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### Unique Free-Volume Change During the Phase Separation of Poly(*N*-isopropylacrylamide) Aqueous Solution Studied by Positron Annihilation Lifetime Spectroscopy

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## **Unique Free-Volume Change During the Phase Separation of Poly(*N*- isopropylacrylamide) Aqueous Solution Studied by Positron Annihilation Lifetime Spectroscopy**

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**Abstract:** The change in free-volume during phase separation of poly(*N*-isopropylacrylamide) (PNIPAM) aqueous solution was studied *in situ* by positron annihilation

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lifetime spectroscopy. The average size of a free-volume nanohole exhibited a co-nonsolvent change, affirming the trans-to-gauche conformational change of PNIPAM chains during phase separation. The results obtained for the *ortho*-positron (*o*-Ps) intensity accounted for the competitive effects of the variations in composition of the free C=O group and the free amino group on the *o*-Ps formation.

**Keywords:** Free volume, phase separation, PNIPAM, positron annihilation lifetime spectroscopy

## INTRODUCTION

Aqueous solutions of poly(*N*-isopropylacrylamide) (PNIPAM) exhibit a phase separation above ca. 32°C. The phenomenon has been explored extensively by use of various experimental techniques, for example, turbidity,<sup>[1]</sup> light scattering,<sup>[2]</sup> calorimetry,<sup>[3]</sup> fluorescence,<sup>[4]</sup> NMR,<sup>[5]</sup> IR spectroscopy,<sup>[6,7]</sup> and Raman spectroscopy.<sup>[8]</sup> NMR studies revealed that not only mobility of the main and side chains of the polymer but also mobility of the surrounding water molecules changed significantly during the phase transition.<sup>[5]</sup> Gauche-to-trans conformational change during the phase transition of PNIPAM was investigated by IR spectroscopy with attenuated total reflection (ATR) method and density functional theory (DFT) calculations.<sup>[6]</sup> 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 during the phase separation of PNIPAM aqueous solution.

The positron has been recently used as a nanoprobe *in situ* through positron annihilation lifetime spectroscopy (PALS) for determination of the distribution of free-volume size and characterization of microstructure in various materials like polymers, zeolites, metal alloys, and others. The great advantage of this technique is its enormous sensibility for the free-volume determination with dimensions up to some tens of angstroms. Due to its short lifetime ( $10^{-10}$  to  $10^{-9}$  s) and the low activity of the positron source, the PALS technique does not change the material properties. In this work, we used PALS to study the change in free-volume during the phase separation of PNIPAM aqueous solution. Unique nanohole volume change was observed compared with the macroscopic volume change of PNIPAM aqueous solution. The formation and/or break of hydrogen bonds (the variations in composition of the free C=O group and the free amino group) were also reflected by the observed changes of the *ortho*-positron intensity.

## MATERIALS AND METHODS

The unfractionated PNIPAM ( $M_\eta \sim 5 \times 10^6$ ) was obtained by redox polymerization in distilled water at 29°C initiated with potassium persulfate (KPS) and *N,N,N',N'*-tetramethylethylenediamine (TEMED) under nitrogen.<sup>[9]</sup>

