Free Volume and Swelling Dynamics of the Poly[(2-dimethylamino)ethyl methacrylate]-*l*-polyisobutylene Amphiphilic Network by Positron Annihilation Investigations

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ABSTRACT: The poly[(2-dimethylamino)ethyl methacrylate]-*l*-polyisobutylene (PDMAEMA-*l*-PIB) amphiphilic network (APN), a new class of cross-linked systems, was synthesized by the use of methacrylate−telechelic PIB obtained via quasiliving carbocationic polymerization. The swelling dynamics and the free volume changes of this APN was followed by simultaneous swelling and positron annihilation measurements. It was found that the lifetime of ortho positrons (o-Ps) increases with increasing swelling ratio (R), reaches a maximum at relatively low R, and decreases to a constant value at equilibrium swelling. These findings indicate the collapse of the hydrophobic PIB domains and expansion of the hydrophilic PDMAEMA phase in the network upon contacting with water. After reaching the maximum, the decrease of the lifetime parameter is caused by filling the free volume with water in the network. A striking observation was obtained for the o-Ps formation intensity as a function of time (or swelling ratio): the intensity rapidly decreases, and it reaches a minimum at very low R, at ~10% of the equilibrium swelling ratio, and then increases to a constant value. These phenomena reveal important aspects of the structure of the free volume in the APN and provide fundamental information about the swelling dynamics. The minimum of the o-Ps intensity is reached at around 1:1 water/monomer units molar ratio in the network. Surprisingly, a similar phenomenon was observed when the monomer itself was mixed with water. Molecular modeling by ab initio calculations indicates that a 1:1 ringlike cluster may be formed between water and DMAEMA. On the basis of these results it is concluded that the surface of the free volume units in the APN become covered with water molecules quickly by interacting with the PDMAEMA chains at the beginning of swelling. This indicates that the free volume in the PDMAEMA-*l*-PIB APN is not composed of independent pores but of interconnected channels which allow rapid diffusion of water molecules to cover the surface of the free volume units. This fast process results in a quick surface structure reorganization, i.e., enrichment of the surface of the channels by PDMAEMA segments leading to the corresponding rapid decrease of o-Ps formation intensity, and to the simultaneous collapse of PIB domains yielding increase of free volume in the network and positron lifetime at the beginning of swelling. Results of this study also allow us to predict that the combined method presented here, i.e., simultaneous swelling kinetics and positron annihilation investigations, can be widely applicable for gaining new information on free volume structure, swelling dynamics, and interactions between material components and swelling agents for a large variety of networks, gels, polyelectrolytes, amorphous materials, blends, composites, etc.

Introduction

Recent rapid developments in the field of quasiliving polymerizations have led to a wide variety of novel functional polymers, such as macromonomers, telechelic polymers, macromolecules with a large selection of desired pendant groups (e.g., liquid crystalline polymers, macromolecules with nonlinear optical properties, etc.), new block copolymers, and macrocycles.[1−10] Among these materials exact telechelic polymers and oligomers, i.e., macromolecules bearing reactive functional termini, are the most desired polymers as building blocks for a variety of new bi- and multicomponent polymeric architectures.[1,4−10] One of the most interesting recent advancements based on the availability of well-defined telechelic polymers with controlled molecular weight (MW) and narrow molecular weight distribution (MWD) is reproducible synthesis of amphiphilic networks, a new class of cross-linked polymeric systems.[11−28] An amphiphilic network (APN) is composed of covalently bonded hydrophilic and hydrophobic chain segments. Due to synthetic difficulties caused by macroscopic phase separation between hydrophobic and hydrophilic polymers, only sporadic reports appeared on APNs in the past,[29−33] and systematic research has started in the field of these new materials only in recent years.[11−28,34−37]

As recent investigations with polyisobutylene- (PIB)-based APNs indicate, the covalently bonded immiscible hydrophilic and hydrophobic chains yield unique nanostructured molecular composites with co-continuous microphase separated morphology.[11−16,37] This special structure is most likely the major factor determining bulk and surface structure and properties obtained by contact angle measurements,[35] X-ray photoelectron spectroscopy, and atomic force microscopy[36] and the excellent biocompatibility[34] and blood compatibility[35] of PIB-based APNs. It has been demonstrated that APNs are swellable both in hydrophilic and hydrophobic solvents,[11−18,26−28] and the equilibrium swelling is controlled by composition. One of the unique aspects of the swelling process of APNs is that the polymer phase with opposite philicity of the solvent is expected to collapse or shrink during swelling.

