# Free Volume and the Mechanism of Plasticization in Water-Swollen Poly(vinyl alcohol)

**R. M. Hodge,*[†,‡] T. J. Bastow,[§] G. H. Edward,[‡] G. P. Simon,[‡] and A. J. Hill[§,||]**

*Department of Mechanical Engineering, Victoria University, P.O. Box 14428 MMC, Melbourne VIC 3000, Australia, Department of Materials Engineering, and Faculty of Engineering, Monash University, Clayton VIC 3168, Australia, and Division of Materials Science and Technology, CSIRO, Private Bag 33, South Clayton MDC, Clayton VIC 3169, Australia*

*Received July 25, 1995; Revised Manuscript Received September 9, 1996*[⊗]

ABSTRACT: Poly(vinyl alcohol), PVOH, films have been studied as a function of water content. The states of water present in the polymer (bound or free) have been characterized and are a function of water content. The effects of water content (and hence state) on the free volume, chain mobility, and glass transition ($T_g$) behavior have been studied by positron annihilation lifetime spectroscopy, $^{13}$C solid state nuclear magnetic resonance, and dynamic mechanical analysis. The addition of approximately 30 wt % water results in a marked increase in free volume cavity size and polymer chain mobility and a corresponding decrease in $T_g$. The water is in a molecular, nonfreezable state for water additions up to approximately 30 wt %, hence it is postulated that nonfreezing water is responsible for the majority of the plasticization in this system. The plasticization is attributed to the increasing free volume and lubrication provided as the water swells the polymer and disrupts polymer−polymer hydrogen bonding. A limited equivalence between the action of water on the polymer and the action of temperature (thermal energy) is proposed.

## Introduction

Poly(vinyl alcohol) (PVOH) is perhaps the simplest of the water soluble/hydrophilic polymers from a structural point of view, and like many other water soluble polymers, it has found wide acceptance as a material for adhesive, hydrogel, membrane, and other applications.[1−4] In addition, PVOH exhibits considerable potential as a material for high modulus, creep resistant films and fibers. Much of the work to date has concentrated on the hydrogel and adhesive applications of PVOH,[5−12] as well as some recent work related to solid state fiber production.[5,13−19]

PVOH is typically produced by hydrolysis of poly(vinyl acetate) (PVAc) and is mutually soluble with water, although the degree of solubility is dependent on degree of hydrolysis, among other factors. Fully hydrolyzed samples are completely soluble in water above the dry glass transition temperature ($T_g$ = 85 °C)[4] of the polymer and are plasticized by water at ambient temperature. Samples with differing degrees of hydrolysis exhibit different hot and cold water solubility characteristics.

It has been established that, although water progressively destroys the crystalline regions in PVOH, the water molecules themselves do not inhabit intact crystallites.[20] Plasticization occurs in the amorphous region only, such that the degree of hydration is quoted as water content in the amorphous region. It is also important to note the state of water in the polymer, whether bound or free. The three states of water in PVOH have been previously defined as follows: [21] (1) *nonfreezing water*, water that is strongly bound to hydroxyl groups and shows no thermal transition by differential scanning calorimetry (DSC); (2) *freezable bound water*, water that is weakly bound to the polymer chain (or weakly bound to the nonfreezing water) and that melts on heating at temperatures greater than 0 °C due to these bonding interactions; and (3) *free water*, water that has the same phase transitions as bulk water. As shown in the present work, the nonfreezing water is the state of water which is the most effective plasticizer of PVOH.

The samples studied in this work have been previously characterized by wide angle X-ray diffraction (WAXD), DSC, and thermogravimetric analysis (TGA) in order to determine degree of crystallinity and the amount and state of water in the films.[22] In the present work, morphological, free volume, and mobility-related parameters are measured as a function of water content by positron annihilation lifetime spectroscopy (PALS), solid state $^{13}$C nuclear magnetic resonance (NMR), and dynamic mechanical analysis (DMA). These characterization techniques are complementary in that DMA probes the bulk material, averaging over the sample, while PALS and NMR offer site specific characterization. The techniques are combined to elucidate the effects of water on the macro- and microstructure. A physical model explaining the mechanism of plasticization as a function of water content in semicrystalline PVOH is proposed which is consistent with the experimental results.

## Experimental Section

The polymer used in the study was Elvanol grade HV poly(vinyl alcohol) (PVOH) from DuPont chemicals. The material is derived from poly(vinyl acetate) (PVAc) by hydrolysis and is supplied in powder form. The DuPont data sheet states that the degree of hydrolysis for Elvanol HV is 99.8% (0.2% residual acetate groups) and the molecular weight is 105 600−110 000 (weight average). Because of the hydrophilic nature of the polymer, the unprocessed powder contains approximately 6.5 wt % water at ambient temperature.[22]

Films were prepared by casting a 10 wt % aqueous solution of PVOH (mechanically mixed at room temperature) onto a glass plate at 22 °C, followed by conditioning at 22 °C for 2

---

[†] Victoria University.

[‡] Department of Materials Engineering, Monash University.

[§] CSIRO.

[||] Faculty of Engineering, Monash University.

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1996.

S0024-9297(95)01073-4 CCC: $12.00

**Table 1. Water Content and Degree of Crystallinity of PVOH Films**

| wt % $H_2O$ total (±0.5) | % crystallinity (±4) | wt % $H_2O$ in amorphous regions |
|---|---|---|
| 2.5 | 29 | 3.5 |
| 5.3 | 24 | 7.0 |
| 6.8 | 23 | 8.8 |
| 13.1 | 18 | 16.0 |
| 18.0 | 14 | 20.9 |
| 30.7 | 7 | 33.0 |
| 46.0 | 3 | 47.4 |
| 62.0 | 0 | 62.0 |

weeks at 50% relative humidity (RH) to allow the water concentration to equilibrate. Samples were subsequently either further dried under vacuum at 55 °C to remove residual water or immersed in distilled water at 22 °C for various times until samples with a variety of water contents were available for testing. Film thickness in the equilibrium state (5.3 wt % water, 22 °C, 50% RH) was 0.9 ± 0.1 mm.

