of EFV, corresponding to different components in the PAL spectrum, are comparable. In this case, the fraction of big holes in the integral specific free volume is roughly proportional to R_5^3 and amounts to 95%. On the other hand, it is reasonable to suppose, that this additional (compared to CPS(0.3)) free volume is responsible for the difference in the densities of CPS(0.3) and CPS(0.3)-66E samples. In this case, the additional specific free volume V_f per cm^3 in CPS(0.3)-66E can be estimated from (12) with $\rho_{0.3} = 1.05$ g/cm^3 and $\rho_{66} = 0.77$ g/cm^3:

$$V_f = (\rho_{0.3} - \rho_{66})/\rho_{0.3} = 0.27 \qquad (12)$$

The number of the largest EFV is

$$N_5 = 3V_f/4\pi R_5^{\,3} = 2.3 \times 10^{19}\ \text{cm}^{-3} \qquad (13)$$

Table 3. Effect of Oxygen on the PAL Spectra in Hyper-Cross-Linked Networks

sample	conditions	τ_3, ns	τ_4, ns	τ_5, ns	I_3, %	I_4, %	I_5, %
CPS(0.3)-25E	vac	2.276 ± 0.009	11.625 ± 0.485		31.17 ± 0.08	1.66 ± 0.06	
	air	2.224 ± 0.011	9.241 ± 0.357		32.27 ± 0.09	2.13 ± 0.09	
CPS(0.3)-43E	vac	1.489 ± 0.070	3.806 ± 0.094	23.487 ± 0.391	11.60 ± 0.46	14.66 ± 0.61	5.73 ± 0.10
	0.1 atm of O_2	1.274 ± 0.074	3.452 ± 0.083	18.200 ± 0.340	10.41 ± 0.37	15.40 ± 0.55	5.37 ± 0.10
	air (0.2 atm of O_2)	1.188 ± 0.068	3.371 ± 0.071	17.439 ± 0.314	10.87 ± 0.34	16.38 ± 0.48	5.44 ± 0.10
	1.0 atm of O_2	2.015 ± 0.022	7.054 ± 0.105		17.34 ± 0.11	6.70 ± 0.14	
	5.0 atm of O_2	2.140 ± 0.010			10.77 ± 0.06		
CPS(0.3)-66E	vac	1.594 ± 0.064	5.492 ± 0.133	38.283 ± 0.336	7.54 ± 0.17	9.20 ± 0.21	13.09 ± 0.07
	air (0.2 atm of O_2)	1.244 ± 0.057	4.633 ± 0.101	27.735 ± 0.244	8.15 ± 0.24	9.98 ± 0.19	11.83 ± 0.08
CPS(0.3)-100E	vac.	1.225 ± 0.050	5.579 ± 0.111	39.489 ± 0.279	6.76 ± 0.24	7.67 ± 0.10	14.99 ± 0.06
	air (0.2 atm of O_2)	1.176 ± 0.053	5.097 ± 0.111	30.995 ± 0.220	6.95 ± 0.26	7.89 ± 0.12	14.18 ± 0.07
	0.4 atm of O_2	1.087 ± 0.073	4.218 ± 0.129	22.207 ± 0.200	7.17 ± 0.43	7.90 ± 0.19	12.39 ± 0.10

Correspondingly, from (10)

$$N_4 = N_5\frac{I_4R_5}{I_5R_4} = 4.5 \times 10^{19}\ \mathrm{cm}^{-3},\qquad N_3 = N_4\frac{I_3R_4}{I_4R_3} = 7.3 \times 10^{19}\ \mathrm{cm}^{-3} \quad (14)$$

On the other hand, concentration of elementary free volumes N_5 for CPS(0.3)-66E can be formally found from the apparent inner surface area S (Table 1) and from the effective surface s of EFV ($s = 4\pi R_5^2$), since the surface is determined mostly by the largest free volumes (provided that the numbers of the voids are of equal order of magnitude, which is the case (see eqs 13 and 14):

$$N_5 = S/4\pi R_5^{\,2} = 3 \times 10^{19}\ \mathrm{g}^{-1} = 2.3 \times 10^{19}\ \mathrm{cm}^{-3} \quad (15)$$

Estimations of the size (eq 9) and number (eqs 13 and 14) of elementary free volumes for CPS(0.3)-66E, using positron annihilation data and some additional information, are listed in Table 2. Naturally, results of estimations using (13) and (15) are very close.

