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Change in free volume during volume phase transition of poly(*N*-isopropylacrylamide) gel as studied by positron annihilation lifetimes: temperature dependence

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Abstract

Macroscopic volume shrinkage and swelling of a poly(*N*-isopropylacrylamide), PNIPA, gel on heating was studied and the microscopic structural change during volume phase transition in water was correlated to variations of size, concentration and size distribution of free volume of the PNIPA gel estimated by positron annihilation lifetime measurement. An average free volume size of 0.28 nm radius of the swollen PNIPA gel coincided with that obtained in pure water below a transition temperature (33°C), whereas, in the collapsed state, two kinds of annihilation lifetimes of *ortho*-positronium were observed. This result implies that a nanoscopic phase separation occurs maybe because of the newly appeared free volumes of respective sizes, 0.18 nm and 0.33 nm in radius, by decreasing the motility of water molecules, accompanied with an aggregation of the polymer network and a significant expansion of the polymer network mesh size, although the macroscopic volume dramatically decreased. Nanoscopic inhomogeneity was discussed in terms of free volume size distribution. These results suggested that an inhomogeneity of the collapsed gel clearly differs from that of the swollen gel. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(*N*-isopropylacrylamide) gel; Volume phase transition; Free volume

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1. Introduction

Volume phase transition (VPT) of polymer gels, such as a poly(*N*-isopropylacrylamide) (PNIPA) gel, a polyacrylamide (PAAm) gel and their derivatives induced by temperature [1], solvent composition [2] and other physical and chemical parameters [3] has been attracting much attention for its scientific and technological importance. As the molecular mechanistic origin of the phenomenon is not yet clear, it has become more important for practical applications, recently. The VPT were studied hitherto mainly from the view point of macroscopic properties, both empirically and theoretically, employing statistical thermodynamic theory for polymer solutions developed by Flory and Huggins [4,5], and it was interpreted as a result of the change in the balance between the attractive and repulsive interactions among polymer segments and solvent molecules [6]. These phenomena of hydrogels were assigned to primitive interactions in biological parameters, i.e. four types of intermolecular forces — van der Waals, hydrophobic, hydrogen bond, and repulsive or attractive ionic forces [7]. PNIPA gel exhibits the VPT at a specified temperature depending either on the content of acrylate ion [1] or on the content of residues promoting or inhibiting hydrogen bonding between the polymer networks and solvent molecules [8]. Recently, numerous investigations on microscopic properties of the polymer gel have been performed by means of dynamic and/or statistic microprobes, such as small angle neutron scattering [9], nuclear magnetic resonance (NMR) spectrometry [10–13], and fluorescent technique [14–16]. These studies have enhanced drawing a novel image of a local structure at the molecular level, suggesting that free volume property plays a significant role in the change of various physical properties. We studied the VPT from the microscopic view point utilizing the free volume properties obtained by positron annihilation lifetime technique [17]. Systematic discussion with the previous researches in the microscopic range may lead us to clearer microscopic images of the polymer gels during the VPT.

The positron annihilation lifetime technique is a powerful

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Table 1
Definition of three kinds of water inside hydrogels

Name	Definition	Relevant terminology appeared in the literature
Bound water	Bound to gel-networks	Non freezable water
Associated water	Associated to bound water	Trapped or glass-state water
Free water	Bulk water	Pure water, freezable water

method to estimate the free volume parameters in an amorphous region of polymers and solutions [17–26]. A *ortho*-positronium (*o*-Ps: the triplet bound-state of positronium of a positron and an electron) probe has a relatively small diameter (0.106 nm) and a repulsive nature compared with the atoms and molecules in a substance, thus one can obtain information on defect, atomic vacancy, void, nanocage, and free volume, much sensitively and exactly than that from other methods. The free volume parameters obtained by this technique have been utilized to explore a change of physico-chemical properties such as glass transition, thermal expansion, and local structure-relaxation at lower temperature in polymers. Further, a free volume distribution, which associates with a nanoscopic inhomogeneity, was utilized in the discussion of its theoretical validities [24]. Recent improvement in the stability and time resolution of this technique facilitated its use in the study of microscopic free volume in both organic and inorganic polymers, such as amorphous silica [18], polysiloxane [19], polyethylene [20], polypropylene [21,22], polystyrene [23–24], ionomer [25], and polymethylmethacrylate [26] as a function of temperature, degree of crosslinkage and molecular structures.