Solid state $^{13}C$ cross-polarization–magic angle spinning (CP-MAS) spectra were collected on a Bruker 400 MSL NMR spectrometer using an MAS probe with a double bearing gas turbine using 4 mm PSZ rotors at a rotational frequency of 6.3 kHz. Chemical shifts for $^{13}C$ are quoted relative to $Me_4Si$ (TMS). Comparison of sample weight before and after measurement confirmed that the water content did not change during the experiment.

The PALS system used in the study was a thermally stabilized automated EG&G Ortec fast–fast coincidence system with a $^{22}Na$ resolution of 250 ps. Data were collected at 22 °C using a 30 $\mu$Ci $^{22}Na$ Ti foil source sandwiched between two identical PVOH/water samples sealed in an air-tight bag. Error bars in the PALS figures are population standard deviations for 7–10 spectra. The lifetime characteristics of PVOH did not vary with source contact time and individual spectra took from 0.4 to 2 h to collect approximately 1 million total counts from annihilation events. The spectra were analyzed using the program PFPOSFIT.[23] No source correction was used, based on the single lifetime ($\tau$ = 0.166 ns) spectra collected for annealed 99.99% pure Al using the same Ti foil source.

$T_g$ values reported are the peak of the tan $\delta$ versus temperature curves for DMA measurements. Samples were tested with an oscillating hemispherical probe at a frequency of 1 Hz between −80 and 100 °C at a heating rate of 2 °C/min. The testing was performed with a dynamic load amplitude of 1000 mN, and the DMA software was configured to maintain a static load of 1100 mN to ensure that probe contact was maintained with the specimen at all times. The sample chamber was cooled with liquid nitrogen and maintained in a dry helium atmosphere to ensure good heat conduction at low and high temperatures and to prevent fouling of the probe assembly by moisture condensation.

## Results and Discussion

Table 1 contains the degree of crystallinity as a function of water content for the PVOH films.[20,22] The WAXD spectra revealed a decrease in conventional three-dimensional crystallinity as water content increased from 6.5 to 35 wt %, and these results are discussed in detail elsewhere.[20] The WAXD data are used to calculate the weight percent water in the amorphous regions. Amorphous region properties such as $T_g$ and amorphous free volume are then plotted as functions of water content in the amorphous regions. NMR results are presented as a function of total water content because the chemical shifts represent nuclei in the amorphous and crystalline regions.

DMA heating traces taken from samples with different water contents reveal a single glass transition temperature (evidenced by a single tan $\delta$ peak) for each water content. Figure 1 shows the variation of measured $T_g$ with water content along with values theoretically predicted from the Gordon–Taylor equation[24] (eq 1):

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{1}$$

where $T_g$, $T_{g1}$, and $T_{g2}$ are the glass transition temperatures of the system, component 1 (PVOH, $T_{g1}$ = 85 °C),[4] and component 2 (water, $T_{g2}$ = −139 °C),[25,26] respectively, and where $w_1$ and $w_2$ are the mass fractions of components 1 and 2, respectively. The experimental data indicate that the $T_g$ for the system has a minimum value of −32 °C when the water content in the amorphous region has reached 42 wt %, whereas eq 1 predicts no such minimum. Equation 1 predicts a monotonic decrease in $T_g$ with increasing water content (see Figure 1).

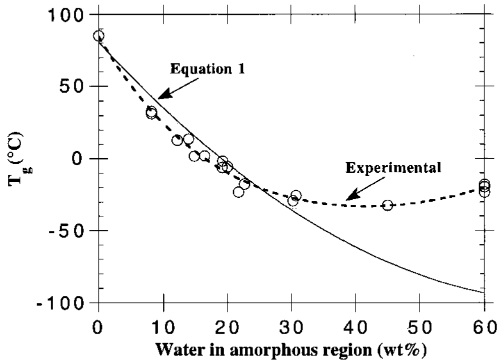

**Figure 1.** Plasticization of PVOH by water measured by glass transition temperature variation. The solid line is predicted by eq 1.

Equation 1 assumes intimate mixing of two components to produce a single amorphous phase and considers only the plasticization effects associated with the amorphous region of the polymer. If one component of the system undergoes a freezing transition and is in a frozen (crystallized) state at the time of measurement, then the composition of the amorphous region (weight percent water) must be corrected to reflect this crystallization. It has been shown previously[20] that frozen water does not exist in these films until the total water content is greater than 30 wt % and the temperature is below 2 °C. At water concentrations greater than 30 wt %, the water molecules are able to freeze, thus indicating a saturation of the nonfreezing water content in the amorphous region and contributing to the deviation of the experimental curve from the theoretical curve, as shown in Figure 1. Using only the nonfreezing components[20] of the total water content in eq 1 results in the modified form of the predicted curve modeling the experimental data far more closely, as illustrated in Figure 2. Some of the remaining variation between the experimental data and that predicted by the modified Gordon–Taylor equation may be accounted for by two considerations: (a) the Gordon–Taylor equation assumes volume additivity of the constituents[24] and (b) the reinforcing effect of water crystals may affect $T_g$. As will be shown in this work, the assumption of volume additivity is not valid for this system, as nonfreezing water addition causes a greater than additive increase in specific volume and free volume.

