



Thermal Expansion of the Free Volume in Poly (Vinyl Alcohol) Using Positron Annihilation Technique and Group Contribution Method

Hossam B. Alaa¹, Hamdy F. M. Mohamed^{2*} and E. E. Abdel-Hady²

¹El-Minia High Institute of Engineering & Technology, Minia, Egypt

²Physics Department, Faculty of Science, Minia University, P.O. Box 61519 Minia, Egypt.

POSITRON annihilation lifetime (PAL) as a function of temperatures were measured to determine the thermal expansion coefficient (α) of the ortho-positronium (*o*-Ps) hole volume for poly(vinyl alcohol), PVA. On the other hand, the thermal expansion coefficient (α) of the bulk volume of PVA has been calculated from measuring the bulk volume as a function of temperature. The group contribution method is used for the calculation of the fractional of the free volume in the glassy and the rubbery states. For the glassy and rubbery states, the ratio of the thermal expansion coefficient of the bulk volume to that of the total free volume is calculated. There is an agreement between these ratios in glassy and rubbery states and those outcomes acquired from the PAL and the substance volume information. This indicated that the *o*-Ps lifetime is a sign to the free volume in the sample which is also proportional to the total free volume.

Keywords: Poly (vinyl alcohol), Positron annihilation lifetime, Bulk volume, Group contribution method, Thermal expansion coefficient.

Introduction

Positron annihilation in polymeric materials attracted much interest because it is expected to bring more information about the volume of the microstructure. The positron behaviour in these materials is much more complex than in metal crystals because a certain fraction of positrons abstract electron to form positronium atom (Ps). Ps atom is formed in two different ground states, depending on the spin orientations of the positron and the electron. The antiparallel spin forms para-positronium (*p*-Ps) with probability 0.25 and annihilates within ~ 125 ps by emitting two photons. The parallel spin orientation form, ortho-positronium (*o*-Ps), with probability 0.75 annihilating to three photons with theoretical lifetime of 140 ns in vacuum [1, 2]. However, within condensed media, the *o*-Ps typically decays via "electron pick-off", i.e. an electron from the surrounding medium annihilates with the positron, emitting two photons with a lifetime approximately two orders of magnitude less than the theoretical value [3].

Poly (vinyl alcohol) (PVA) is a polymer of considerable importance due to its great film shaping and physical properties, high hydrophilicity, processability, biocompatibility, and great compound resistance [5, 6]. It is a semi-crystalline polymer, containing crystalline and amorphous phases. At the point when such a polymer is doped with a reasonable dopant, it might associate either in the formless portion or in the crystalline fraction of the polymer and in both cases its diverse physical quantities are changed relying on the basic change. Hence the complete information about PVA helps in tailoring those polymer properties for particular applications [7-10].

It has been pointed out that the thermal expansion coefficient of the volume determined by the *o*-Ps lifetime is about one order of magnitude larger than that of the bulk (i.e., total volume) substance [11, 12]. Also, the *o*-Ps hole has been taken as the free volume in the matter without a proof. So, the aim of this study is to obtain some insight which will shed some light on the

*Correspondence: Tel: +201208281849, Fax: +20862363011.

E-mails: hamdyfm@gmail.com & hamdy.farghal@mu.edu.eg

Received : 21/6/2020; accepted : 7/7/2020

DOI : 10.21608/ejphysics.2020.33422.1045

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nature of the free volume measured by the *o*-Ps lifetimes using the PAL and the substance volume measurements. Those have been performed over a wide range of temperature. Also, the thermal expansion coefficients were deduced from the PAL and the substance volume and a comparison is held with the data calculated from the group contribution method.

Experimental

Poly (vinyl alcohol) powder was purchased from Hayashi Pure Chemical Industries Ltd, Japan, with an average degree of polymerization 1700. It was dissolved in distilled water by gently heating in a water bath until the PVA powder is completely dissolved and form a clear viscous solution. The viscous PVA solution was coated onto Teflon plates and left to dry in air for three days.

Conventional fast-fast coincidence spectrometer [13-15] was used for measuring the positron annihilation lifetime (PAL). The positron source was prepared by depositing about 20 μ Ci aqueous $^{22}\text{NaCl}$ on a Kapton foils of 7 μm thickness and 10x10 mm^2 area. It was sandwiched between two identical samples of PVA. The time resolution of the PAL system was 240 ps.