In the present article, a non-ionized PNIPA gel was studied by the positron annihilation lifetime measurement. Temperature dependence of the average size, numerical concentration and size distribution of the free volume in the PNIPA gel were investigated in water. The change of sub-nano-environment inside the PNIPA gels, and the origin and location of the free volumes were discussed on the VPT induced by the change of an interaction between water molecules and the polymer chains of the PNIPA in terms of the hydrophobic interaction. It is expected that the states of water molecules inside hydrogels are different from those of bulk water, as many previous studies suggested [13, 27, 28]. We, therefore, paid attention to the state of water by assuming the degree of an interaction to polymer chains or neighboring water molecules as was previously predicted elsewhere [28]. To clarify the discussion, we define three kinds of water in the present article, and tabulate them in Table 1. The relationship between the free volume parameters — the size, numerical concentration and size distribution — and the macroscopic volume change were deduced in terms of the interactions between the gel-network and the solvent molecules and microscopic structural changes inside the PNIPA gels around a transition temperature (33°C). Discussions about the observed data were also connected with previous results from positron annihilation [29], NMR measurement [12] and diffusivity measurement [30,31].

2. Experimental

2.1. Gel preparation

All reagents and solvents were obtained from commercial suppliers (Tokyo-Kasei, Co. Ltd) and were purified before use in a conventional manner. *N*-isopropylacrylamide (NIPA) was purified by precipitation in hexane from benzene solution. The PNIPA gels were prepared by free radical copolymerization of NIPA (7.9 g, 70 mmol) and *N*,N′-methylenebisacrylamide (BIS, 0.13 g, 0.86 mmol) using 0.04 ml of tetramethylethylenediamine (TEMED, 0.27 mmol) as an accelerator and 20 mg of ammonium persulfate (0.088 mmol) as an initiator. All reagents, with the exception of TEMED and ammonium persulfate, were dissolved in DMF/water (2/3 volume ratio). The solution was flushed with nitrogen for 30 min. TEMED and ammonium persulfate were added, and the solution was made up to 100 ml with the DMF/water. After stirring for 15 min, the solution was flushed again with nitrogen. The pre-gel solution was kept standing for several days at room temperature to complete polymerization. The polymerized PNIPA gels contained 1.2 mol% of BIS crosslinking reagents.

2.2. Instruments

The decay curves of positron annihilation were observed with a conventional fast–fast coincident system with a time resolution of 290–300 ps FWHM (full-width at half-maximum). The positron source was 7.5 × 10^5Bq ^{22}NaCl contained in Kapton foils with a thickness of 7.5 μm. Correction of data, i.e. the subtraction of the error caused by positron annihilation in the sealing films of ^{22}NaCl was carried out at the computer fitting step. Samples (5 × 10 mm^2, and 2 mm thickness) in a cell were separated from ^{22}Na source by sealing it with a Ni foil (thickness of 10 μm) in order to avoid contamination of sample gels by ^{22}Na. Decay curves with total counts of more than 1×10^6 were fitted by non-linear least-square method and resolved into three or four components by using PATFIT-88 [32] computer program with a good statistical precision. Inverse Laplace transformation of positron annihilation decay curve accumulating 8–9 million counts were deconvoluted using

Table 2
Positron annihilation lifetime parameters analyzed by non-linear least-square method for PNIPA gels

T/°C	τ_1/ns	Error	τ_2/ns	Error	τ_{3a}/ns	Error	τ_{3b}/ns	Error
20	0.183	± 0.005	0.522	± 0.019			1.89	± 0.02
30	0.181	± 0.005	0.532	± 0.020			1.90	± 0.02
40	0.122	± 0.020	0.370	± 0.027	1.13	± 0.23	2.61	± 0.25
50	0.181	± 0.014	0.429	± 0.052	1.17	± 0.25	2.67	± 0.25

T/°C	I_1/%	Error	I_2/%	Error	I_{3a}/%	Error	I_{3b}/%	Error
20	44.1	± 2.2	36.2	± 1.9			19.7	± 0.4
30	45.2	± 2.2	35.7	± 2.0			19.1	± 0.4
40	31.8	± 2.8	43.0	± 1.2	15.1	± 1.6	10.2	± 2.8
50	38.7	± 5.7	36.6	± 2.4	13.8	± 0.7	11.0	± 2.8

CONTIN program to procure a probability density function (PDF) of annihilation rate, $\alpha(\lambda)$ [33–39]. This process of obtaining the lifetime distribution of *o*-Ps in polymers have been discussed by Jean's group [40–45].