It was stressed above that the formation of localized Ps in a polymer requires both spur electrons and EFV. Therefore, it was interesting to compare N_5 with local spin density n_e in the positron terminal spur. Reasonable estimations, supposing several electrons in the vicinity (50 Å) of thermalized e^+, give 10^{19} cm^{-3}. This value is comparable with N_5, and we conclude that nearly each free volume is suitable for the formation of localized Ps. Correspondingly, the mean distance L that positron (positronium) has to diffuse to form localized Ps is about 50 Å. Diffusion coefficient of precursor of localized Ps $D = L^2/6\tau = 1.1 \times 10^{-4}$ cm^2/s. Here τ is annihilation lifetime of nonlocalized precursor, which is about the same (~0.3 ns) for nonlocalized e^+ and Ps. This diffusion coefficient (~10^{-4} cm^2/s) is too small for nonlocalized e^+ in molecular substances (10^{-1} cm^2/s for polyethylene[18,19]) and corresponds more likely to the mobility of the nontrapped Ps.[6]

3.3. Quenching of o-Ps by Oxygen. Effect of o-Ps quenching (shortening of o-Ps pick-off annihilation lifetime τ_4 and τ_5) by oxygen is shown in Table 3 for CPS(0.3)-25E, CPS(0.3)-43E, CPS(0.3)-66E, and CPS(0.3)-100E polymers. There is no influence of oxygen in the original CPS(0.3) sample. The effect is similar to that observed recently by some authors[20,21] for the typical glassy polymer membrane material poly(trimethylsilyl propine) PTMSP. However, in the case of hyper-cross-linked polymers, vacuum lifetimes are still longer. Quenching effect is explained by the spin-exchange between o-Ps (triplet Ps) and paramagnetic oxygen:

$$^{T}\mathrm{Ps}(\downarrow\downarrow) + \mathrm{O}_2(\uparrow) \rightarrow {}^{S}\mathrm{Ps}(\uparrow\downarrow) + \mathrm{O}_2(\downarrow) \quad (16)$$

Arrows show here spins of electrons and the positron. Quenching is due to Ps transition from the long-lived triplet state to the short-lived singlet state. The rate constant k of Ps interaction can be found from the known eq 17 of positronium chemistry

$$\tau_{4,5}^{\ -1}(\mathrm{ox}) = \tau_{4,5}^{\ -1}(\mathrm{vac}) + k[\mathrm{O}_2];\qquad k = 4\pi D_{\mathrm{loc}}^{\mathrm{Ps}}(R_{\mathrm{Ps}} + R_{\mathrm{ox}}), \quad (17)$$

where $D_{\mathrm{loc}}^{\mathrm{Ps}}$ characterizes the mobility of Ps atom localized in a pore, and [O_2] means concentration of oxygen molecules; $R_{\mathrm{Ps}} = 0.53$ Å, and $R_{\mathrm{ox}} = 1.2$ Å. This consideration infers, as in some previous publications,[20,22] that, after localization in one of elementary free volumes, o-Ps is capable of changing the place of its initial location. This change may happen several times. Therefore, quenching is a result of Ps staying, for some time, next to an oxygen molecule and, for the rest of its lifetime, in an empty free volume. Otherwise, in the case of complete localization of some of the trapped Ps in EFV occupied by oxygen, the effect would look like inhibition of Ps formation.