The prepared sample (PVA foils/positron source/PVA foils) was put in the holder of a heating chamber which was evacuated all the time during the PAL was measured. The measurements were performed starting from 30 up to 160 $^{\circ}\text{C}$ and then in a cooling direction from 160 $^{\circ}\text{C}$ to room temperature at 5 or 10 degrees steps. Each PAL spectrum, having about one million total counts, was analysed using the PALSfit [16] program into three lifetime components which give smaller variances ratio of the fits ($\chi^2 \sim 1.2$). The length dilation of the sample from the same sheet was measured as a function of temperature by using cathetometer between 30 and 160 $^{\circ}\text{C}$.

For the determination of the volume expansion coefficient, a long sheet of PVA was hanged in a constant temperature box (controlled to ± 0.1 degree) and then the length of the sheet was measured through the glass window by using a cathetometer.

The wide-angle x-ray diffraction (WAXD) patterns of pure PVA as received and after heated at 160 $^{\circ}\text{C}$ were recorded using JEOLJSX-600 PA diffractometer with $\text{CuK}\alpha$ ($\lambda=1.54184\text{\AA}$) incident

radiation. The WAXD peaks were recorded in the 2θ range of 5-50 $^{\circ}$. The measurements were done at a temperature of 25 $^{\circ}\text{C}$ and relative humidity of 25%.

Results and Discussion

Three lifetime components were obtained from the PAL spectra. The lifetimes and intensities of the short-lived component ($\tau_1 = 0.15 - 0.20$ ns, $I_1 = 40-55\%$) and the intermediate lifetime component ($\tau_2 = 0.40 - 0.50$ ns, $I_2 = 35 - 45\%$) are attributed mainly to *p*-Ps and direct annihilation of positrons, respectively. The long-lived component, with lifetime $\tau_3 = 1.2 - 2.0$ ns and intensity $I_3 = 14 - 19\%$, is due to *o*-Ps annihilation in free volume holes. Figure (1) presents the behaviour of the *o*-Ps parameters (*o*-Ps lifetime τ_3 , and its intensity I_3) as a function of temperature. Clearly there are two regions with different temperature dependences of τ_3 . The *o*-Ps lifetime τ_3 increases slightly with increasing the temperature up to 80 $^{\circ}\text{C}$ and then starts to rise with a steeper slope. The meeting point of these two regions is the glass transition temperature T_g (80 $^{\circ}\text{C}$). The present data agrees with data of Chen and Zhang [17] who found that the glass transition temperature for pure PVA is 79.6 $^{\circ}\text{C}$ by using a differential scanning calorimeter measurement. The glass transition temperature T_g is conventionally assigned to the onset temperature of micro-Brownian motion of the amorphous main chain. The *o*-Ps intensity I_3 also appears to be composed of two regions as for the *o*-Ps lifetime τ_3 , where the meeting point is at 80 $^{\circ}\text{C}$. It is clear that I_3 value before T_g is larger than those values above T_g , because the Ps formation probability, represented by I_3 , has become smaller due to enhanced crystallinity which has been confirmed by both density and WAXD measurements.

The density of the fresh and the heated at 160 $^{\circ}\text{C}$ samples were measured by the floating method using benzene and carbon-tetrachloride. The density of the fresh sample increased with heating (from $\rho = 1.2860$ to 1.2975 g/cm^3) indicating the development of crystallization. The degree of crystallinity X_c was calculated as [18, 19];

$$X_c = (\rho - \rho_a) / (\rho_c - \rho_a) \quad (1)$$

Where ρ is the specific density of the PVA sample, ρ_a is the density of the fully amorphous PVA (1.269 g/cm^3), and ρ_c is that for the fully