2.3. Data analysis

The results obtained from PATFIT analysis of the decay curves, assuming three or four components, were shown in Table 2. Variance of fit (V.O.F. = χ^2/N, where N is the number of fitted channels), as fitting parameter, was less than ∽ 1.1 and assured the reliability of the data. In the process of PATFIT analysis, all parameters of lifetimes were unfixed. The shortest lifetime (τ_1: ∽ 180 ps) and its intensity (I_1: 32%–45%) are because of self-annihilation of *para*-Ps (*p*-Ps) and free annihilation of positrons with an electron belonging to atoms in the bulk of the sample. The high yield of the first component is because of thin Ni foils between gel samples and the source. The poor separation of short-term components, $\tau_1$and τ_2, is because of the time resolution of the lifetime apparatus. We assumed that a contribution of Ni foil to I_1 was 36 ± 2% by a separate experiment. The second shortest component (τ_2: 370–530 ps, I_2: 36%–43%) is assumed to be associated either with the annihilation of positrons at free volumes in amorphous phases or with the interface between amorphous and crystalline regions. The third component (τ_{3a}: ∽ 1.1 ns, I_{3a}: 14%–15% above 33°C) has not yet been clearly attributed, leaving a possibility as a result of the annihilation of excited Ps and the pick-off annihilation of *o*-Ps in small free volumes. The longest component, τ_{3b}, and its intensity, I_{3b}, is attributed to a pick-off reaction of *o*-Ps in free volumes present in the amorphous region.

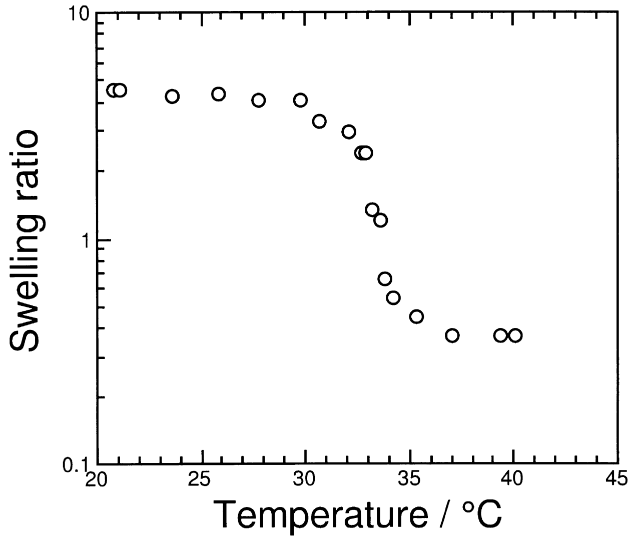

Fig. 1. Macroscopic swelling curve of PNIPA gel in water as a function of temperature [15].

2.4. Quantitative estimation of free volume size from o-Ps lifetime

By using a simple model, assuming an infinite spherical potential well based on quantum mechanics, a relationship between annihilation lifetime of *o*-Ps, τ, and cavity radius, R, was proposed as follows [46, 47]:

$$\tau = 0.5\left[1 - \frac{R}{R + 0.166} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R + 0.166}\right)\right]^{-1}, \quad (1)$$

where τ and R are expressed in ns and nm, respectively. A formation of a 'Ps-bubble' could be predicted in the system of a solution, like a liquid or fluid, because a difference of kinetic energies of the zero-point motion of *o*-Ps obtained by expanding the size of a sub-nano order hole is substantially larger than the thermal energy size of atoms or molecules [48]. Thus an observed size estimated from an annihilation lifetime of *o*-Ps in a solution is bigger than the free volume size obtained from the speed of sound [49]. However, a strong correlation between the observed free volume sizes from the two methods in common liquids was confirmed, both theoretically and experimentally [49], indicating that the free volume size and the size of 'Ps-bubble' may be controlled by the same physico-chemical properties such as surface tension (which is microscopically reflected by the cohesive energy size) and viscosity. In addition to this, an excellent correlation is found between 'Bondi' free volumes in various liquids and polymers and

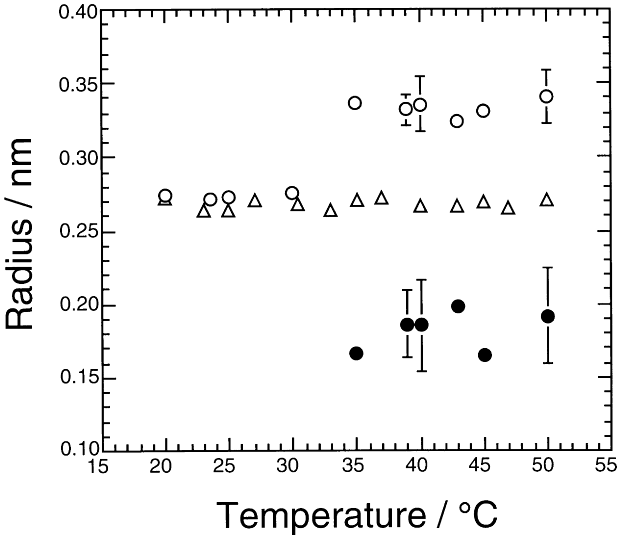

Fig. 2. Changes in an average radius of the free volume in the PNIPA gels and pure water as a function of temperature (●: 3a component of the PNIPA gel, R_{3a}, ○: 3b component of the PNIPA gel, R_{3b}, △: pure water). Data were obtained by using non-linear least-square method.

the cavity volumes obtained from Eq. (1) [50]. We concluded that an obtained cavity size by the positron annihilation could reflect a free volume hole size in the gels.