The polymer was redissolved in distilled water with 7.36 wt% for further use. The lifetime spectra were obtained using an ORTEC (ORTEC Co., USA) fast-fast coincidence circuit, with 280 ps of time resolution, from the  $^{60}\text{Co}$  prompt curve. Carrier-free  $^{22}\text{NaCl}$ , with an activity of 40  $\mu\text{Ci}$ , was immersed in the solution as the positron source after being sandwiched between two 3- $\mu\text{m}$  nickel foils and sealed with 15- $\mu\text{m}$  polyethylene (PE) films. To avoid any distortion in the spectra due to non-Gaussian distribution of the counts in each channel, the integrated counts were kept at about  $10^6$ .<sup>[10,11]</sup> The temperature range (25.0–50.0°C) was investigated by using a thermostatically controlled copper vessel, with an accuracy of  $\pm 0.1^\circ\text{C}$ . After changing the temperature, the device was maintained for 30 min to make the sample solution equilibrate at that temperature. The same experiments were carried out for distilled water. The lifetime spectra were satisfactorily analyzed in three components using the PATFIT program (Riso National Laboratory, Roskilde, Denmark), leading to the intensities ( $I_i$ ) and lifetimes ( $\tau_i$ ) of the various positron states: subscripts 1, 2, and 3 refer to *para*-positronium (*p*-Ps), free positron, and *ortho*-positron (*o*-Ps), respectively. The *o*-Ps lifetimes ( $\tau_3$ ) and intensities ( $I_3$ ) were determined with all  $\tau_i$  free. Variance of fit (V.O.F. =  $\chi^2/N$ , where  $N$  is the number of fitted channels), as fitting parameter, was less than  $\sim 1.1$  to ensure the reliability of the data. The turbidity was monitored as a function of temperature at a fixed wavelength of 586 nm on a 756PC UV-vis spectrophotometer (Shanghai Spectrum Instruments Inc., China), equipped with a circulating water bath. The phase separation temperature ( $T_p$ ) was defined as the onset temperature of the turbidity-versus-temperature curve. The sol-gel transition was determined by a test-tube-inclining method. The 4-mL vial (diameter 1.1 cm) containing 2 mL of polymer solutions was immersed in a water bath at a designated temperature for 15 min. The transition temperature was determined by flow (sol)–no flow (gel) criterion when the vial was inclined using a temperature increment of  $0.5^\circ\text{C}$  per step.

## RESULTS AND DISCUSSION

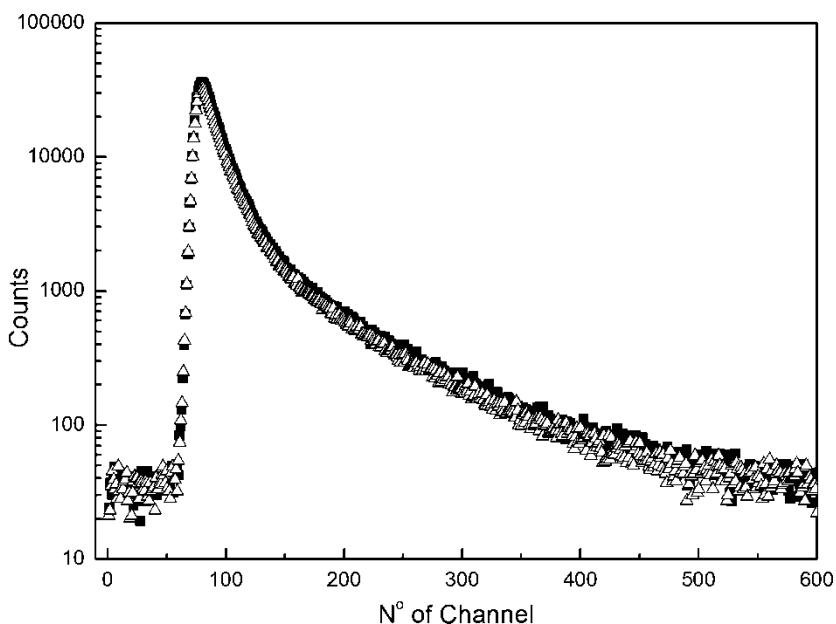
The free-volume cell model for the positron annihilation was proposed by Brandt et al.<sup>[12]</sup> to explain the observed *o*-Ps lifetimes in molecular solids and polymers, which gives a simple correlation curve, derived by Tao<sup>[13]</sup> and Eldrup et al.,<sup>[14]</sup> using a rigid spherical potential of radius  $R$  with an electron layer of thickness  $\Delta R$ . By the application of this model, assuming an infinite spherical potential well based on quantum mechanics, a relationship between  $\tau_3$  and cavity radius,  $R$ , was proposed as follows:

$$\tau_3 = 0.5 \left[ 1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R + \Delta R}\right) \right]^{-1} \quad (1)$$