As stated earlier, care must be taken in the interpretation of the $T_g$ data and in relating the data to mechanical properties and physical characteristics at subambient temperatures due to the complicating factor of the freezing of water. A sample containing 60 wt %

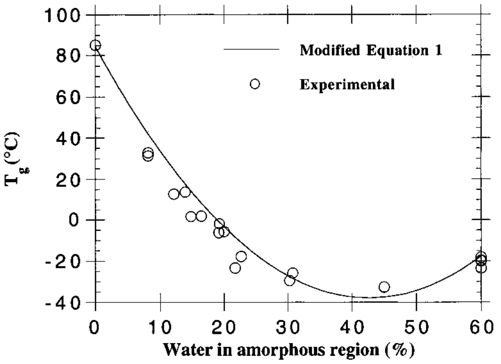

**Figure 2.** Plasticization of PVOH by water measured by glass transition temperature variation. The solid line is predicted by eq 1, modified to include only the contribution from nonfreezing water.

water is extremely flexible and rubbery at room temperature, while a sample containing 45 wt % water is noticeably less flexible and less plasticized under the same conditions. Considering the form of the curve in Figure 2, however, it is tempting to conclude that the 45 wt % water sample would behave in a more rubbery fashion than the 60 wt % sample, as room temperature is further above the measured $T_g$ of the 45 wt % sample than the 60 wt % sample. However, at room temperature, no water is in a frozen state, regardless of the relative proportions of each state of water indicated by (subambient temperature) DSC traces.[20] At room temperature, water is in a highly mobile state and the samples with a higher water content exhibit more flexibility than those with lower water contents. The data above 30 wt % water in Figure 2 are only of experimental relevance for experiments performed below the freezing point of water.

The free volume of the system was probed at room temperature by PALS, which can give two free volume-related parameters: the ortho-positronium (oPs) pickoff lifetime, $\tau_3$, which is related to the mean radius of the free volume cavities, and the associated intensity, $I_3$, which is related to the concentration of free volume cavities.[27] The oPs pickoff lifetimes ($\tau_3$) and intensities ($I_3$) were measured as functions of water content. In order to interpret the PALS parameters in terms of the free volume model,[27,28] it is important to confirm that oPs inhibition is not being caused by changes to the system chemistry. In some cases, changes in the $I_3$ parameter can be associated with oPs inhibition and not changes in free volume concentration.[29] Free water is known to cause positronium (Ps) inhibition.[30] In the present work, lack of Ps inhibition is confirmed by the approximately constant para-Ps component intensity with increasing water content. It must be remembered that these PVOH films do not contain any free water until the water content is greater than 30 wt %. Another important factor affecting the oPs pickoff component is the degree of crystallinity. Several studies have shown a linear relationship between the degree of crystallinity and the oPs intensity $I_3$, representative of the relative number of free volume sites in the volume probed.[27,31–33] As discussed elsewhere,[31] crystalline corrections can be applied to polymers where there is a nonzero contribution from the crystalline regions to the total number of oPs pickoff annihilations occurring in the polymer. PVOH samples of varying percent crystallinity were prepared by annealing in air at 55 °C for varying times producing a range of crystallinities from 42% to 53%. It was experimentally determined[22] that the crystallites in PVOH contribute 10.2 ± 0.5% (absolute percent) toward the total $I_3$ values recorded, and so the correction proposed for semicrystalline polymers[31] was applied to the $I_3$ data.

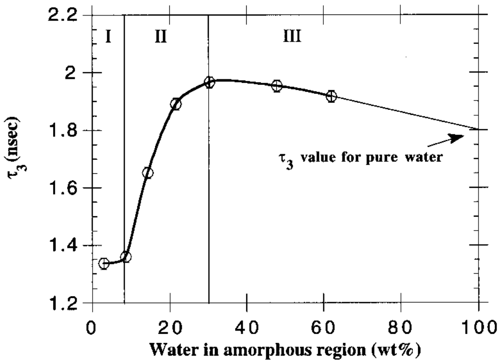

**Figure 3.** Measured oPs pickoff lifetimes for the PVOH/water system as a function of water content.

Figure 3 shows the variation in $\tau_3$ with water content for the system. The data may be divided into three distinct regions: an initial region, where the $\tau_3$ values are essentially constant (region I), followed by a range of water contents between approximately 8 and 30 wt %, where $\tau_3$ increases (region II) before undergoing a gradual decrease for water contents above 30 wt % (region III). An implicit assumption is that water predominantly swells the amorphous region only. The data in Figure 3 have therefore been presented as a function of water in the amorphous region.

As mentioned previously, $\tau_3$ has been shown to be related to the mean free-volume cavity radius.[27,28] Figure 3 indicates that the mean size of the free volume cavities is essentially unchanged during the initial stages of water absorption corresponding to region I. The data in region II indicate a significant increase in free volume cavity size until the water content reaches approximately 30 wt %. At this point (region III), the curve is at a maximum and begins a gradual decrease over all subsequent amounts of water absorption up to 60 wt % water. Extrapolation of the curve beyond 60 to 100 wt % water gives a value for pure liquid water consistent with the published values of $\tau_3 = 1.8$ ns.[34,35]

The water enters initially as molecular water and hydrogen bonds to the hydroxyl groups. Calculation of the water content for one water molecule per hydroxyl group indicates that the first 29 wt % of water is in this strongly bound state.[22] The increase in water content in the amorphous region from 4.5 to 8 wt %, however, does not appear to alter the average electron density "seen" by the oPs localized in free volume cavities. This result may indicate that either the oPs localizes in sites that are sufficiently removed from the bonding sites of the first 8 wt % of water so that the local electron density at the oPs sites is not altered (in other words the oPs does not localize near hydroxyl groups) and/or the water does not alter the mean cavity radius (average for all the free volume cavities probed) within the standard deviation of the $\tau_3$ component (0.03 ns) for the first 8 wt % of water.