3. Results and discussions

3.1. Dependence of bulk VPT of PNIPA gel on temperature.

A swelling ratio V/V_0, where V and V_0 are the volumes of PNIPA gels after swelling and the time of preparation, respectively, was determined by measuring a sample diameter, D, after reaching swelling equilibrium, thus the swelling ratio is expressed by $V/V_0 = (D/D_0)^3$, where D_0 is the sample diameter at the time of preparation. Fig. 1 shows the bulk VPT of the PNIPA gel in pure water as a function of temperature [14]. The PNIPA gel without acrylate anion showed VPT at ∽ 33°C, and was in a swollen state below 33°C, and in a collapsed state above 33°C.

3.2. Change in free volume size of PNIPA gel with temperature.

The changes in the average size of a free volume in the PNIPA gel and pure water with an increase of temperature are shown in Fig. 2. Temperature dependence of the free volume size calculated by using Eq. (1) showed a critical change at 33°C, which is coincident with that of the macroscopic VPT temperature. Below the VPT temperature, the free volume size is equal to that of pure water, or 0.28 × 2 nm in diameter, indicating that the interaction between water molecules and network atoms hydrated into the gel network is soft enough as not to affect the hydrogen bonding among water molecules taken into the gel-network.

In the collapsed state above 33°C, the third component, τ_3, is split into two components, one ($\tau_{3a} =$ 1.0–1.2 ns) attributable to the free volumes by the size of ∽ 0.18 × 2 nm in diameter and another ($\tau_{3b} =$ 2.6 ns) attributable to the free volumes by the size of 0.33 × 2 nm in diameter, suggesting that a nanoscopic phase separation occurred by an aggregation of the gel-network because of the VPT. Obtained lifetime of the 3a component seems to be much shorter than that of*o*-Ps as was observed in the amorphous phase. Two possibilities, one arising from the formation of 'Bloch-type Ps', and the other from the pick-off reaction of *o*-Ps in small free volumes (0.18 × 2 nm in diameter) can be speculated as its origin. *o*-Ps is inclined to move to bigger free volume holes or enlarge the Ps cavity volume to be stabilized energetically. If the voids or free volumes are arrayed periodically, a wave function of *o*-Ps spread in the periodic potential to form 'Bloch-type Ps', which is a delocalized Ps state analogous to a positron in Bloch state, and *o*-Ps can exist in a smaller free volume. The former prediction, therefore, suggests the generation of a periodic structure of water molecules arrayed along the polymer chain, which produces periodically arrayed free volumes from the water molecules with reduced size and favors the formation of 'Bloch-type Ps'. The average diameter of the free volumes estimated by Eq. (1), 0.18 × 2 nm, coincides well with that for ice at 0°C (0.13 × 2 nm) observed by Brandt, et al. [29]. The stronger interaction between the water molecules associated with the polymer chains aggregated by the hydrophobic interaction caused the shorter periodical array and produced a new assembly of water clusters similar to that of the ice structure. Thus, a formation of clusters of water molecules by shrinkage of the PNIPA gel produces the free volumes with a reduced size. The proposed model does not contradict previous concepts and the formation of the periodical arrayed free volume of the small size is plausible.

By contrast, the τ_{3b} component, because of free volume of 0.33 × 2 nm in diameter, is bigger than the τ_3 component in the swollen state whereas the macroscopic volume has dramatically decreased. This result suggests that the origins of these free volumes are different. It seems that the newly appeared free volumes could be attributed to the free volumes that existed in an aggregation of the hydrophobic polymer chains, because the smaller free volumes in the region, where the water molecules highly exist, was attributed to the 3a component. Moreover, a size of the 3b component is approximately in same range as that of many common polymers in the rubbery state [23]. This prediction is partially supported by a result concerning with a motility of *iso*-propyl groups of the PNIPA obtained from ^{13}C NMR measurement. The result indicated that the rotational mobility of *iso*-propyl groups increases in the collapsed state [11]. Further, the observation by the authors does not come into conflict with the speculation, which is deduced from the result of a larger diffusion coefficient of acetaminophen in the collapsed PNIPA gel than that predicted by the free volume theory of Yasuda et al. reported by Gehrke [30,31].