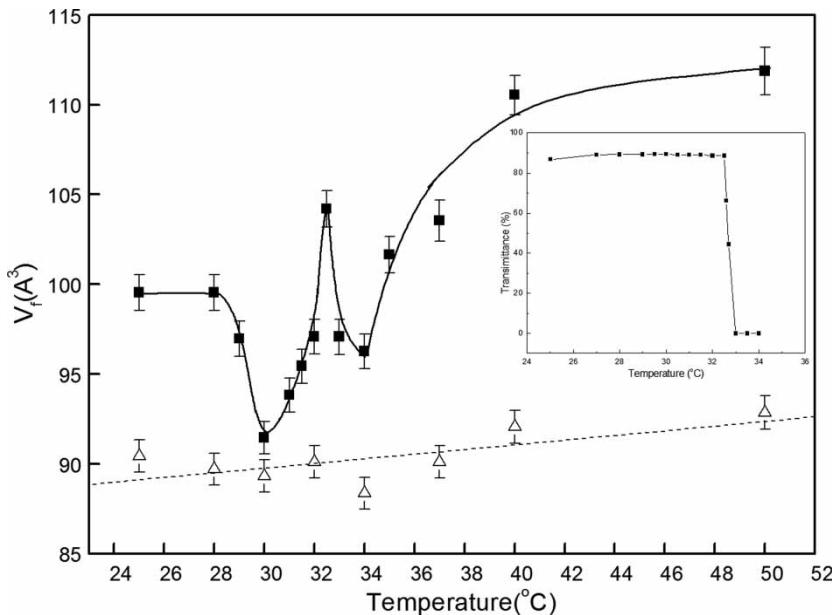
Here,  $\Delta R$  is the width of the electron layer where the *o*-Ps annihilates by pick-off, which is fitted to be 0.166 nm;  $\tau_3$  and  $R$  are expressed in nanoseconds and nanometers, respectively.

In the system of a solution, an observed size estimated from an annihilation lifetime of *o*-Ps is bigger than the free-volume size obtained from the speed of sound, due to the formation of "Ps-bubble."<sup>[15]</sup> However, a strong correlation between the observed free-volume sizes from the two methods was confirmed in common liquids, both theoretically and experimentally,<sup>[16]</sup> indicating that the free-volume size and the size of Ps-bubble may be controlled by the same physicochemical properties such as surface tension and viscosity. Furthermore, an excellent correlation is found between "Bondi" free-volumes in various liquids and polymers and the cavity volumes obtained from Eq. (1).<sup>[17]</sup> Thus, it could be concluded that cavity size obtained from the positron annihilation lifetime could reflect a free-volume hole size in the solution.

The positron lifetime spectra for the PNIPAM aqueous solution and distilled water at 32.5°C are shown in Fig. 1. The changes in the average size of a free-volume ( $V_f$ ) in the PNIPAM aqueous solution and distilled water as a function of temperature are shown in Fig. 2.  $V_f$  in distilled water gradually increases with increasing temperature due to some source correction effects for 15-μm PE films used. Co-nonsolvency is observed in the case of PNIPAM aqueous solution:  $V_f$  first decreases from 28.0°C toward the minimum at 30.0°C followed by an increase toward the maximum at 32.5°C and then decreases again followed by an increase from 34.0°C.