After approximately 8 wt % water addition, the proximity and concentration of the strongly bound water molecules must be such that the local electron density seen by the oPs decreases (as illustrated in Figure 3 by the increase in $\tau_3$ in region II). This increase in mean free volume cavity radius is only likely to occur if the water molecules are expanding the inter- or intrachain distances. Density measurements of PVOH films as a function of water content[36] indicate an initial increase in density due to the filling of free volume cavities with no swelling of the polymer, followed by a decrease in density due to hydrogen bond disruption and gradual swelling of the polymer. These density results support the postulation that the $\tau_3$ increase reflects larger free volume cavities due to swelling of the polymer. The disruption of inter- and intrachain hydrogen bonding increases polymer mobility, resulting in a decrease in $T_g$. Figures 1 and 2 show that samples with water content >10 wt % are above $T_g$ at the PALS measurement temperature (22 °C), so the increase in $\tau_3$ observed from region I to II could be an indication of the glass transition. PALS studies of polymers and plasticizers have shown an increase in $\tau_3$ as the polymers go from the glassy to the rubbery state.[37] Hence, the $\tau_3$, $T_g$, and density behaviors for increasing nonfreezable water contents (up to 30 wt %) suggest plasticization of the polymer by swelling. The variation in $\tau_3$ for water contents greater than 30 wt % is now addressed.

Figure 3 illustrates the variation of $\tau_3$ for the amorphous polymer/water system as a whole. If it is assumed that the observed value of $\tau_3$ may be taken as the sum of the weighted contributions from the polymer and water, with the measured value of oPs lifetime biased increasingly toward that of pure water, the individual contributions from water and polymer to $\tau_3$ for the system can be calculated from

$$\tau_{3(\mathrm{net})} = A\tau_{3(\mathrm{water})} + (1 - A)\,\tau_{3(\mathrm{polymer})}, \qquad (2)$$

where $A$ is the amount of free water in the system (for reasons discussed directly) and $\tau_{3(\mathrm{net})}$, $\tau_{3(\mathrm{water})}$, and $\tau_{3(\mathrm{polymer})}$ represent the mean oPs pickoff lifetimes for the system (measured), water, and polymer, respectively.

To separate the individual contributions, it must be considered that oPs can annihilate in water by the "bubble" mechanism,[38] whereby it is proposed that the oPs effectively blows a bubble around itself before annihilating by the pickoff mechanism and can therefore do this only when there is a sufficient amount of water to completely surround it, i.e. when the water forms clusters. According to the bubble model, the value of $\tau_3$ in free water reflects the cohesive energy density of the liquid rather than the free volume cavity size (as in a polymer). This model also implies that the molecular, or nonfreezing, water has insufficient aggregate size to allow oPs annihilation associated solely with bound water. Other workers have postulated that the bound water effectively acts as a filler in the polymer free volume cavities, decreasing the amount of free volume in the system.[39,40] Therefore, in eq 2, "$A$" represents the amount of free water in the amorphous regions of the system, and not the total water content. Equation 2 can be applied to data recorded for water contents above 30 wt % to deduce the nature of the variation of the relative size of the free volume cavities in the polymer, removing the direct contribution to the oPs lifetimes from annihilations in the water clusters within the polymer. Figure 4 shows the results of this separation of contributions, including the behavior of the system as a whole for comparison. Figure 4 illustrates that the mean free volume cavity size in the polymer increases most significantly during the stages of water absorption where the water in the polymer is contained as nonfreezing water (<30 wt %). Using a semiempirical model[27] to convert $\tau_3$ to a cavity radius and spherical cavity volume, $V_h$, indicates an increase in free volume cavity size from 0.04 to 0.10 nm$^3$ as the polymer goes from 5.3 wt % water to 30 wt % water. Johnson et al.[41] have suggested that free water can only exist in the polymer when there is a sufficient free volume size available. In the present case, that sufficient size would correspond to 0.10 nm$^3$ and a total of three to four water molecules to fill that space and constitute free water. At water concentrations where the polymer begins to contain free water (>30 wt %), the mean free volume cavity size has almost reached its maximum value, and the curve begins to flatten out.

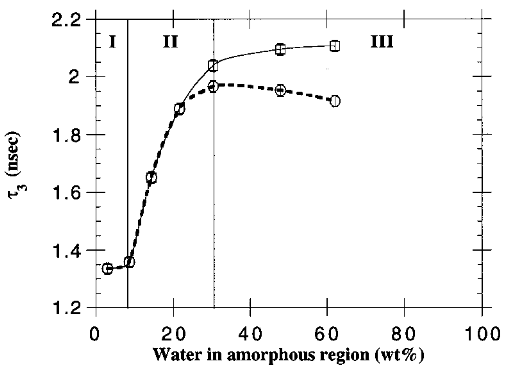

**Figure 4.** The variation in oPs pickoff lifetime with water content for the PVOH component of the PVOH/water system, calculated from eq 2. ☐ represents calculated data for the polymer component, and ○ represents the measured data for the system, included for comparison.

The sigmoidal variation in $\tau_3$ with water content shown in Figure 4 is similar to the form of the variation of $\tau_3$ with temperature in PVOH reported by other workers.[42,43] The similarity in the form of the temperature and water curves may be expected, considering that a major contributor to the increase in free volume cavity size in PVOH is the disruption of hydrogen bonds. As the temperature is raised such that there is sufficient thermal energy in the system to overcome hydrogen bonding, the amount of free volume in the polymer would be expected to increase accordingly.[42] In the present work, water addition, rather than thermal energy, disrupts the hydrogen bonding and swells the polymer, thus enlarging the free volume cavities. The equivalence between the action of water and temperature in PVOH is limited by their very different effects on the crystallinity of the polymer.[44] Water addition reduces crystallinity, while thermal energy (over a range of crystallization temperatures) increases crystallinity. As mentioned previously, the value of $\tau_3$ has been shown to be independent of degree of crystallinity in numerous polymers while the value of $I_3$ reflects the degree of crystallinity.[27,31,32] The variation in $I_3$ (related to free volume concentration) with water content is now addressed.