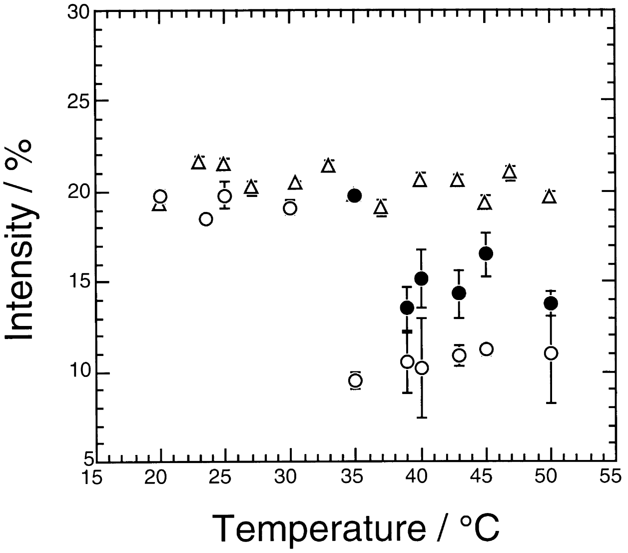

Fig. 3. Changes in numerical concentration of the free volume (I_3) in the PNIPA gels as a function of temperature (●: 3a component of the PNIPA gel, I_{3a}, ○: 3b component of the PNIPA gel, I_{3b}, △: pure water).

3.3. Change in numerical concentration of free volume in PNIPA gel with temperature

As described above, *o*-Ps tends to localize in a free space hole having a lower electron density because of the repulsive nature of diamagnetic atoms in the bulk. Thus a relative intensity of *o*-Ps, $I_{3,}$ could correspond to a numerical concentration of free volumes in the sample, if a chemical character of the sample inducing a chemical quench of Ps would not change. Temperature dependencies of the intensities, I_{3a} and I_{3b}, of the PNIPA gel and that of pure water are shown in Fig. 3. The results show that I_{3b} of the PNIPA gel below the VPT temperature were coincident with that of pure water as the annihilation lifetimes were. The fact that I_{3b} is smaller than I_{3a} in the collapsed state suggests that the free volumes formed in water clusters around the gel-network are much more numerous than those in the network of the PNIPA gel. I_{3a} gradually decreased at temperatures above 33°C, implying a decrease of water clusters having a periodical structure, while I_{3b} slightly increased. The authors previously reported a relationship for the dependence between intensity of *o*-Ps and the enthalpy of the hydrogen bond between water molecule and hydroxyl group of a polymer chain of the polyvinylalcohol (PVA) in the system of PVA gel [51], resulting that the intensity of *o*-Ps (I_3) considerably correlated to an amount of the hydrogen bond. Variation of a ratio of I_{3a} to I_{3b} may reflect a significant change of such interactions in the PNIPA gel as water molecule-polymer chain, polymer chain-polymer chain and water molecules-water molecules. However, an accurate attribution of the result may be subject to further investigation in this line.

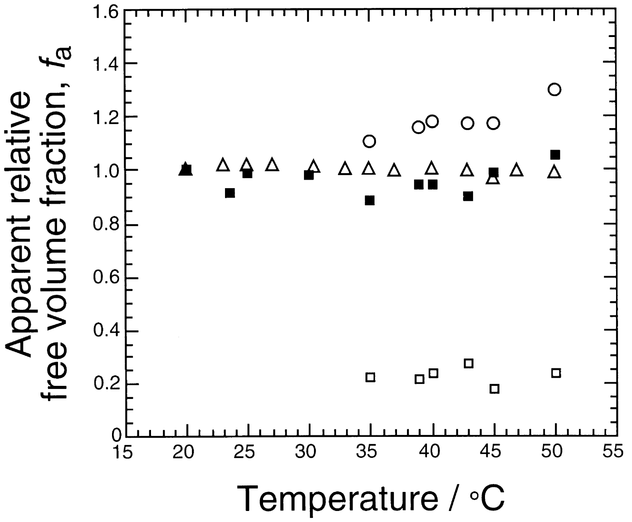

Fig. 4. Apparent relative free volume fraction, f_a, in the PNIPA gels and pure water as a function of temperature (○: entire $f_a = f_a^{3a} + f_a^{3b}$,□: 3a component, f_a^{3a},■: 3b component,f_a^{3b}, for the PNIPA gel, respectively and △: for the pure water).

3.4. Change in apparent free volume fraction in PNIPA gel by temperature

Free volume fraction (f) of polymers was proposed to be for many kinds of polymers,

$$f = 0.025 + \alpha(T - T_g) - \beta P, \tag{2}$$

where α is the thermal expansion coefficient in the rubbery state and β the compressibility of free volume [52–54]. In a previous article [55], the results obtained by the positron annihilation lifetime technique suggested that a value of I_3 could be proportional to the fractional number (C_f) of free volumes in organic polymer systems. The relationship between C_f and intensities of *o*-Ps (I_3) was discussed by Jean, et al. [55] for epoxy polymer systems. In the literature, f was defined by,

$$f \equiv V_f C_f = V_f(A \times I_3 + B), \tag{3}$$

where V_f was the size of free volume estimated from annihilation lifetime of *o*-Ps applying Eq.(1). A and B are constants, but cannot be obtained for specified polymer gels quantitatively from independent physical characteristics. Therefore, we calculated an apparent relative free volume fraction (f_a),$V_f(T)I_3(T)/V_f(20)I_3(20)$, by assuming A and B as 1 and 0, respectively. The result is shown in Fig. 4 as a function of temperature.