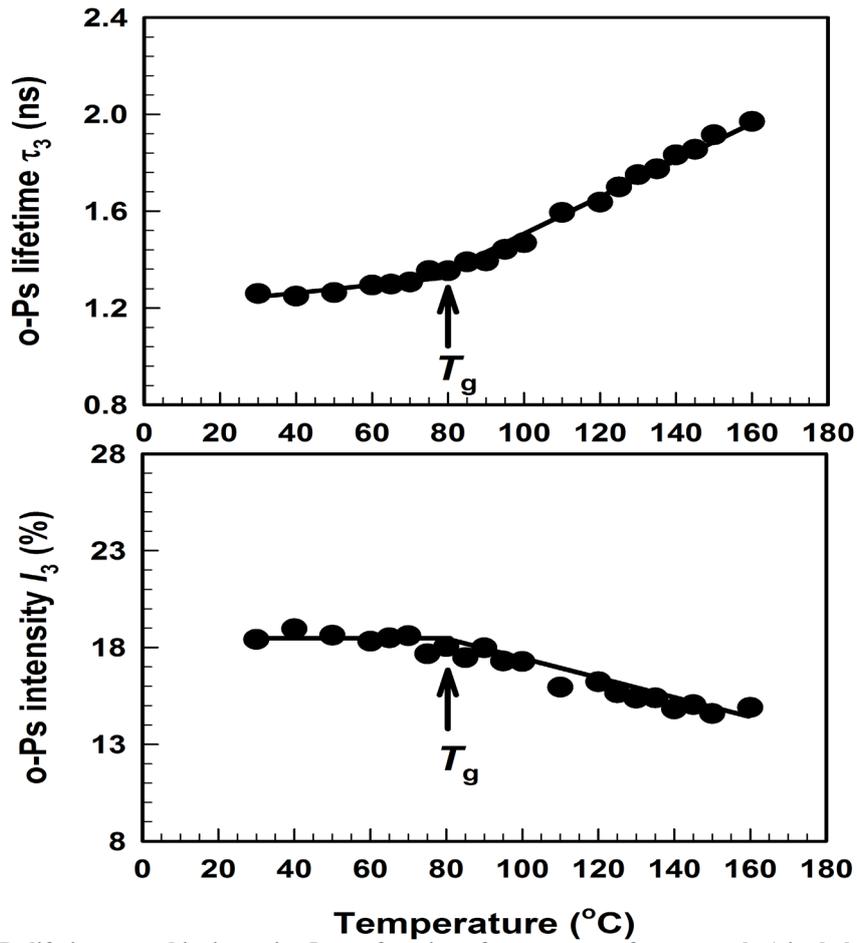


Fig. 1 . The *o*-Ps lifetime τ_3 and its intensity I_3 as a function of temperature for pure poly (vinyl alcohol).

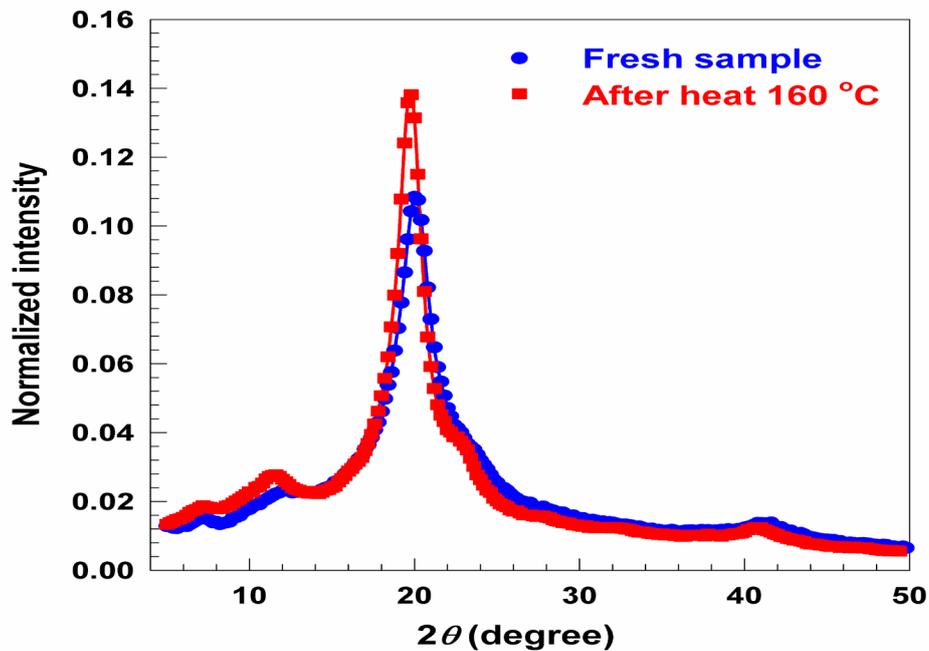


Fig. 2. The WAXD for pure poly(vinyl alcohol) fresh and heated at 160 °C.

crystalline PVA (1.345 g/cm³) [20-22]. The resultant crystallinity was 22.4 and 37.5% for the fresh and the heated samples, respectively. Also, wide angle x-ray diffraction (WAXD) patterns for the fresh and heated samples confirmed that the degree of crystallinity was increased as shown in Fig. 2.