The variation of $I_3$ with water content, corrected in accordance with the findings of other workers,[31] is shown in Figure 5. As with Figure 3, the form of the curve in Figure 5 is such that it may be divided into three distinct regions. Region I shows that, at low water contents, the $I_3$ values are essentially constant. In region II, $I_3$ decreases markedly up to a water content of approximately 30 wt %, after which the curve increases (region III).

As in the case of $\tau_3$, region I (including water contents up to approximately 8 wt %) corresponds to an essentially constant value of $I_3$, indicating that the relative number of oPs pickoff annihilations in the amorphous region is unchanged. Figure 5 suggests that in the early stages of water absorption either the nonfreezable water

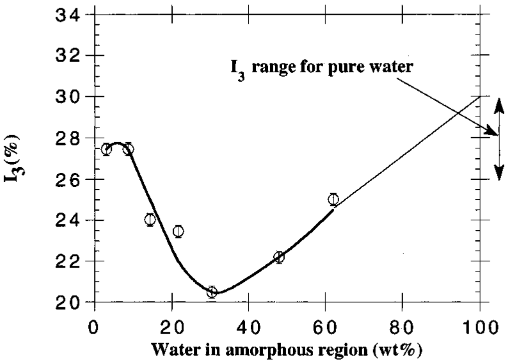

**Figure 5.** Measured oPs pickoff intensities for the PVOH/water system as a function of water content.

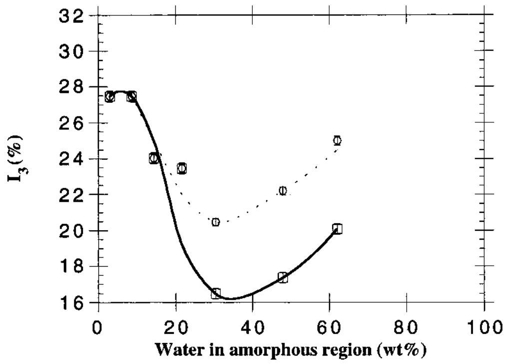

**Figure 6.** oPs pickoff intensities in PVOH as a function of water content. □ represents calculated data for the polymer component, and ○ represents the measured data for the system, included for comparison.

partially occupies free volume cavities such that the relative number of cavities available for localization of oPs does not change or the initial nonfreezable water occupies sites unfavorable for oPs localization (such that these sites are not probed by oPs). Hence the $\tau_3$ and $I_3$ results for water contents less than 8 wt % suggest that the initial nonfreezing water can act as a plasticizer without appreciably changing the relative size or number of free volume cavities probed by oPs. Density measurements,[36] however, indicate an initial increase in density. Thus it appears that nonfreezable water can increase the density of PVOH without decreasing the free volume as measured by PALS. The addition of 8 wt % nonfreezable water results in a decrease in $T_g$ from 85 to 30°C. In these PVOH films the results indicate that the initial decrease in $T_g$ occurs due to interuption of intrachain hydrogen bonding without the increase in free volume normally associated with plasticization. A greater than additive change in density while $T_g$ decreases due to initial water absorption has also been observed in polyamides.[40]

Region II of Figure 5, between approximately 8 and 30 wt % water, shows that the relative number of free volume cavities decreases with increasing water content before increasing gradually in region III (corresponding to water contents in excess of 30 wt %). The decrease in the value of $I_3$ in region II seems initially to be at odds with the contention that water acts to plasticize PVOH. However, the data contained in Figure 5 are corrected for crystallinity and consider only the oPs annihilations in the amorphous regions of the polymer. It is shown elsewhere[20] that crystalline regions within the polymer are gradually destroyed by attack from water. The dissolving crystallites are constrained on one side by intact crystallites and on the other by swollen amorphous region. It is suggested that these dissolving crystalline regions pass through a state of order intermediate between that of planar zigzag crystallite and completely random amorphous (perhaps a helical configuration), before assuming completely amorphous configuration. Hence an increasing proportion of the amorphous region (the prior crystalline regions) is of a higher structural order (greater packing efficiency). This higher structural order may effectively exclude these prior crystalline regions from the same degree of positron sampling (in terms of oPs pickoff annihilations) as the amorphous material. The crystalline correction to $I_3$ considers these prior crystalline regions to be amorphous in nature, and the net effect is a lower proportion of oPs annihilations occurring by pickoff in the amorphous region and a corresponding decrease in the value of $I_3$. A decrease in $I_3$ with temperature is also shown in the data of Suda et al.[42] and Mohamed et al.[43] for PVOH. This decrease may be due to increasing crystallinity at the temperatures above $T_g$ in the amorphous regions or due to the increased molecular mobility above $T_g$ causing the free volume cavities to appear occupied due to segmental mobility at frequencies $>10^9$ Hz. The latter explanation is also a possibility in the present work. Forsyth et al.[29] have shown that $I_3$ can decrease due to plasticizer addition since the plasticizer effectively occupies (from the oPs viewpoint) dynamic free volume at frequencies $>10^9$ Hz.