Existence of some EFV free of oxygen follows from the shortening of o-Ps lifetimes (τ_4, τ_5) with the increase of oxygen pressure (see Table 3). Unfortunately, the concentration of oxygen molecules in hyper-cross-linked networks under different pressures is not known now, and we cannot calculate the diffusion coefficient of trapped Ps $D_{\mathrm{Ps}}^{\mathrm{loc}}$ from the quenching data. However, if this coefficient is about the same as in PTMSP (3.8×10^{-5} cm^2/s [20]), the concentration of dissolved oxygen molecules C_{ox} in CPS(0.3)-66E, for example, under atmospheric conditions can be estimated from eq 18

$$\mathrm{C}_{\mathrm{ox}} = [\tau_5^{\ -1}(\mathrm{air}) - \tau_5^{\ -1}(\mathrm{vac})]/[4\pi(R_{\mathrm{Ps}} + R_{\mathrm{ox}})D_{\mathrm{Ps}}^{\mathrm{loc}}]. \quad (18)$$

Equation 13 gives for the air $C_{\mathrm{ox}} = 1.2 \times 10^{18}$ cm^{-3}; in CPS(0.3)-100E at $P_{\mathrm{O}_2} = 0.4$ atm, C_{ox} is twice as large: 2.4×10^{18} cm^{-3}.

High resolution of several components of the o-Ps lifetime distribution, along with certain Ps mobilities between EFV, probably means that o-Ps does not move between free volumes of different size (an assumption, accepted in system 3), but it is able to meet similar free volumes during its lifetime. This fact implies that free volumes of different size are distributed inhomogeneously. In other words, there are microregions of larger free volumes and those of smaller free volumes. Prob-

Table 4. Effect of Very Dense Cross-linking

	CPS(0.3)-150E, $\rho = 0.71$ g/cm^3, $S = 1200$ m^2/g					
conditions	τ_3, ns	τ_4, ns	τ_5, ns	I_3, %	I_4, %	I_5, %
air	1.432 ± 0.188	5.256 ± 0.308	22.367 ± 0.189	4.36 ± 0.47	5.41 ± 0.23	16.00 ± 0.16
vac	1.690 ± 0.152	5.306 ± 0.324	16.558 ± 0.328	7.27 ± 0.36	8.33 ± 0.33	9.52 ± 0.33
air again	1.786 ± 0.140	6.558 ± 0.335	20.900 ± 0.351	5.61 ± 0.25	7.82 ± 0.21	11.30 ± 0.31
N_2, 1 atm	1.840 ± 0.149	6.813 ± 0.342	21.575 ± 0.417	5.69 ± 0.27	8.25 ± 0.22	10.33 ± 0.32
O_2, 0.6 atm	1.772 ± 0.137	5.737 ± 0.436	15.208 ± 0.490	7.37 ± 0.31	7.97 ± 0.32	7.96 ± 0.55
O_2, 1 atm	2.656 ± 0.060	9.858 ± 0.103		9.81 ± 0.13	9.85 ± 0.14	