The *o*-Ps hole volume ($V_{o-Ps} = 4/3\pi R^3$) which is probed by the *o*-Ps lifetime was calculated from the following relation between τ_3 and the average radius (R) of the hole [23, 24];

$$\tau_3 = 0.5 \left\{ 1 - \frac{R}{R_o} + \frac{1}{2\pi} \sin \left(\frac{2\pi R}{R_o} \right) \right\}^{-1} ns, \quad (2)$$

where $R_o = R + \Delta R$ and $\Delta R = 1.656 \text{ \AA}$ is the thickness of the homogenous electron layer in which the positron annihilates [25]. The temperature dependence of the calculated *o*-Ps hole volume V_{o-Ps} is shown in Fig. 3. As can be seen from this figure, there are two linear parts intercepted at the glass transition temperature ($T_g = 80 \text{ }^\circ\text{C}$) similar to Fig. 1. Below T_g , the *o*-Ps hole volume increases slightly with increasing the temperature. Above T_g , the matrix becomes rubbery and the *o*-Ps hole volume increases dramatically with increasing the temperature. A linear correlation between the *o*-Ps hole volume and temperature was observed with a definite slope ($\Delta V_{o-Ps}/\Delta T$) in the glassy and the rubbery states. The thermal expansion coefficient of the *o*-Ps hole volume, α' , can be estimated as [26];

$$\alpha' = \frac{1}{V_{o-Ps}} \cdot \left(\frac{\Delta V_{o-Ps}}{\Delta T} \right). \quad (3)$$

The values of the thermal expansion coefficient of the *o*-Ps hole volume in the glassy (α'_g) and the rubbery states (α'_r) were calculated to be $(5.1 \pm 0.8) \times 10^{-3} / ^\circ\text{C}$ and $(2.7 \pm 0.1) \times 10^{-2} / ^\circ\text{C}$, respectively.

Figure 4 represents the variation of the length of the PVA sheet with temperature. Again, the same behaviour as Fig. 3 is observed with different slopes. It is well known that the volume thermal expansion coefficient is equal to three times of the linear thermal expansion coefficient. So, three times the slope of their linear fits should yield the volume thermal expansion coefficients of the bulk substance α_g and α_r for the glassy and the rubbery states, respectively. The value of the volume expansion coefficient for the rubbery state was obtained in this way but for the glassy state, the literature value [27] is used since the present

measurements have a large experimental error. The values of the thermal expansion coefficient of the bulk substance in the glassy and rubbery states are $2.7 \times 10^{-4} / ^\circ\text{C}$ and $(2.2 \pm 0.2) \times 10^{-3} / ^\circ\text{C}$, respectively.

By comparing the thermal expansion coefficient of the *o*-Ps hole and the bulk volume values, it is obvious that the thermal expansion coefficient of the free volume is larger than that of the total volume by one order of magnitude. This is in agreement with the previous results [12]. On the other hand, the thermal expansion coefficient of the *o*-Ps hole volumes is 19 (12) times larger than that of the bulk volume for the glassy (rubbery) state. This large difference comes from the fact that only the free volume is measured by the PAL while the size of the excluded volume is included in the case of the bulk expansion. In order to consider this in detail, the total volume of the polymer, V_T , is divided into two components; one is the temperature independent part (V_o) and the other is the temperature dependent part (V_f); i.e.

$$V_T = V_o + V_f. \quad (4)$$

Simply, V_o corresponds to the excluded volume (the volume occupied by the molecules at 0 K per mole of the repeated unit of the polymer) while V_f corresponds to the free volume.