At approximately 30 wt % water (region III), the vast majority of crystallinity has been destroyed, and water begins to form in the polymer as free water. The oPs annihilates in free water in the polymer as well as in the polymer free volume. As the free water content increases in region III, more water is available to contribute to the overall $I_3$ value. The net $I_3$ value is biased increasingly toward that of pure water (28 ± 2%)[35,45] in much the same way as in the case of $\tau_3$ in region III of Figure 3. Additionally, during this stage of water absorption, it is proposed that the prior crystalline regions with intermediate order have become less constrained and have adopted a completely random configuration. It is possible that an increase in the relative amorphous concentration of the polymer also contributes to the overall increase in the value of $I_3$ in region III.

In a similar manner to that described for $\tau_3$ in eq 2, the individual contributions to $I_3$ of the polymer and free water can be calculated. The result, illustrated in Figure 6, shows that the value of $I_3$ for the polymer increases as free water increases (>30 wt %, region III). This result supports the postulation that, as the prior crystalline regions convert from the intermediate order described above and adopt a completely amorphous structure, the effective number of free volume sites increases.

The PALS results can be compared to those of other researchers who have studied water absorption in molecular solids. The observed $\tau_3$ variation with water is similar in nature to that reported in DNA,[45,46] proteins,[47] nylons,[39,48] and other polyamides.[40] These polymer systems exhibit two-stage behavior approximating that observed in regions I and II as defined in this study. Only DNA[45] exhibits behavior similar to that defined in this study by region III, where the observed $\tau_3$ decreases gradually after reaching a maximum value in the latter stages of region II. PALS data were collected in DNA over the entire range of water contents up to and including 100% water.[45] Other

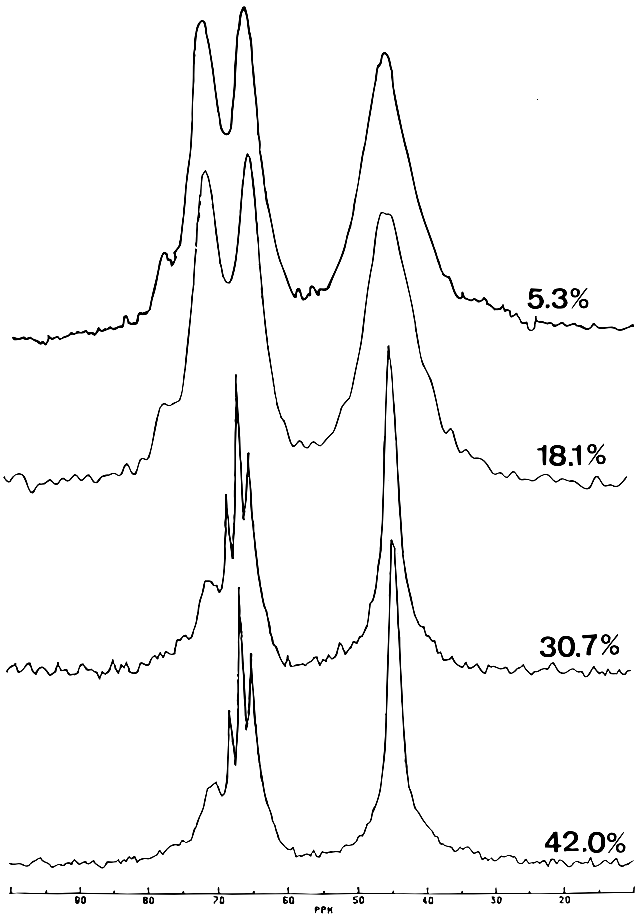

**Figure 7.** Selected $^{13}C$ spectra of PVOH films at varying water content. Chemical shifts are relative to TMS standard.

workers have reported results in systems with a maximum level of hydration below 25%, such that there may be insufficient free water contained in these systems to allow for the formation of water clusters in which the oPs can localize. The data presented for DNA[45] exhibit equivalent trends to those observed in this study for both $\tau_3$ and $I_3$, with both parameters at high water contents gradually approaching the respective values reported for pure water.

Solid state NMR can be used to verify the plasticizing effects of water by examining the polymer mobility. The changing nature of the $^{13}C$ spectrum as a function of water content is shown in Figure 7. The spectra initially reveal four peaks which remain essentially unchanged for water contents up to approximately 30 wt %. The lowest chemical shift peak at 44.7 ppm is attributed to the $CH_2$ carbon, and the triplet peaks at 64.6, 70.6, and 77.0 ppm are associated with the CHOH carbon.[49−51] At approximately 30 wt % water, all peaks narrow significantly, and the triplet peaks abruptly collapse into a different configuration and exhibit a fourth peak at 66.6 ppm.

The dry samples show a broad peak at a chemical shift of 44.7 ppm, and the components of the triplet are broader, more widely spaced and located at higher frequency than found for the CHOH carbon resonance in the solution spectrum.[52] The broader nature of the triplet peaks, wider spacing and shift to higher frequency are due to the presence of intramolecular hydrogen bonding between OH groups on the PVOH chain molecules. The peaks, in order of increasing shift, correspond to OH groups hydrogen bonded to zero, one, and two nearest neighbor hydroxyl groups.[49,51] Such a bonding environment is experienced in syndiotactic, atactic, and isotactic PVOH sequences, respectively, as discussed elsewhere.[51]