In the swollen gels, f_a coincided well with that of pure waters. Different observation by positron annihilation was previously reported by the authors in the PNIPA gel with the methanol-water system, i.e., the apparent free volume fraction of the PNIPA gel swollen with pure methanol was bigger than that of pure methanol [56]. This result shows that solvent molecules could have a different free volume property in polymer gels than in the pure solvent, because there exists a significant interaction between a polymer chain and a solvent molecule. Nonetheless, the agreement

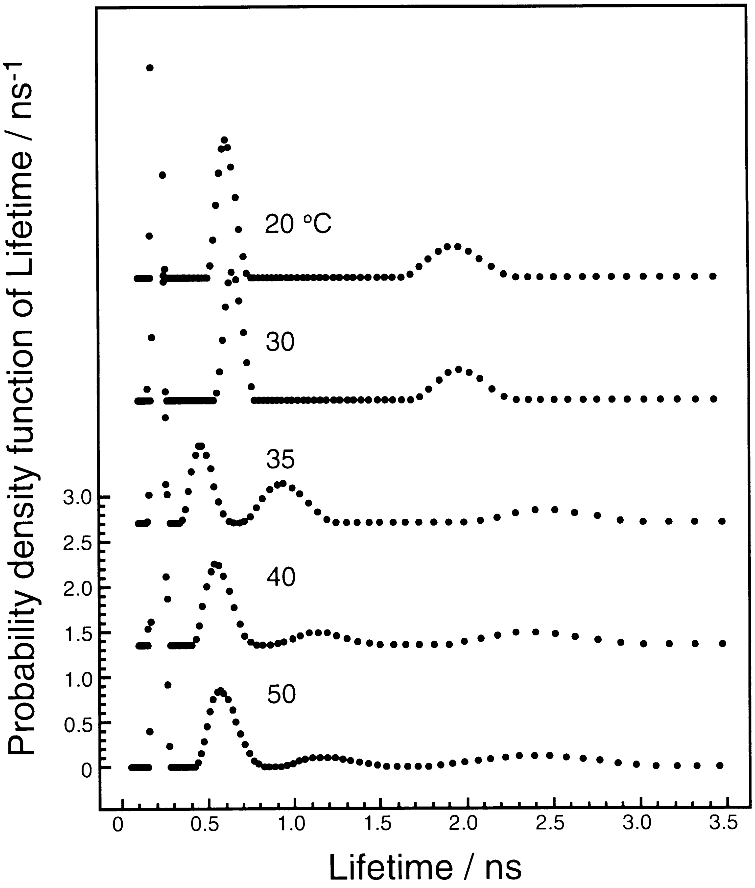

Fig. 5. Temperature dependencies of the lifetime distribution of positron and positronium for the PNIPA gels.

of f_a in this study suggests that an average state of interaction between the water molecules is not influenced by the existence of polymer chains, or the interaction between the water molecules and the polymer chains is almost same as that between water molecules, as an interaction between water molecules is adequately strong.

The entire relative fractional free volume, $f_a^{3a} + f_a^{3b}$, is bigger than the relative fractional free volume of pure water in the swollen PNIPA gel. A f_a^{3b}, which has a different origin from that of pure water, nearly agrees with a value of f_a in pure water. A value, $f_a^{3a} : f_a^{3b} \approx 1 : 4.3$, indicates that the entire free volume fraction in the collapsed PNIPA gel is roughly controlled by the τ_{3b} component. It could be expected that the molecular motion is suppressed by an aggregation of gel-network, and has some kind of periodical structure as the 3a component appeared newly, suggesting that f_a^{3a}, has a different nature from that of a free volume around flexible molecular chains or atomic groups.

Some of the most essential interaction which induces the VPT are production and destruction of the hydrogen bonding among polymer chains and solvents. A serious discrepancy was observed between the macroscopic volume and nanoscopic fractional free volume behavior on their temperature dependencies. It is expected that intermolecular interactions change significantly above and below the VPT temperature. It is also indicated that the liberation of associated water clusters from the network of the PNIPA gel occurs. This speculation agrees with the suggestion that the volume phase change results from the balance between the effective attractive and repulsive interactions between polymer segments and the water molecules. An estimated bonding energy between the PNIPA and the water molecule at 33°C would be less than the energy of the hydrogen bond (∽ 0.25 eV) and more than the vibration energy of atoms (∽ 0.026 eV).

