# Investigation of Hydrogen-Bonding Structure in Blends of Poly(*N*-vinylpyrrolidone) with Poly(vinyl acetate-*co*-vinyl alcohol) Using Positron Annihilation

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ABSTRACT: The effect of hydrogen bonding on the free volume in polymer blends is reported using infrared spectroscopy and positron annihilation lifetime spectroscopy (PALS). The system under investigation comprised blends of poly(*N*-vinylpyrrolidone) with poly(vinyl acetate-*co*-vinyl alcohol) containing varying ratios of vinyl acetate:vinyl alcohol. Infrared spectroscopy revealed the presence of hydrogen bonding in the blends as a shift to lower wavenumbers of the pyrrolidone carbonyl and the alcohol hydroxyl bands. PALS revealed an increase in free volume, in comparison to the individual components, of the polymer blends with increase in the hydrogen bonding, but this is followed by an unexpected “collapse” of the network structure above a critical value of hydrogen bonding.

## Introduction

In recent years considerable progress has been made in recognizing the importance of specific interactions in the phase behavior of polymer blends, and one of the most important intermolecular interactions is the hydrogen bond between a proton donor and proton acceptor. The hydrogen bond can be responsible for the miscibility of otherwise incompatible polymer blends, as well as enhancing the miscibility of partially miscible systems.[1−6] Altering the degree of intermolecular hydrogen bonding in a polymer blend might also be expected to change the free volume of the blend. Previous work in this group has shown that increasing the strength of hydrogen-bonding interactions in polymer blends produces changes in the network structure.[7]

A recently developed technique that may be used to probe free volume in polymers is positron annihilation lifetime spectroscopy (PALS).[8−11] This measures the time difference between the emission of a positron from a radioactive source and its subsequent annihilation. The lifetime of a positron at any particular point in a material is inversely proportional to the electron density at that point, i.e., on the probability of coupling with an electron to form either an orthopositronium atom (o-Ps) or a parapositronium atom (p-Ps). PALS spectroscopy effectively quantifies three characterstic lifetimes: $\tau_1$ attributable to p-Ps annihilation, $\tau_2$ due to annihilation of free positrons, and $\tau_3$ the lifetime of o-Ps. The relatively long-lived o-Ps tend to localize in cavities where electron density, and hence chance of annihilation, is relatively low, and so $\tau_3$, along with the corresponding lifetime intensity $I_3$ which is proportional to the number of annihilations, may be used to estimate the mean size and relative number of free volume cavities in a polymer sample.

There are numerous studies of polymer blends using positron annihilation, and these show that changing the ratio of the blend components can have a marked effect on the free volume of the blend. Free volume in blends has been observed to change linearly with changing polymer ratio[12,13]as well as showing positive[7,14,15] and negative[16−18] deviations from linearity. There has been no study, so far, that has used PALS to examine the free volume change of a polymer blend with varying amounts of hydrogen bonding. In this work PALS is used to measure the free volume in polymer blends in which the amount of hydrogen bonding is changed by varying the relative content of hydroxyl groups. The system investigated was poly(*N*-vinylpyrrolidone) (PVP) blended with random copolymers of vinyl acetate and vinyl alcohol (PVAc(*x*%)VA) in which the mole percent of vinyl alcohol content is indicated by *x*.

## Experimental Section

**Materials.** Poly(*N*-vinylpyrrolidone) (PVP) and poly(vinyl acetate) (PVAc) were obtained from BDH and were used as received. Molecular weights were 44 000 and 45 000 g mol$^{-1}$, respectively. Poly(vinyl acetate) samples hydrolyzed to varying degrees were obtained from the Harco Chemical Co. Ltd. Samples with degrees of hydrolysis 20% and 35% were supplied as 25% w/v solutions in methanol and were dried under vacuum at 40 °C prior to use. A sample with 55% hydrolysis was obtained as a dispersion of 40% weight in water and was dried under vacuum at 40 °C prior to use. A sample with 85% hydrolysis was obtained as a solid and was used as received. All copolymers were stated by the supplier to be random. Blends coreresponding to 50/50 wt % were prepared by melt blending the components 50 K above their $T_g$ values in a die under 10 tons static pressure. The resultant sample disks were 14 mm in diameter and had a thickness of between 1 and 2 mm. For each PALS measurement two disks were prepared and placed on either side of the positron source.