The evolution of the $^{13}C$ spectra of PVOH as a result of water addition reveals a trend in behavior that is essentially two-stage in nature. The $^{13}C$ spectra remain essentially identical for water contents up to about 30 wt %. At a water content of 30 wt %, the triplet has collapsed into a spectrum closely resembling that of the solution spectrum. The sharp peaks of the 30 wt % spectrum indicate solution-like behavior, arising from large scale free-rotation about the C−C covalent bonds. A necessary condition for this free rotation is disruption of the vast majority of hydrogen bonds (both inter- and intramolecular). For water contents greater than 30 wt %, the intensities of the peaks associated with the CHOH carbons[49−51] in isotactic (two nearest neighbor OH hydrogen bonds) and atactic (one nearest neighbor hydrogen bond) sequences are significantly reduced, and the triplet peaks at high chemical shift, which are characteristic of the solid state, are replaced by narrow, closely spaced and lower chemical shift triplet peaks, characteristic of the solution spectrum and the rubbery material. Hence the solid state NMR data indicate that at approximately 30 wt % water, the vast majority of the hydrogen bonding has been destroyed by the water, allowing greater macromolecular mobility. Similar trends have been reported in the solid state NMR spectra of dry PVOH as a function of temperature.[50] The similarities between the NMR spectra at high temperatures and those at high water contents is further evidence of the proposed temperature/water content equivalence for the PVOH system discussed previously with reference to PALS data. Again, this equivalence is limited by the difference in the action of water and temperature on crystallinity. The disruption in hydrogen bonding and the increase in mobility (as indicated by NMR data) are gradual with increasing temperature due to the crystals[44,52] and abrupt (at 30 wt % water as indicated by NMR data) with increasing water content and lack of crystallinity.[44]

On the basis of the assumption of a single water molecule hydrogen bonding to each available OH group, one can calculate that complete hydroxyl hydrogen bond saturation occurs at a level of 29 wt % water. This value compares well with the water content required (∼30 wt %) to cause the collapse of the $^{13}C$ spectra into the solution-like spectrum. This value also compares well with the maximum amount of nonfreezing water that is proposed[20] to be intimately associated with the polymer chains.

It is interesting to note that the PALS free volume data indicate an increasing free volume cavity size between approximately 8 and 30 wt % water. The DMA data indicate that the $T_g$ is lowered to room temperature (22 °C) with the addition of 10 wt % water; hence, the majority of the free volume cavity size increase takes place once the polymer enters the rubbery state. However, the $^{13}C$ NMR data show no appreciable change for water contents below 30 wt %. The gradual increase in free volume cavity size and decrease in $T_g$ with increasing molecular, or nonfreezing, water content can be contrasted with the abrupt line narrowing of the $^{13}C$ peaks at approximately 30 wt % water. It is postulated that the PALS parameters are sensitive to the gradual effect of molecular water on the inter- and intrachain separation and the chain conformations while the $^{13}C$ NMR is sensitive to the complete disruption of interand intrachain hydrogen bonding, apparently requiring full hydrogen bond saturation to achieve the free chain motion necessary to yield a liquid-like spectrum. The experimental results indicate that maximum main chain mobility is reached only after a certain level of plasticization is achieved, defined at the point where saturation of hydroxyl bonds by the water molecules has occurred and also by the point of maximum free volume cavity size.

## Conclusions

The data in this investigation support the contention that water contributes to the plasticization of PVOH in a 2-fold manner. The PALS data indicate that water addition increases the size of free volume cavities of the polymer. The solid state NMR data indicate that water provides a lubrication effect that promotes chain mobility and disrupts hydrogen bonding, removing further barriers to bond rotation and chain mobility. The DMA data show that water content results in a marked decrease in the $T_g$ of the polymer.

The PALS and NMR data indicate that, of the various states of water present in PVOH, the nonfreezing water contributes most to the plasticization process. The freezing water is present at water contents greater than approximately 30 wt %. The critical experimental value of 30 wt % water corresponds well with the theoretical water content for complete hydroxyl site saturation (and therefore also theoretical maximum nonfreezing water content). Hence, the nonfreezing water is responsible for the majority of the plasticization (increase in free volume and chain mobility) indicated by the PALS and NMR data.

Both the $^{13}$C spectra and the PALS parameter variations with water content in this investigation are similar in form to the corresponding variations with temperature reported in the literature,[41,42,51] indicating that increasing temperature has an effect equivalent to increasing water content in PVOH. This investigation has shown that water disrupts hydrogen bonding and creates free volume in the polymer, increasing the mobility of the polymer chains and plasticizing the system in a manner similar to that of increased thermal energy provided by raising the temperature. It was noted, however, that the equivalent effects of water and temperature are limited by the fact that water can decrease the degree of crystallinity while temperature can increase the degree of crystallinity.[44]

**Acknowledgment.** Insightful comments by the reviewers of the original version of the manuscript are appreciated. The support of the Australian Wool Research Council and the Australian Research Council is gratefully acknowledged. R.M.H. and A.J.H. are grateful to Dr. K. J. Heater of METSS, Columbus, OH, for helpful discussions and for providing unpublished data.