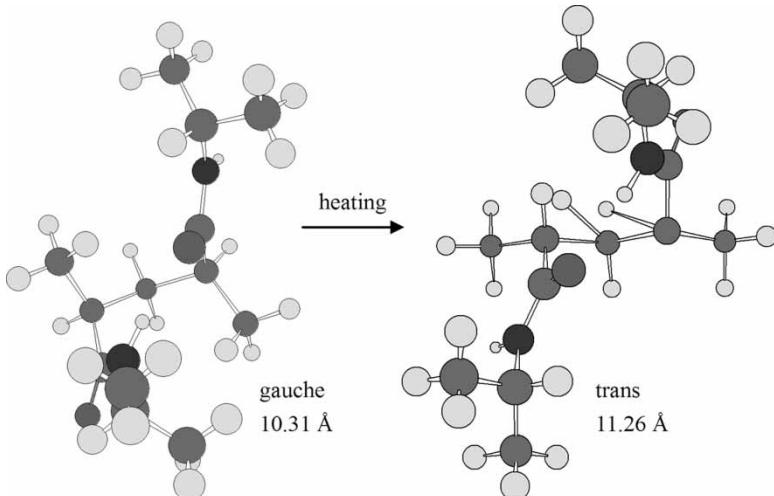


**Figure 1.** Positron annihilation lifetime spectra for the PNIPAM aqueous solution (square) and distilled water (triangle) at 32.5°C.



**Figure 2.** Variations of free-volume size for the PNIPAM aqueous solution (square) and distilled water (triangle) as a function of temperature. The inset is the turbidity results for the PNIPAM aqueous solution.

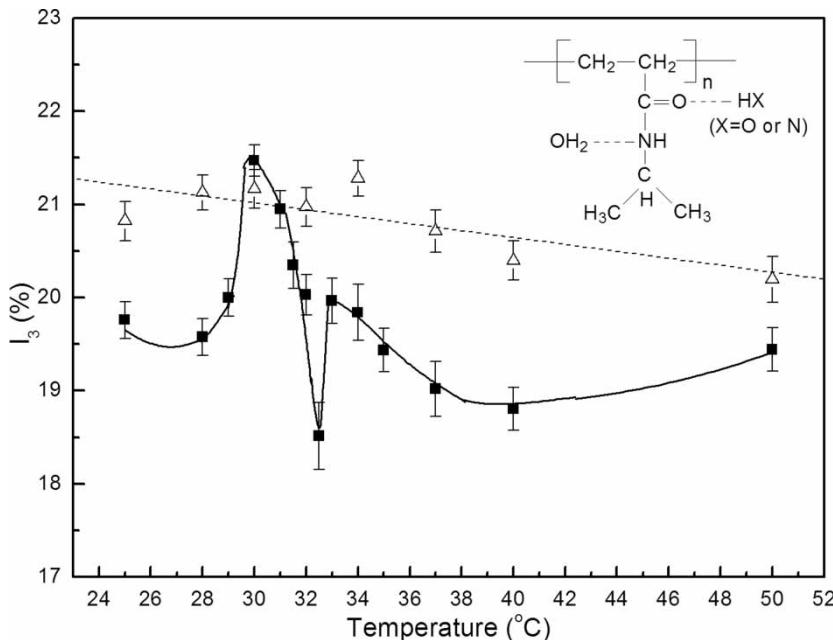
Compared with the results in distilled water, the data in PNIPAM aqueous solution are confirmed to be related to the free-volume changes caused by PNIPAM. The phase transition of aqueous solutions of PNIPAM has been explained by a theory of coil–globule transition, which insists that dehydration of the polymer chain above the lower critical solution temperature (LCST) induces the segmental interactions of the polymer to be attractive and to collapse the coiled polymer chain into a global conformation. The gyration radius of PNIPAM becomes small gradually below the LCST and then shows an abrupt change in the vicinity of the transition temperature, which could cause the decrease of  $V_f$ .<sup>[2]</sup> Recently, Katsumoto et al. investigated the conformational change in the coil–globule transition of PNIPAM with ATR/IR spectroscopy and DFT calculations.<sup>[6]</sup> The results indicate that the gauche conformation decreases and the trans conformation increases when PNIPAM changes into the globule state. Figure 3 shows the dimer models of these two conformations of PNIPAM and the corresponding diameters. The diameter of trans-conformation dimers is larger than that of gauche-conformation dimers, which illuminates that the gauche-to-trans transition would make  $V_f$  in the PNIPAM aqueous solution increase. Thus, the changes of  $V_f$  from 28.0°C to 32.5°C could be considered as a result of the coexistent effects of the collapse and the gauche-to-trans transition of



**Figure 3.** Conformational change of dimer models of PNIPAM during the phase separation. The conformations were optimized by DFT calculations at the B3LYP/6-31G(d) level.