**Positron Annihilation Lifetime Spectroscopy.** The positron lifetime measurements were obtained using a fast−slow coincidence system employing time-to-pulse height conversion and multichannel analysis.[19] The PALS system uses cylindrical (40 mm diameter × 15 mm thick) $BaF_2$ scintillators arranged at 90° to each other to avoid pulse pile-up problems. The front and sides of the scintillators were wrapped with PTFE tape; this has high UV reflectance and improves time and energy resolution. A count rate of 150−300 cps was

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**Table 1. FTIR Peak Positions, $T_g$ Values, and Positron Lifetimes for Copolymers and Blends**

| copolymer/blend | carbonyl (cm$^{-1}$) | | hydroxyl (cm$^{-1}$) | $T_g$/K | lifetime/ns 303 K |
|---|---|---|---|---|---|
| | acetate | pyrrolidone | | | |
| PVAc | 1737 | | | 312 | 1.89 |
| PVP | | 1679 | | 428 | 1.99 |
| PVAc(20%)VA | 1737 | | 3462 | 318 | 1.79 |
| PVAc(35%)VA | 1737 | | 3396 | 320 | 1.99 |
| PVAc(55%)VA | 1737 | | 3392 | 322 | 1.75 |
| PVAc(85%)VA | 1737 | | 3350 | 337 | 1.77 |
| PVP/PVAc | | | | 333 | 1.93 |
| PVP/PVAc(20%)VA | 1738 | 1675 | 3455 | 342 | 2.02 |
| PVP/PVAc(20%)VA | 1738 | 1763 | 3388 | 356 | 2.08 |
| PVP/PVAc(55%)VA | 1737 | 1644 | 3386 | 361 | 1.86 |
| PVP/PVAc(85%)VA | | | | 361 | 1.86 |

achieved with a $^{22}$Na source and an instrument resolution of 220−240 ps for a 50 $\mu$Ci source. Benzophenone was used to determine the resolution and source correction. The lifetime components were calculated using the program POSITRONFIT.[20] A fixed analysis was used, with $\tau_1$ equal to 0.125 ns (p-Ps), $\tau_2$ equal to 0.360 ns (free e$^+$), and a ratio of $I_3/I_1$ at 3:1. Prior to measurements all samples were heated to above their glass transition temperatures to erase previous thermal history.

**Differential Scanning Calorimetry.** Glass transitions ($T_g$) were determined by differential scanning calorimetry (DSC) using a Perkin-Elmer Pyris 1 calorimeter. The values reported are enthalpic $T_g$s, averaged over five scans, obtained by integration of the $C_p$ curves.[21] The point of intersection of the liquid and glassy enthalpy lines extrapolated into the transition region is taken to be a more reliable measure of the glass transition since it should be independent of scan rate and sample size.

**Infrared Spectroscopy.** Infrared spectra were recorded on a Perkin-Elmer 1720X FTIR spectrometer in transmission mode. Samples were cast from 1 wt % solutions in methanol onto NaCl disks and dried at 350 K prior to examination.

## Results and Discussion

The infrared data establish the presence of hydrogen bonding in the blends, although spectra were unobtainable for the PVP/PVAc(85%)VA blend because of the insolubility of the sample. The positions of the acetate and the pyrrolidone carbonyl bands, and the hydroxyl bands of the copolymers and blends, are collected in Table 1, along with the $T_g$ values. The entries in this table show that the acetate carbonyl position changes very little (at most ~1 cm$^{-1}$), either in the copolymer series or in the blends. This band does, however, broaden on the low frequency side as the proportion of vinyl alcohol in the copolymer increases, indicating that an increasing fraction of the carbonyls are involved as hydrogen bond acceptors. The pyrrolidone carbonyl band, on the other hand, shifts measurably to lower frequency in the blend series, in line with the OH content of the blends.

Hydroxyl bands in condensed systems tend to be broad, but nevertheless will also respond to their hydrogen-bonding environment. In the copolymers this band shows the expected shift to lower wavenumbers as the number of OH groups in the system increases, indicating a corresponding increase in the extent of association via hydrogen bonding. Blending the copolymers with PVP leads to a further shift to lower wavenumbers at each composition of ~7 cm$^{-1}$. This, along with the displacement of the pyrrolidone carbonyl position, indicates that PVP, acting as a proton acceptor, is hydrogen bonded to the copolymer in this blend system to a significant degree.