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The positron lifetime technique has recently been used widely for studying the structure of polymers,[38−44] providing a unique possibility to investigate the free volume through the lifetime of positronium atoms. Positronium is formed by an electron and a positron and it can be considered as a very light hydrogen atom. It has two ground states (a triplet and a singlet) but only the triplet state has a practical advantage for investigating the polymer structure. Usually 10−30% of the injected positrons form triplet positronium (ortho-positronium, o-Ps) in polymers.[45] The usual lifetime of o-Ps is around 1.5−3 ns. The most important factors determining the formation of lifetime parameters of o-Ps atoms are the chemical composition of the material and the size of free volume units. According to the simplest Ore model[46] the positronium formation is determined mainly by the gap between the binding energy of the ground state of positronium and the ionization energy of the material. The changes of this value are reflected by the changes of the Ps-formation intensity.

In a vacuum where the electron density is zero, the o-Ps has a very long lifetime (141 ns), but in a condensed material, the lifetime is decreased by about 3 orders of magnitude by the finite electron density. In this case the annihilation of o-Ps takes place by external electrons, and the changes of the electron density yield changes in the actual lifetime value. This fact makes the o-Ps useful for studying the free volume: any change of the free volume size changes the average electron density in the material affecting the lifetime of o-Ps. According to calculations performed on the basis of the free volume model of Ps formation, the positronium atoms are localized in the free volumes.[47] Their annihilation usually takes place in this localized state, providing direct information about the size of the free volume units. Several authors published correlation functions between the lifetime of o-Ps and the size of free volume units in molecular systems.[45] However these correlations are valid only for similar chemical compositions. Even if such relationships are not available, processes connected with free volume changes can be followed by changes in the lifetime of o-Ps.

This study concerns the applicability of the positron annihilation technique for investigating structural changes occurring during swelling of the poly[2-(dimethylamino)ethyl methacrylate]-*l*-polyisobutylene (PDMAEMA-*l*-PIB; where *l* stands for *linked*)[48] amphiphilic network in order to obtain new insight into these phenomena.

Results and Discussion

APNs are special nanostructured molecular composites providing unique hydrogels upon swelling these new materials in water. It has been found that PIB-based APNs with 40−60% hydrophobic component exhibit the most attractive properties, such as biocompatibility and blood compatibility in the swollen state in water and/or under physiological conditions.[34,35] The structure of APNs under equilibrium swelling conditions determining the properties of the resulting hydrogels is the consequence of specific processes occurring during swelling due to the coexistence of chain segments with opposite philicity in these materials. However, information on these processes is practically not available yet. Therefore, investigations have been carried out in our laboratories with the PDMAEMA-*l*-PIB APN containing 48% PIB by following the swelling kinetics and the free volume changes with conventional water uptake measurements and simultaneous positron annihilation experiments, respectively. This network has microphase separated morphology[32] indicated by two glass transition temperatures (T_g) for the hydrophobic PIB and hydrophilic PDMAEMA segments at −60 and +30 °C, respectively.