The volume expansion coefficient is defined as $\alpha = \frac{1}{V_T} \frac{\Delta V_T}{\Delta T}$ which could be reduced to $\frac{1}{V_T} \frac{\Delta V_f}{\Delta T}$. Let F be the fraction of the volume seen by the *o*-Ps in the total free volume then, V_{o-Ps}

= F V_f assuming that the *o*-Ps is a measure of a fraction but not of all the free volume. When the fraction is a constant independent of temperature,

the volume expansion of the *o*-Ps hole volume, $\alpha' = \frac{1}{V_{o-Ps}} \frac{\Delta V_{o-Ps}}{\Delta T}$, reduces to $\frac{1}{V_f} \frac{\Delta V_f}{\Delta T}$. Thus,

a simple relationship is obtained for the ratio of the thermal expansion coefficient of the *o*-Ps hole volume to the thermal expansion coefficient of the bulk volume as

$$\alpha' / \alpha = V_T / V_f = [V_T / (V_T - V_o)] = [1 - V_o / V_T]^{-1}. \quad (5)$$

In order to estimate the temperature dependent term V_o , the Bondi's group contribution method [28] is applied, where each functional group of the

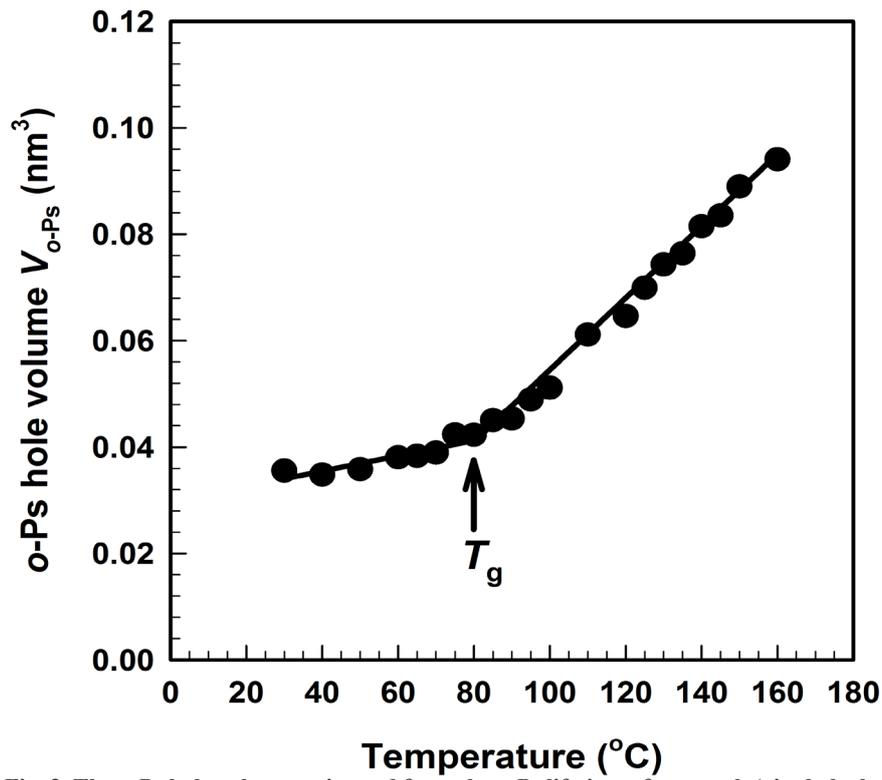


Fig. 3. The o -Ps hole volume estimated from the o -Ps lifetime of pure poly(vinyl alcohol).

The straight lines are the results of the linear fit.