3.5. Variation of size distribution of free volume size with temperature

Several results of typical inverse Laplace transform of positron annihilation decay curves for the swollen and collapsed PNIPA gels using the CONTIN computer program is shown in Fig. 5. The abscissa represents the positron/positronium lifetime and the ordinate expresses $\lambda^2\alpha(\lambda)$, PDF of the annihilation lifetime, to balance the intensities of τ_1, τ_2 and τ_3 components. In the collapsed state, a distribution of PDF of annihilation lifetimes was clearly separated into four components, as was a result of the non-linear least-square analysis. The average lifetime of each component agrees well with those of non-linear

Table 3
Positron annihilation lifetime parameters analyzed by inverse Laplace transformation method for the PNIPA gels

T/°C	τ_1/ns	Error	τ_2/ns	Error	τ_{3a}/ns	Error	τ_{3b}/ns	Error
20	0.207	± 0.001	0.612	± 0.004			1.94	± 0.02
30	0.209	± 0.001	0.649	—			1.97	± 0.02
40	0.205	± 0.001	0.563	± 0.21	1.14	—	2.39	± 0.07
50	0.207	± 0.001	0.609	± 0.015	1.58	± 0.07	2.40	± 0.08

least-square method within the range of error (Table 3). This result again shows that the existence of a small free space correlated with a lifetime of ∽ 1.0 ns of *o*-Ps in the collapsed PNIPA gel.

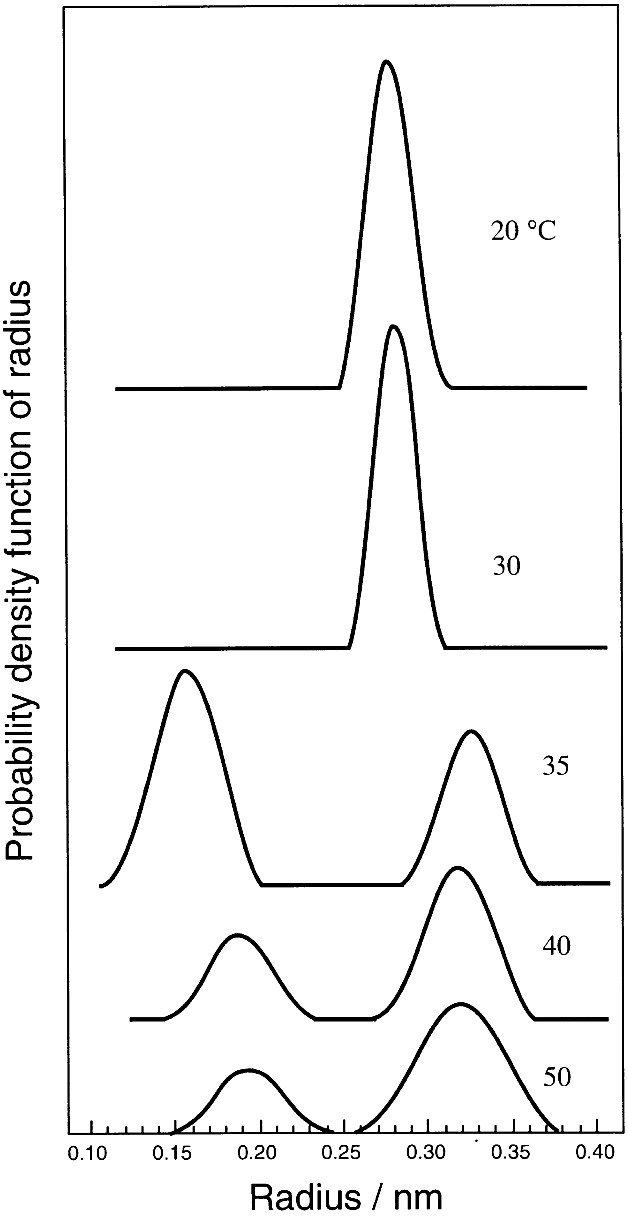

Fig. 6. Size distributions of free volume radius for the PNIPA gels as a function of temperature. Corresponding temperatures were indicated beside the curves.

A change in size distribution of free volume of the PNIPA gel against temperature is shown in Fig. 6. A PDF of the free volume radius, $R_{\mathrm{f\ pdf}}(R)$, was calculated by the following expression derived from Eq. (1):

$$R_{\mathrm{f\ pdf}}(R) = -\alpha(\lambda)\frac{\mathrm{d}\lambda}{\mathrm{d}R} \tag{4}$$

$$R_{\mathrm{f\ pdf}}(R) = -0.331\left[\cos\left(\frac{2\pi R}{R+0.166}\right)-1\right]\frac{\alpha(\lambda)}{(R+0.166)^2}. \tag{5}$$

A dispersion of the size distribution reflects a microscopic structural fluctuation in the gel. The free volume size increased and the distribution range of the free volume size did not change substantially with the increasing temperature except for the drastic change at the VPT temperature. The existence of two stable states of water, as a result of the association between water molecules and the molecular chains of the PNIPA gel, are believed to cause the VPT. The increase of the short lifetime component in the collapsed state with increasing temperature suggests that increase in the thermal motion of water molecules leads to their release from the gel-network resulting in the destruction of periodical structure in the cluster of water molecules. A comparison of the size distribution of the free volume in the PNIPA gel with that of pure water is shown in Fig. 7. Because the PNIPA gel contains more than 95% water molecules in the swollen state, it is not unexpected that the distribution of the swollen gel agrees with that of pure water. However, the size distribution of the free volume in the PNIPA gel changes drastically at the VPT temperature, implying that the nanoscopic inhomogeneity of the shrinking PNIPA gel clearly differs from that in the swollen PNIPA gel.