Table 5. Effect of the Nature of the Link

	annihilation characteristics					
atmosphere	τ_3, ns	τ_4, ns	τ_5, ns	I_3, %	I_4, %	I_5, %
CPS(0.3)-150E, $\rho = 0.71$ g/cm^3, $S = 1200$ m^2/g (vac)						
vac	1.690 ± 0.152	5.306 ± 0.324	16.558 ± 0.328	7.27 ± 0.36	8.33 ± 0.33	9.52 ± 0.33
LPS-150X, $\rho = 0.6$ g/cm^3, $S = 1600$ m^2/g (vac)						
vac.	1.226 ± 0.056	6.118 ± 0.171	52.126 ± 0.237	5.47 ± 0.22	5.20 ± 0.09	29.29 ± 0.06
air	0.919 ± 0.045	5.241 ± 0.129	39.287 ± 0.158	7.70 ± 0.57	5.83 ± 0.08	28.09 ± 0.07
LPS-150XT (1 h, 190 °C), $\rho = 0.6$ g/cm^3, $S = 1500$ m^2/g (vac)						
vac	0.951 ± 0.052	5.256 ± 0.120	51.781 ± 0.219	6.55 ± 0.54	5.54 ± 0.08	28.60 ± 0.05
CPS(0.3)-100E, $\rho = 0.76$ g/cm^3, $S = 1000$ m^2/g (vac)						
vac	1.225 ± 0.050	5.579 ± 0.111	39.489 ± 0.279	6.76 ± 0.24	7.67 ± 0.10	14.99 ± 0.06
LPS-100X, $\rho = 0.74$ g/cm^3, $S = 1200$ m^2/g (vac)						
vac	1.420 ± 0.058	5.233 ± 0.130	41.084 ± 0.251	7.64 ± 0.17	8.02 ± 0.19	18.39 ± 0.06
air	1.024 ± 0.046	4.297 ± 0.085	30.336 ± 0.162	9.41 ± 0.44	9.19 ± 0.16	18.01 ± 0.06

ably, these sites translate into each other continuously, with no sharp borders between the regions, since our samples were optically transparent. Furthermore, sizes of micro regions l are larger, than localized Ps diffusion length $l \geq (6D_{Ps}^{loc}\tau_i)^{1/2} = 560$ Å. Parameter τ_i here is the lifetime of once-trapped o-Ps. This is new structural information, which can be inferred from the quenching effect.

3.4. Effect of the Highest Density of Cross-Linking. There was one sample, among the cross-linked polystyrenes examined (CPS(0.3)-150E), with a degree of linking higher than 100%. This strange statement means in fact that half of the benzene rings were linked twice by methylene groups in this material. The effect of the additional linking is not obvious, especially in the case of short methylene bridges. Some characteristics of this sample are shown in Table 4. Contrary to other samples, evacuation of the sample does not lead to an increase of o-Ps lifetime. Furthermore, the longest Ps lifetime τ_5 drops down from 22.367 ± 0.189 to 16.558 ± 0.328 ns. The same is related to the intensity I_5. This effect was repeatedly observed several times for the same sample. Filling of the sample with air or nitrogen gave longer lifetimes and higher intensities. PAL characteristics of CPS(0.3)-150E sample were observed to be slightly changing with time. For instance, after the transition from vacuum to air, the lifetime was observed to change over a number of hours from 18.495 ± 0.415 to 20.90 ± 0.351 ns. Intensity was going up from 9.46 ± 0.58% to 11.30 ± 0.315%. For some reason or another, in air, in the presence of nitrogen, Ps did not contact oxygen. At higher pressures of pure oxygen (0.6, 1.0 atm), Ps quenching by oxygen becomes obvious. The reason for the effect has to be additionally studied in experiments with gas sorption. Probably it has something to do with the presence of a substantial number of sites that retain oxygen even in the vacuum exposed situation. Indeed, first results of testing materials cross-linked with excessive amounts of MCDE by using gas and liquid chromatography techniques, reveal the extreme affinity of these materials to polar compounds, especially oxygen-containing ones. We suggest formation of anthracene-like condensed aromatic systems after bridging of two phenyl rings by two *o*-methylene links, which should be favored at cross-linking densities that high as in the CPS(0.3)-150E material. Because of strong $\pi-\pi$-interactions with electronic systems of condensed aromatics, oxygen, like carbonyl-containing compounds, may form sorption complexes of enhanced stability. With *p*-XDC as the cross-linking agent, condensed aromatic systems are less likely to form. As we will see below, the transition to XDC-links transforms the CPS(0.3)-150E system into sorbent LPS-150X (apparent specific surface area, 1600 m^2/g) that behaves normally from the point of view of Ps quenching by oxygen.