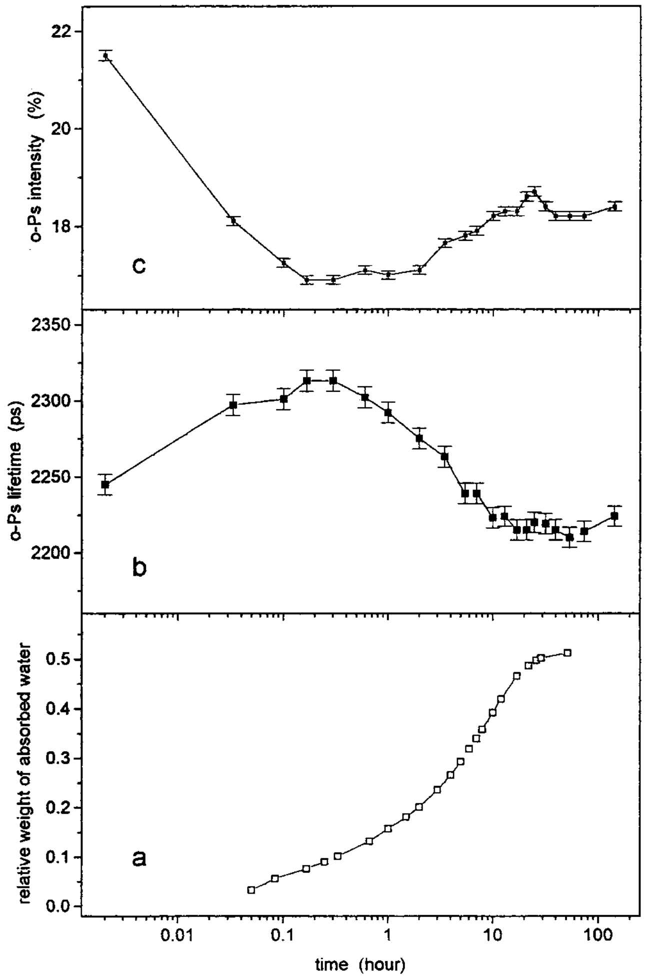

Figure 1. Swelling kinetics of the PDMAEMA-*l*-PIB amphiphilic network followed gravimetrically (a) and by positron lifetime spectroscopy (b, c).

As exhibited in Figure 1a, the usual swelling ratio measurement shows that the investigated PDMAEMA-*l*-PIB is able to absorb relatively large amounts of water.[55] The water uptake is relatively quick at the beginning but saturation (equilibrium) occurs only after ≈50 h soaking at 52% swelling ratio (R = weight of absorbed water/weight of dry PDMAEMA-*l*-PIB) at room temperature. There are significant changes in the lifetime and the intensity of o-Ps as a function of swelling time as shown in parts a and b of Figures 1. At the beginning of the swelling process, i.e., at low swelling ratios, the o-Ps lifetime increases by about 70 ps, and then it reaches a maximum and decreases to a constant value. This latter phase, the decrease of the lifetime is the expected phenomenon, and it is related to filling the free volume by water. As the water molecules fill the free volumes in the network by reaching equilibrium swelling, the o-Ps lifetime approaches the value measured in pure water (about 1800 ps).

The increase of the lifetime at very low swelling ratios indicates that the average size of free volume sites increases in the PDMAEMA-*l*-PIB network as water

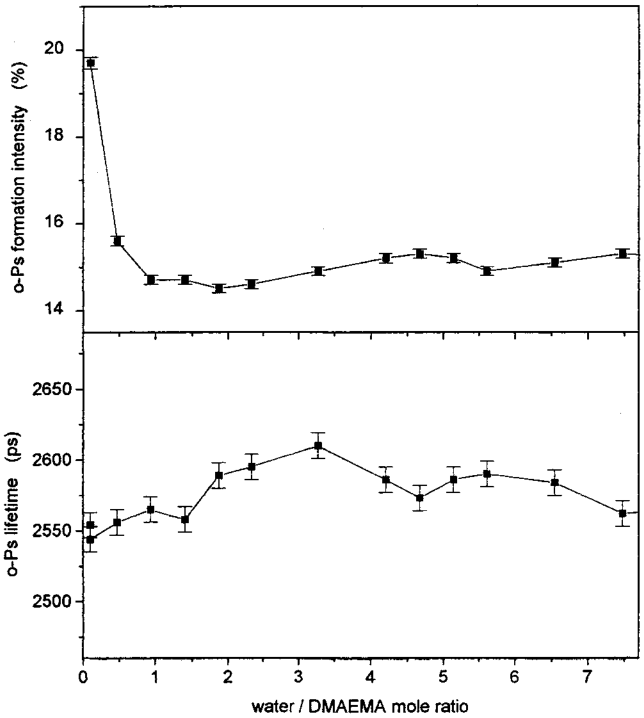

Figure 2. Positron lifetime parameters in the mixtures of the DMAEMA monomer and deionized water.

start to diffuse in the material. Surprisingly, these dynamic structural changes occur fast at the very beginning of the swelling process and at low swelling ratios. The free volume model of o-Ps annihilation[47] suggests that the size of free volume units in the PDMAEMA-*l*-PIB APN increased by about 5% in the first 10 min. Considering the amphiphilic nature of the PDMAEMA-*l*-PIB sample, this observation can be explained by a quick rearrangement of the phases with opposite philicity in this APN. The PDMAEMA phase expands whereas the PIB phase shrinks upon contacting with water.[34−37] Both effects yield increase of the size of free volume units. The fact that this is a fast process indicates rapid reorientation of the hydrophilic PDMAEMA segments toward the surface of free volume units in this network.

As shown in Figure 1c, the o-Ps formation intensity rapidly decreases at the beginning of the swelling process, and after reaching a minimum, it increases again. The interpretation of the decrease of the o-Ps formation intensity is not as straightforward as that of the lifetime changes. It cannot be explained either by the free volume increase or by the direct effects of water; i.e., the increase of free volume size does not have a significant effect on Ps formation, and the Ps formation intensity is higher in pure water than in the network.