4. Conclusion

We reported experimental evidence of the change of the free volume parameters during the VPT of the PNIPA gel, which was carried out by means of positron annihilation lifetime technique. A critical change of free volume size was found at the VPT temperature, 33°C. Free volume is composed of water molecules inside the PNIPA gel below the VPT temperature. Two phases of the microscopic structure was observed by the annihilation lifetime of *o*-Ps in the collapsed state. The formation of ‘Bloch type Ps’ and/or the

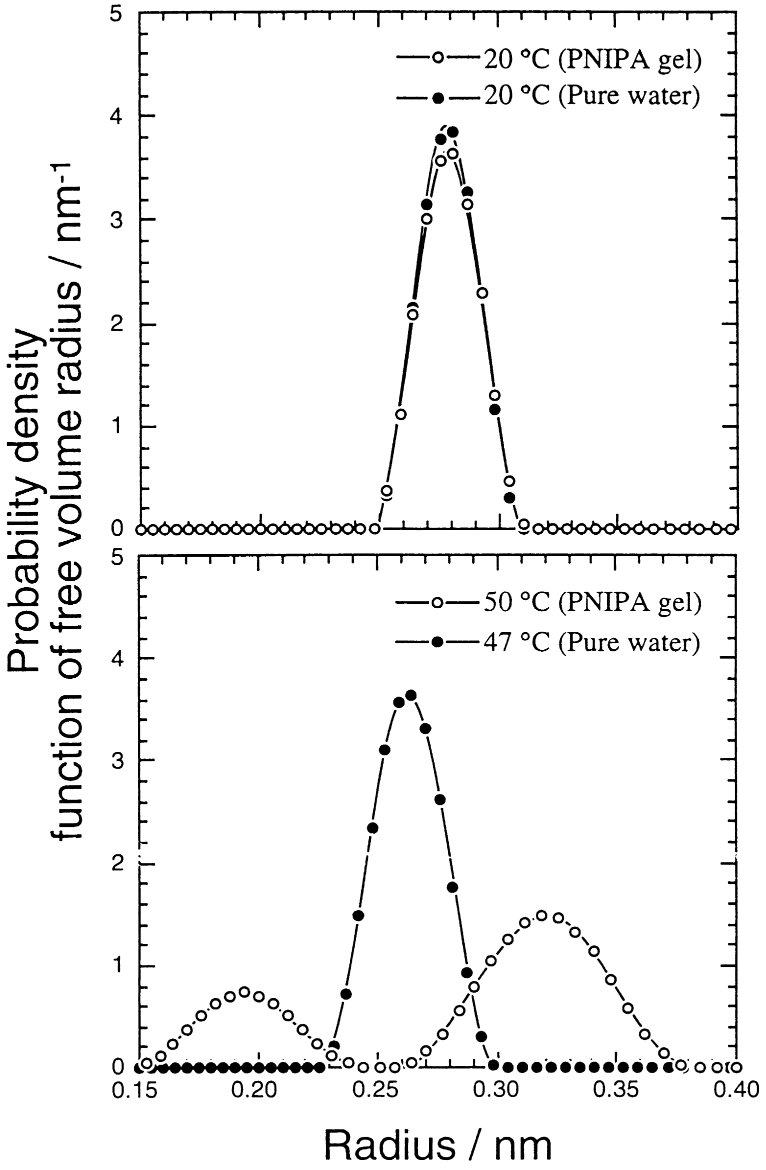

Fig. 7. Comparison of the lifetime distribution of the PNIPA gels with that of pure water below and above the VPT temperatures.

pick-off reaction of *o*-Ps in small free volumes was revealed above the VPT temperature, suggesting the presence of clusters of water molecules with a periodical structure in the shrunk phase of the PNIPA gel with a average diameter of the free volumes of 0.18 × 2 nm. The free volumes with average diameter of 0.33 × 2 nm are attributed to a nanoscopic aggregation of the polymer chains of the PNIPA. The results suggest that the change of the nanoscopic free volume during the VPT was as a result of the liberation of associated water clusters from the PNIPA network and the aggregation of the polymer chain. The data in this study may become a basis for the interpretations of the static structure and the interactions between solvents and solutes in polymer solution or in crosslinked polymer gels in the order of molecular dimensions.

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