PNIPAM. The phase separation temperature ( $T_p$ ) of the PNIPAM aqueous solution was measured to be about 32.5°C from the turbidity results (as shown in the inset of Fig. 2). The chain mobility of PNIPAM would be constrained above 32.5°C due to the gelation of the sample; as a result, the  $V_f$  in the sample would decrease suddenly. Compared with the cross-linked PNIPAM gel, the physical gel possessed less inhomogeneities in collapsed state due to the existence of two kinds of annihilation lifetimes of *o*-Ps of collapsed cross-linked gel.<sup>[18]</sup> Further phase separation of the PNIPAM gel above 34.0°C would cause the amount of water buried in the free-volume cavities of the PNIPAM to reduce. Accordingly, the size of free-volume cavities increases.

The results obtained for the *o*-Ps intensity in the PNIPAM aqueous solution and distilled water are showed in Fig. 4.  $I_3$  exhibits a first increase with increasing temperature followed by a decrease below the LCST, and a similar variation is observed above the LCST for the PNIPAM aqueous solution, while  $I_3$  in distilled water gradually decreases with increasing temperature. Interpretation of  $I_3$  is complicated by its dependence on relative free-volume element concentration and the probability of *o*-Ps formation. During the spur processes, Ps formation takes place in the positron terminal spur where electron-ion recombination and scavenging and trapping of electrons and/or positrons are competing. Thus, the Ps formation process is strongly affected by many factors, such as free radicals, chemical functional groups, hydrogen bonds,<sup>[19]</sup> and so on. For the PNIPAM aqueous solution, the lone electron pairs of the amino group and those of the doubly bonded oxygen of



**Figure 4.** Variations of *o*-Ps intensity for the PNIPAM aqueous solution (square) and distilled water (triangle) as a function of temperature. The inset is the hydrogen-bonded chemical structure of PNIPAM in aqueous solution.

the carbonyl group play a significant role in the *o*-Ps formation. The location of these lone electron pairs could result in the decrease of the *o*-Ps formation. The hydrogen-bonded chemical structure of PNIPAM in aqueous solution is shown in the inset of Fig. 4. Thermal micro ATR/FT-IR spectroscopic studies of the PNIPAM aqueous solution revealed that there was an initial decrease of the composition of the free  $\text{C}=\text{O}$  group below  $\sim 33^{\circ}\text{C}$  (break of hydrogen bonds) followed by an increase as the temperature increased above  $\sim 33^{\circ}\text{C}$  (formation of hydrogen bonds), while the composition of the free amino group exhibited an opposite result.<sup>[7]</sup> However, the changing rates of the free  $\text{C}=\text{O}$  group and the free amino group were not consistent at different temperatures and their effects on the Ps formation could not compensate exactly, which resulted in the observed changes of  $I_3$ .

In conclusion, the changes in free-volume during phase separation of PNIPAM aqueous solution were investigated *in situ* by PALS. The observed variations of the *o*-Ps intensity were related to the formation and/or break of the intramolecular and intermolecular hydrogen bonds (the variations in composition of the free  $\text{C}=\text{O}$  group and the free amino group). 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 gels of the order molecular dimensions.