Lifetime measurements were also made with water/DMAEMA mixtures in order to study the intensity decrease phenomenon. As exhibited in Figure 2, the observed results show that similar intensity decrease occurs by adding water in the DMAEMA monomer as in the APN. The o-Ps formation intensity decreases until the water/DMAEMA molar ratio reaches one, and then further addition of water does not affect this parameter significantly. These results suggest that the "adsorption" of the first water molecule changes the electronic structure of DMAEMA molecules so that it provides smaller probability for o-Ps formation.

Table 1. Total Energies for Different 1:1 DMAEMA:Water Clusters Obtained by Different ab Initio Methods[a]

	total energy (hartree)		
level of calculation	N- -H−O	O- -H−O	N- -HOH- -O
HF/3-21G	−588.6787	−588.6819	−588.6900
HF/6-31G**	−591.8868	−591.8870	−591.8905
MP2/6-31G**	−593.7232	−593.7210	*b*
DFT (B3LYP)/6-31G**	−595.5127	−595.5127	−595.5278

[a] All data refer to the optimum geometry of the given calculation level. [b] The optimum geometry was not found although several initial configurations were tested.

To find a reasonable explanation for the exceptional role of 1:1 molar ratio quantum chemical ab initio calculations were performed for the DMAEMA monomer. It was supposed that H-bonded clusters were formed in the mixtures, and 1:1 clusters are the most stable among them. To confirm this assumption, optimum geometries and total energies were calculated for 1:1 clusters of different structures. The most evident assumption for explaining the stability of 1:1 clusters is that the hydrogen bonds formed by the nitrogen and oxygen atoms of the DMAEMA monomer are different. However, the calculations disproved this assumption. No matter what levels of theory or how large sets of functions were used, the total energies of the N- -H−O and the O- -H−O clusters differed only very slightly. As is shown in Table 1 the calculated energy differences are too small to result in the exceptional stability of 1:1 clusters.

There are two other possible cluster structures which distinguish the 1:1 ratio of water and DMAEMA. The first is a chainlike structure in which DMAEMA and water molecules are ordered alternately connected to each other by H-bonds. Carbonyl and amino groups are supposed to alternate randomly in the chain. Although this structure contains water and DMAEMA in 1:1 a ratio, it does not explains the unexpected stability of 1:1 clusters on the expense of DMAEMA molecules hydrated separately. In the latter case the energy gain should be the same, but the water:DMAEMA ratio should be 2:1, indicating a second distinguished concentration. Moreover, the formation of chains should significantly change the free volume structure of the mixtures but the small change of the o-Ps lifetime does not indicate such a large scale structural change (Figure 2). Another reason against chainlike clusters is provided by the polymer sample. The 1:1 water:DMAEMA ratio is also distinguished in this case, although the random orientation of DMAEMA monomers prevents the formation of H-bonded chains.

The second possible explanation for the exceptional role of the 1:1 concentration is the formation of an H-bonded ring of DMAEMA and water (Figure 3). The total energy of the ringlike cluster is significantly lower than that of other studied structures (Table 1). The calculated energy gain (several kilojoules per mole) might be enough to stabilize the N- -HOH- -O structure at the expense of other clusters. It should be noted that the formed clusters do not necessarily live forever but their lifetime is long enough to affect positronium formation intensity.

In accordance with the results of the ab initio calculations, an approximate mechanism can be suggested for the hydration of the DMAEMA monomer. When water is added to the liquid monomer, each DMAEMA molecule forms hydrogen bond by its amino and carbonyl

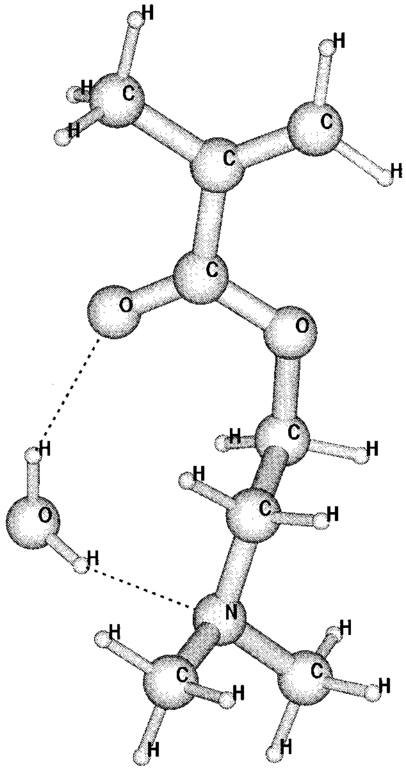

Figure 3. Structure of the DMAEMA:water hydrogen-bonded cluster. The figure represents the optimized geometry calculated by DFT(B3LYP)/6-31G** (see also Table 1).