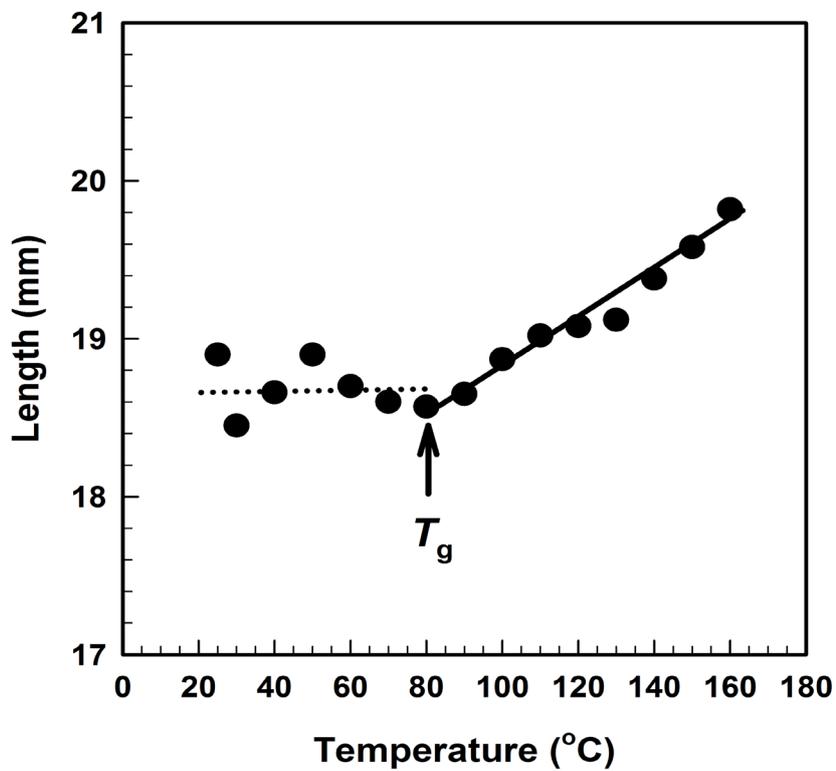


Fig. 4. The length of the sheet of pure poly(vinyl alcohol) as a function of temperature.

polymer chain is given a specific van der Waals volume, V_w . The Sum of V_w of all the groups per unit of chain multiplied by 1.3, taking into account the density, gives the zero-point volume V_o , corresponding to the volume at absolute zero temperature; i.e.,

$$V_o = 1.3 \sum V_w \quad (\text{cm}^3/\text{mol}) \quad (6)$$

From the molecular weight ($M_w = 44.05$ g/mol for PVA) and the density ρ of the sample, the total volume, V_T , is given by

$$V_T = M_w (\text{g/mol}) / \rho (\text{g/cm}^3), \quad (\text{cm}^3/\text{mol}) \quad (7)$$

Substituting Eqs. (6&7) into Eq. (5), one can obtain

$$\alpha' / \alpha = [1 - 1.3 \rho V_w / M_w]^{-1}. \quad (8)$$

The chemical structure of PVA is $[\text{CH}_2\text{CHOH}]_n$. The V_w of the groups CH_2 , CH , and OH according to Bondi are 10.23, 6.78, and 8.04 cm^3/mol , respectively and the contribution per hydrogen bond is -1.05 cm^3/mol [29]. From these values, the V_w for PVA is 24 cm^3/mol , where the density of the sample in the glassy state was measured to be 1.3 g/cm^3 and the density for the rubbery state, taken from literature [30], was 1.2274 g/cm^3 . So, the ratio (α' / α) is 13 for the glassy and 10 for the rubbery states.

There is some correlation between the ratio of the thermal expansion coefficients obtained from the *o*-Ps parameters to the bulk volume (α' / α) and the data calculated by using the group contribution method in the glassy and rubbery states. Also, the ratio (α' / α) obtained from the *o*-Ps data are larger than the corresponding values calculated from Eq. (8). It can be indicated that the hole volume which is calculated from the *o*-Ps lifetime is larger than the original hole volume in the polymer chain. It can be attributed to a possibility of increasing the hole volume after positronium get in.

Conclusions

The thermal expansion coefficient was determined by three different methods; the *o*-Ps hole volume, the bulk volume, and the group contribution. A correlation between these methods has been experimentally observed. The values of the thermal expansion coefficient from the PAL measurement appear to be in accord with the other methods. This shows that the *o*-Ps lifetime is an indication to the free volume in the sample which is also proportional to the total free volume. The obtained results also reveal that the

positron annihilation technique is a powerful tool in revealing the nature of the free volume.