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## REFERENCES

1. Fujishige, S.; Kubota, K.; Ando, I. Phase transition of aqueous solutions of poly(*N*-isopropylacrylamide) and poly(*N*-isopropylmethacrylamide). *J. Phys. Chem.* **1989**, *93*, 3311–3313.
2. Wang, X.; Qiu, X.; Wu, C. Comparison of the coil-to-globule and the globule-to-coil transitions of a single poly(*N*-isopropylacrylamide) homopolymer chain in water. *Macromolecules* **1998**, *31*, 2972–2976.
3. Inomata, H.; Goto, S.; Otake, K.; Saito, S. Effect of additives on phase transition of *N*-isopropylacrylamide gels. *Langmuir* **1992**, *8*, 687–690.
4. Walter, R.; Rička, J.; Quellet, C.; Nyffenegger, R.; Binkert, T. Coil-globule transition of poly(*N*-isopropylacrylamide): a study of polymer-surfactant association. *Macromolecules* **1996**, *29*, 4019–4028.
5. Tokuhiro, T.; Amiya, T.; Mamada, A.; Tanaka, T. NMR study of poly(*N*-isopropylacrylamide) gels near phase transition. *Macromolecules* **1991**, *24*, 2936–2943.
6. Katsumoto, Y.; Tanaka, T.; Sato, H.; Ozaki, Y. Conformational change of poly(*N*-isopropylacrylamide) during the coil-globule transition investigated by attenuated total reflection/infrared spectroscopy and density functional theory calculation. *J. Phys. Chem. A* **2002**, *106*, 3429–3435.
7. Lin, S.-Y.; Chen, K.-S.; Run-Chu, L. Thermal micro ATR/FT-IR spectroscopic system for quantitative study of the molecular structure of poly(*N*-isopropylacrylamide) in water. *Polymer* **1999**, *40*, 2619–2624.
8. Maeda, Y.; Yamamoto, H.; Ikeda, I. Phase separation of aqueous solutions of poly(*N*-isopropylacrylamide) investigated by confocal raman microscopy. *Macromolecules* **2003**, *36*, 5055–5057.
9. Liu, W.; Zhang, B.; Lu, W. W.; Li, X.; Zhu, D.; Yao, K. D.; Wang, Q.; Zhao, C.; Wang, C. A rapid temperature-responsive sol–gel reversible poly(*N*-isopropylacrylamide)-g-methylcellulose copolymer hydrogel. *Biomaterials* **2004**, *25*, 3005–3012.
10. Dubek, G.; Eichler, S. Do MELT or CONTIN programs accurately reveal the *o*-Ps lifetime distribution in polymers? Analysis of simulated lifetime spectra. *Phys. Stat. Sol. (a)* **1998**, *168*, 333–350.
11. Bockstahl, F.; Duplatre, G.; Miguel, M. d. G.; Burrows, H. D. Probing the size of P84 block copolymer micelles in Pluronic aqueous solution by means of positron annihilation lifetime spectroscopy. *Phys. Chem. Chem. Phys.* **2000**, *2*, 4768–4771.
12. Brandt, W.; Berko, S.; Walker, W. Positronium decay in molecular substances. *Phys. Rev.* **1960**, *120*, 1289–1295.
13. Tao, S. J. Positronium annihilation in molecular substances. *J. Chem. Phys.* **1972**, *56*, 5499–5510.

14. Eldrup, M.; Lightbody, D.; Sherwood, L. N. The temperature dependence of positron lifetimes in solid pivalic acid. *Chem. Phys.* **1981**, *63*, 51–58.
15. Mogensen, O. E. *Positron Annihilation in Chemistry*; Springer: Berlin, 1995.
16. Ujihira, Y.; Ryuo, T.; Kobayashi, Y.; Nomizu, T. Dependence of ortho-positronium pick-off annihilation lifetime on free volume in organic molecular liquids calculated by Kincaid Eyring method, and positronium bubble formation. *Appl. Phys.* **1978**, *16*, 71–74.
17. Kobayashi, Y.; Haraya, K.; Kamiya, Y.; Hattori, S. Correlation between the ortho-positronium pick-off annihilation lifetime and the free-volume in molecular liquids and polymers. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 160–163.
18. Ito, K.; Ujihira, Y.; Yamashita, T.; Horie, K. Change in free volume during volume phase transition of poly(*N*-isopropylacrylamide) gel as studied by positron annihilation lifetimes: temperature dependence. *Polymer* **1999**, *40*, 4315–4323.
19. Süvegh, K.; Domján, A.; Vankó, G.; Iván, B.; Vértes, A. Free volume and swelling dynamics of the poly[(2-dimethylamino)ethyl methacrylate]-l-polyisobutylene amphiphilic network by positron annihilation investigations. *Macromolecules* **1998**, *31*, 7770–7775.