groups producing a complex with nine atoms arranged in a ring (Figure 3). This H-bonded ring is more-or-less stable, and 1:1 water/DMAEMA clusters are formed in the liquid. Positron lifetime data suggest that the addition of further water molecules does not modify the structure of these 1:1 clusters; i.e., the o-Ps formation intensity remains at its lowest value even for a large water excess.

Since the o-Ps formation intensity data of the PDMAEMA-*l*-PIB APN are very similar to those of the water/DMAEMA mixtures, we can assume that the hydration of the APN occurs in a similar way; i.e., the formation of ringlike 1:1 clusters is also the first process in the network. This assumption is confirmed by the fact that the intensity decrease continues in the network till the water/DMAEMA mole ratio reaches the unit value (in about 8−10 min). The fact that the intensity decrease stops at this mole ratio suggests that water molecules are able to reach every DMAEMA unit very quickly at the beginning of the swelling process. If the free volume were composed of independent pores, the intensity decrease would be a slow process and would not stop at 1:1 a water:DMAEMA ratio. On the other hand, the observed changes indicate that the surface of the free volume units become covered with water molecules quickly at the beginning of swelling. This suggests that the free volume in the PDMAEMA-*l*-PIB APN is composed of interconnected channels which allow rapid diffusion of water molecule to cover the surface of the free volume units in the network.

Beside the H-bond formation of DMAEMA units the other process associated with the swelling of the network is the shrinkage of PIB segments. This shrinkage might rearrange the free volume structure. The rearrangement is indicated by the lifetime increase at low swelling ratios (Figure 1b). It should be emphasized at this point that the shrinkage of PIB segments is a fast process and it is coincident with the H-bond formation of DMAEMA units (compare parts b and c of Figure 1).

The hydration mechanism discussed in the previous paragraphs has a consequence on the possible ways of o-Ps formation. At the beginning of the swelling, the electron structure of a DMAEMA unit is changed: the lone electron pair of the amino group and those of the doubly bonded oxygen of the ester group form hydrogen bonds with a water molecule. Due to the localization of these lone electron pairs in the H-bond, the o-Ps formation is decreased by 25%. Consequently, these electron pairs play a significant role in the o-Ps formation process.

Conclusion

It has been shown that positron lifetime spectroscopy is a suitable new technique for obtaining information on the changes in free volume and the swelling dynamics of APNs. In the course of swelling of PDMAEMA-*l*-PIB APN with water, the size of free volume units increases, reaches a maximum, and then decreases. The most plausible explanation for the increase of the free volume size at the beginning of the swelling process in water is the collapse of the hydrophobic PIB phase and the expansion of the hydrophilic PDMAEMA phase in the network. Then further swelling leads to filling of the free volume by water resulting in a lifetime decrease and intensity increase. The changes of the lifetime parameters are continuous until they reach their saturation values at equilibrium swelling.

At low swelling ratios a sharp decrease of o-Ps formation intensity indicates that the free volume of the PDMAEMA-*l*-PIB amphiphilic network is composed of channels rather than independent pores. The surface of the channels is covered by water molecules relatively fast at the beginning of the swelling process resulting in a quick surface structure reorganization, i.e., enrichment of the surface of the channels by PDMAEMA segments leading to the corresponding rapid decrease of o-Ps formation intensity and to the simultaneous collapse of PIB domains, yielding an increase in the free volume in the network and the positron lifetime at the beginning of swelling.

The observed positronium formation intensities suggested that 1:1 water/DMAEMA complexes are formed in both the APN and the DMAEMA/water mixtures. The performed ab initio calculations showed that water molecules are able to form almost identical H-bonds with either the amino or the ester groups of DMAEMA molecules. The lowest energy cluster has a ringlike structure, which explains why the 1:1 mole ratio was found to be exceptional.

Results of this study also indicate that positron annihilation can be successfully applied for obtaining information not only on free volume changes in polymeric materials but also on the dynamics of swelling and the structure of free volume in certain macromolecular systems, such as networks, hydrogels, polyelectrolyte gels, polymer composites, blends, etc., by studying the swelling kinetics and positron lifetime parameters simultaneously. It is also predicted by us that the results of this study can be extended for the investigation of a wide variety of gels and amorphous materials as well.