## References and Notes

(1) Finch, C. A., Ed. *Polyvinyl Alcohol*; Wiley: London, 1973.
(2) Finch, C. A., Ed. *Properties and Applications of Polyvinyl Alcohol*; S. C. I. Monograph No. 30; Society of Chemical Industry: London, 1968.
(3) Pritchard, J. G. *Poly(vinyl Alcohol), Basic Properties and Uses*; Macdonald Technical and Scientific: London, 1970.
(4) Sakurada, I. *Polyvinyl Alcohol Fibres*; International Fiber Science and Technology Series; 6; Marcel Dekker, Inc: New York, 1985.
(5) Peppas, N. A.; Merrill, E. W. *J. Appl. Polym. Sci.* **1976**, *20*, 1457.
(6) Peppas, N. A. *Makromol. Chem.* **1977**, *178*, 595.
(7) Peppas, N. A.; Hansen, P. J. *J. Appl. Polym. Sci.* **1982**, *27*, 4787.
(8) Stauffer, S. R.; Peppas, N. A. *Polymer* **1992**, *33* n18, 3932.
(9) Higuchi, A.; Iijima, T. *Polymer* **1985**, *26*, 1207.
(10) Zhang, W-Z.; Satoh, M.; Komiyama, J. *J. Membrane Sci.* **1989**, *42*, 303.
(11) Mrkvicková, L. *Colloid Polym. Sci.* **1989**, *267*, 28.
(12) Prokopova, E. and Schmidt, P. *Eur. Polym. J.* **1989**, *25*, 1319.
(13) Prokopova, E.; Biros, J.; Lednicky, F.; Sundelöf, L-O. *Eur. Polym. J.* **1988**, *24*, 61.
(14) Cebe, P.; Grubb, D. T. *J. Mater. Sci.* **1985**, *20*, 4465.
(15) Garret, P. D.; Grubb, D. T. *J. Mater. Sci.* **1986**, *1* (6) 561.
(16) Garret, P. D.; Grubb, D. T. *J. Polym. Sci. B. Polym. Phys.* **1988**, *26*, 2509.
(17) Garret, P. D.; Grubb, D. T. *Polym. Commun.* **1988**, *29*, 60.
(18) Van Gurp, M. *Intern. J. Polym. Mater.* **1993**, *22*, 219.
(19) Conibeer, C. J.; Lin, K. Z.; Edward, G. H. *Mater. Forum* **1990**, *14*, 224.
(20) Hodge, R. M.; Edward, G. H.; Simon, G. P. *Polymer* **1996**, *37*, 1371.
(21) Nakamura, K.; Hatakeyama, T.; Hatakeyama, H. *Polymer* **1983**, *24*, 871.
(22) Hodge, R. M. Ph.D. Dissertation, Monash University, Melbourne, Australia, 1994.
(23) Puff, W. *Comput. Phys. Commun.* **1983**, *30*, 359.
(24) Gordon, M.; Taylor, J. S. *J. Appl. Chem.* **1952**, *2*, 493.
(25) Sugisaki, M.; Sugg, H.; Seki, S. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2591.
(26) Argell, C. A.; Sare, J. M.; Sare, E. J. *J. Phys. Chem.* **1978**, *82*, 2529.
(27) Jean, Y. C. *Microchem. J.* **1990**, *42*, 72.
(28) Brandt, W.; Berko, S.; Walker, W. W. *Phys. Rev.* **1960**, *120*, 1289.
(29) Forsyth, M.; Meakin, P.; MacFarlane, D. R.; Hill, A. J. *J. Phys. Condens. Matter* **1995**, *7*, 7601.
(30) Mogensen, O. E., In *International Symposium on Positron Annihilation Studies of Fluids*; Sharma, S. C., Ed.; World Scientific: Singapore, 1988; p 418.
(31) Simon, G. P.; Zipper, M. D.; Hill, A. J. *J. Appl. Polym. Sci.* **1994**, *52*, 1191.
(32) Xie, L.; Gidley, D. W.; Hristov, H. A.; Yee, A. F. *Polymer* **1994**, *35*, 14.
(33) Zipper, M. D.; Simon, G. P.; Cherry, P.; Hill, A. J. *J. Polym. Sci. B. Polym. Phys.* **1994**, *32*, 1237.
(34) Green, R. E.; Bell, R. E. *Can. J. Phys.* **1958**, *36*, 1684.
(35) Fabri, G.; Gemagnoli, E.; Querica, I. F.; Turrisi, E. *Nuovo Cimento* **1962**, *30*, 21.
(36) Iwadere, Y, *Kobunshi Ronbunshu* **1977**, *34*, 475.
(37) Elwell R. J.; Pethrick R. A. *Eur. Polym. J.* **1990**, *26*, 853.
(38) Ferrell, R. A. *Phys. Rev.* **1958**, *110*, 1355.
(39) Heater, K. J., unpublished data, 1991.
(40) Welander, M.; Maurer, F. H. J. *Mater. Sci. Forum.* **1992**, *105−110*, 1815.
(41) Johnson, G. E.; Bair, H. E.; Matsuoka, S.; Anderson, E. W.; Scott, J. E. In *Water in Polymers*; ACS Books: Washington DC, 1980; Chapter 27.
(42) Suda, Y.; Uedono, A.; Ujihira, Y. *Mater. Sci. Forum.* **1992**, *105−110*, 1721.
(43) Mohamed, H. F. M.; Ito, Y.; El-Sayed, A. M. A.; Abel-Hady, E. E. *Polymer* **1996**, *37*, 1529.
(44) Hodge, R. M.; Bastow, T. J.; Hill, A. J in *Preprint of the 4th Pacific Polymer Conf*erence; Baker, M. T., Ed.; Pacific Polymer Federation c/o ACS: Washington, DC, 1995; p 244; full manuscript in preparation.
(45) Warman, J. M.; Eldrup, M. *Biopolymers* **1986**, *25*, 1865.
(46) Gregory, R. B.; Chai, K. J.; Su, W. *Mater. Sci. Forum.* **1992**, *105−110*, 1577.
(47) Gregory, R. B.; Chai, K. J. *J. Phys. Suppl J.* **1993**, *3*, 305.
(48) Singh, J. J.; St. Clair, T. L.; Holt, H. H.; Mock, W., Jr. *Nucl. Instrum. Methods Phys. Res.* **1984**, *221*, 427.
(49) Terao, T.; Maeda, S.; Saika, A. *Macromolecules* **1983**, *16*, 1535.
(50) Horii, F.; Ito, T.; Kitamaru, R. *Polym. Prepr.* **1988**, *29*, 27.
(51) Horii, F.; Hu, S.; Ito, T.; Odani, H.; Matsuzawa, S.; Yamaura, K. *Polymer* **1992**, *33*, 2299.
(52) Wu, T. K.; Ovenall, D. W. *Macromolecules* **1973**, *6*, 582.

MA951073J