References

1. Procházka, I., *Mater Struct.* **8**, 55 (2001)
2. West, R. N., "Positron Studies of Condensed Matter", Barnes and Noble, New York (1974).
3. Lind, J. H, Jones, P. L., and Pearsall, G., *J. Poly. Sci.* **A24**, 3033 (1986).
4. Shehap, A. M., and Akil, D. S., *Int. J. Nanoelectronics and Materials* **9**, 17 (2016).
5. Gomaa, M. M., Hugenschmidt, C., Dickmann, M., Abdel-Hady, E. E., Mohamed, H. F. M., and Abdel-Hamed, M. O., *Physical Chemistry Chemical Physics* **20**, 28287 (2018).
6. Kinadjian, N., Achard, M., Julián-López, B., Maugey, M., Poulin, P., Prouzet, E., and Backov, R., *Advanced Functional Materials* **22**, 3994 (2012).
7. Mohamed, H. F. M., El-Sayed, A. M. A., and Abdel-Hady, E. E., *Journal of Physics: Condensed Matter* **11**, 4461 (1999).
8. Arata, A. K., Abdulkadhimb, D.H., and Rashida, M. H., *Journal of University of Babylon, Pure and Applied Sciences* **26**, 95 (2018).
9. Gomaa, M. M., Hugenschmidt, C., Dickmann, M., Abdel-Hamed, M.O., Abdel-Hady, E. E., and Mohamed, H. F. M., *Acta Physica Polonica A* **132**, 1519 (2017).
10. Abdel-Hady, E. E., Mohamed, H. F. M., Abdel-Hamed, M. O., and Gomaa, M. M., *Advances in Polymer Technology* **37**, 3842 (2018).
11. Jean, Y. C., Mallon, P. E., and Schrader, D. M., "Principles and applications of positron & positronium chemistry", World Scientific, USA (2003).
12. Jean, Y. C., in "Positron and Positronium Chemistry", Jean, Y. C., (Ed.), World Scientific, London (1990).
13. Mohamed, H. F. M., Abdel-Hady, E. E., Abdel-Hamed, M. O., and Said, M., *Acta Physica Polonica A* **132**, 1543 (2017).
14. Mohamed, H. F. M., and Owais, A., *Journal of Polymer Research* **25**, 28-1 (2018).
15. Alharbi, T., Mohamed, H. F. M., Saddeek, Y. B.,

- El-Haseib, A. Y., and Shaaban, Kh. S., *Radiation Physics and Chemistry* **164**, 108345-1 (2019).
16. Olsen, J. V., Kirkegaard, P., Pedersen, N. J., and Eldrup, M., *Phys. Stat. Sol. C4*, 4004 (2007).
 17. Chen, N., and Zhang, J., *Chinese Journal of Polymer Science* **28**, 903 (2010).
 18. Neto, E. S. B, Coelho, L. A. F., Forte, M. M. C., Amico, S. C., and Ferreira, C. A., *Materials Research* **17**, 236 (2014).
 19. Conti, D. S., Yoshida, M. I., Pezzin, S. H., and Coelho, L. A. F., *Fluid Phase Equilibria*. **261**, 79 (2007).
 20. Assender, H. E., and Windle, A. H., *Polymer*. **39**, 4295 (1998).
 21. Stribeck, N., Zeinolebadi, A., Fakirov, S., Bhattacharyya, D., and Botta, S., *Sci Technol Adv Mater*. **14**, 035006 (2013).
 22. Desmaisons, J., Rueff, M., Bras, J., and Dufresne, A., *Soft Matter* **14**, 9425 (2018).
 23. Tao, S. T., *J. Chem. Phys.* **56**, 5499 (1972).
 24. Eldrup, N., Lightbody, D., and Sherwood, J. N., *Chem. Phys.* **63**, 51 (1981).
 25. Nakanishi, H., Wang, S. J., and Jean, Y. C., in Sharama, S. C., (Ed.) "Positron Annihilation Studied of Fluids", *Proc. of Int. Symposium, Arlington, Texas*, P. 292, 1987.
 26. Okamoto, K., Tanaka, K., Katsube, M., Kita, H., and Ito, Y., *Bull. Chem. Soc. Jpn.* **66**, 61 (1993).
 27. Britton, A. T., JR., Sullivan, J. L., and Smith, K. J., JR., *J. Polym. Science. Polym. Phys.* **18**, 537 (1980).
 28. Bondi, A., " Physical Properties of Molecular Crystal, Liquids and Glass", Wiley, New York, 1968.
 29. Bondi, A., *J. Phys. Chem.* **68**, 441 (1964).
 30. Pritchard, J. G., "Poly(Vinyl Alcohol): Basic properties and use", Macdonald Technical & Scientific, London (1973).