Experimental Section

Materials. Solvents, such as hexane and tetrahydrofuran (THF), methacryloyl chloride, and 2-(dimethylaminoethyl) methacrylate (DMAEMA) were purified by conventional distillation procedures. Isobutylene (99.95%; Izobutilen Ltd., Hungary) was passed through a drying column (Labclear gas filter; Aldrich) before condensation under dry nitrogen atmosphere. *N*,*N*-Dimethylacetamide (DMA), allyltrimethylsilane (ATMS), 9-borabicyclo[3.3.1]nonane (9-BBN) in THF, and $TiCl_4$ (all from Aldrich) were used as received. The initiator, 1,3-di(2-chloro-2-propyl)-5-*tert*-butylbenzene (**1**), for living isobutylene polymerization was prepared as described[49] earlier. 2,2′-Azoisobutyronitrile (AIBN) (Aldrich) was crystallized from methanol before use.

Preparation of Methacrylate−Telechelic Polyisobutylene (MA−PIB−MA). Allyl−telechelic polyisobutylene (PIB) was obtained by quasiliving carbocationic polymerization of isobutylene by the **1**/$TiCl_4$ initiating system in the presence of DMA using a simple laboratory process[50] followed by end-quenching with ATMS.[51,52] The allyl termini were converted to primary hydroxyl groups by hydroboration with 9-BBN followed by oxidation with H_2O_2 in the presence of KOH according to a procedure described in the literature.[51−53] The hydroxyl-ended PIB was reacted with methacryloyl chloride to obtain MA−PIB−MA as described.[54] The resulting methacrylate−telechelic PIB was characterized by GPC (M_n = 11 200, M_w/M_n = 1.12) and by ^{1}H NMR for end group functionality (F_n = 2.0).

Synthesis of the Poly[2-(dimethylamino)ethyl methacrylate]-*l*-polyisobutylene (PDMAEMA-*l*-PIB) Amphiphilic Network. MA−PIB−MA was copolymerized with DMAEMA in THF containing 10% of each component with AIBN initiator under nitrogen in a closed Teflon mold at 60 °C for 72 h as described earlier.[11−14] After the reaction was cooled to room temperature, THF was evaporated from the cross-linked gel and the sample was extracted with ethanol for 24 h by Soxhlet extraction resulting in 3.2% soluble material. Then the network was dried in vacuo overnight and subsequently subjected to Soxhlet extraction by hexane for 24 h, giving 2.7% extractables. The resulting network was dried to constant weight in vacuo at 50 °C. The dried PDMAEMA-*l*-PIB film had a thickness of about 1 mm. Composition was determined by elemental analysis giving 52% PDMAEMA and 48% PIB.

Positron Lifetime Measurements. A 3.7×10^5 Bq activity ^{22}Na source was used to produce positrons. Together with the positron, a 1.28 MeV γ-ray is also emitted by ^{22}Na nuclides, marking the “birth” of the positron. Similarly, the 0.51 MeV γ-rays from annihilation mark the “death” of a positron. A coincidence system furnished with a signal delay makes it possible to measure the time elapsed between the start and the stop signals,[56] i.e., the lifetime of the positron. It has to be noted that, in principle, every positron is observed individually and the spectra are constructed from these individual events.

For lifetime measurements a fast−fast coincidence system[39,56] was applied which performs the separation of the different energy gamma rays and their timing in a single step. The output signals of the time-to-amplitude converter (i.e. the spectrum) were collected in the memory of a computer based multichannel analyzer card till 5×10^6 events were observed. The overall time resolution of the system was 210 ps.

The spectra were evaluated by the RESOLUTION computer program.[57] We have found three lifetime components in every case but interpreted only the longest one. This component is characteristic of o-Ps in polymers,[58] and this is the most sensitive to the changes of the size and distribution of free volumes. The other two lifetimes were around 160 ps and 380−400 ps and their intensities were 30% and 50−55%, respectively.

Swelling. For swelling experiments dry samples were placed in deionized water at 20 °C and the swelling was followed gravimetrically as described.[11−14] When the desired soaking time was reached, the swelling process was interrupted by removing the samples from the water container. The surfaces of the samples were dried mildly by a cotton swab, and they were packed into an airtight sample holder together with the positron source. The spectrum collection time was 3 h, and after this time, swelling was continued for another predetermined time interval.

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