3.5. Properties of LPS-100X and LPS-150X. Let us compare now the properties of hyper-cross-linked networks based on styrene-0.3%DVB copolymer CPS-(0.3) and cross-linked with short methylene bridges with the properties of networks on the basis of linear polystyrene cross-linked with *p*-xylylene dichloride that forms longer bridges. From the considerations of data given in Table 5 for CPS(0.3)-100E and LPS-100X, we can conclude that there is no direct correlation between τ_5, I_5 and the length of cross-bridges. We have also never observed other properties of hyper-cross-linked networks, such as swelling, porosity, sorption capacity, and so on, to be associated with the length of bridges. It is not surprising, because many other more powerful factors (e.g., rate of the chemical cross-linking reaction or dilution of the starting system) govern the behavior of hyper-cross-linked materials.

However, the lifetime τ_5 and the intensity I_5 correlate unambiguously with the apparent density of the polymers under consideration. Indeed, the apparent densities of CPS(0.3)-100E and LPS-100X are comparable; still the density of the latter sample is slightly lower, and both τ_5 and I_5 parameters are slightly larger. A dramatic increase in the longest lifetime τ_5, up to 52.126 ± 0.237 ns, is observed for the sample LPS-150X that is characterized by a significantly smaller density, 0.6

g/cm^3, in contrast to 0.71 g/cm^3 for CPS(0.3)-150E. To our knowledge, τ_5 for LPS-150X is one of the longest Ps lifetimes for polymeric compounds that was ever observed. Extremely high is also the relative intensity of this component $I_5 = 29.29 \pm 0.06\%$. Contrary to CPS(0.3)-150E, the effect of oxygen is normal here (shortening of o-Ps lifetime). This result shows again some special "relation" of CPS(0.3)-150E free volumes to oxygen compared to that in all other systems.

Deviations of LPS-100X properties from those of CPS(0.3)-100E are not that strong as for LPS-150X and CPS(0.3)-150E.

3.6. Temperature Treatment. We have studied also the influence of annealing (1 h, 190 °C) on the annihilation characteristics of LPS-150X (Table 5.). The annealed sample is called LPS-150XT here. Though the thermal treatment might be expected to result in the collapse of the porous structure of the network, annihilation characteristics of the latter did not change. This finding corresponds to the previous conclusion that the expanded hyper-cross-linked sorbent matrix, which is formed in the strongly solvated state, is basically free of excessive local tensions[1] and presents a sufficiently stable network.

4. Conclusion

We have studied positron annihilation lifetime (PAL) characteristics of hyper-cross-linked polystyrenes that are known for their highly developed specific surface area. Sensitivity of the PAL technique to the size and number of elementary free volumes is demonstrated. Measurements of o-Ps lifetimes in the polymers allowed detecting definite increase in the size of EFV, due to intensive post-cross-linking of the swollen initial polymer. On transition from the parent sample CPS(0.3) to that with 66% of cross-linking degree, effective radius R_{ef} of EFV is changing from 2 to 3 Å up to 14 Å, but the integral number of EFV remains about the same, on the level of 5×10^{19} cm^{-3}. Additional linking up to 150% gives a further increase in R_{ef} and the number of the largest free volumes sensed by positronium. Thermal treatment (1 h, 190 °C) did not change the characteristics of EFV of the hyper-cross-linked polymer networks.

Though the positron annihilation technique is considered to provide reliable information on the porous structure of polymeric materials, the structural information obtained in this study has to be compared elsewhere with that resulting from several other methods, as small-angle X-ray scattering, adsorption isotherms, size exclusion chromatography, NMR spectroscopy of adsorbed molecules, etc.

Acknowledgment. Financial support from the Russian Foundation for Basic Research (grants 00-15-97427, IR 97-1525, and 02-03-33061) is greatly acknowledged. The authors thank Prof. Yu. P. Yampolskii for useful discussions.

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MA020615B