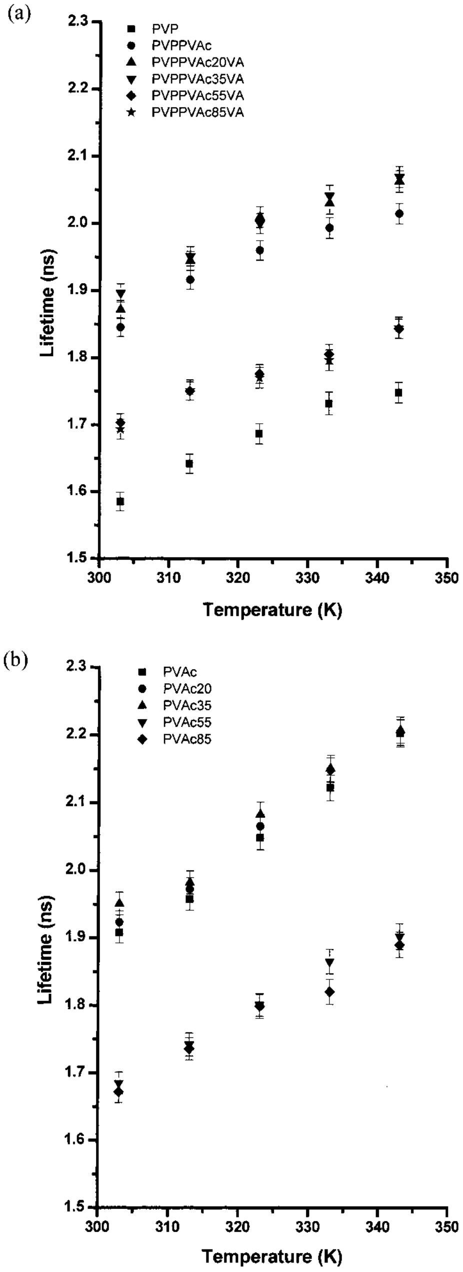

**Figure 1.** Positron annihilation lifetime ($\tau_3$) as a function of temperature for (a) PVP and polymer blends and (b) PVAc and VAc/VA copolymers. Key is given in the figure.

PALS spectra were measured over the temperature range 303−343 K, and the results are shown in Figure 1. For both the polymers, and the blends, an increase in temperature brings about longer positron lifetimes corresponding to a free volume increase. A possible change of slope, which could be associated with $T_g$, is discernible only in the data for PVAc, PVAc(20%)VA, and PVAc(35%), but otherwise it is impossible to determine $T_g$ positions over the narrow temperature range covered here. Positron lifetimes for the blends and the copolymer series are compared at 303 K in Figure 2, and the glass transition temperatures are shown in Figure 3. The glass transition of poly(vinyl alcohol) is not calorimetrically detectable in this highly crystalline polymer, and the point shown in Figure 3b refers to the value of 358 K obtained by dynamic mechanical measurement.[22] On this basis, the copolymer $T_g$s exhibit a negative deviation from linearity. The blends of the

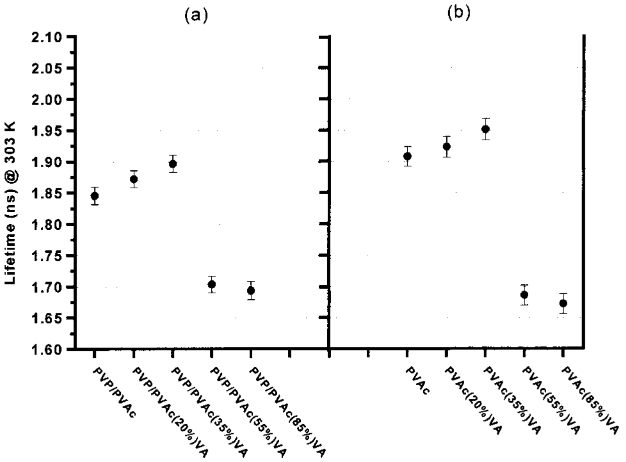

**Figure 2.** Positron annihilation lifetimes ($\tau_3$) at 303 K for (a) polymer blends and (b) VAc/VA copolymers.

vinyl acetate–vinyl alcohol copolymers with PVP are single phase at the level of discrimination afforded by DSC, and their $T_g$–composition behavior, shown in Figure 2a, exhibits a positive departure from linearity, although here we must extrapolate to an estimated PVP/PVA blend $T_g$ in the region of 360 K.

Deviations of the glass transition from linearity, in either blends or copolymers, are ascribed to relatively lower, or higher, barriers to main chain mobility than expected from simple additivity of the components. The opposed trends, shown in Figure 3, emphasize that a balance of structural effects *and* intermolecular interactions must be considered to explain such behavior since enhanced hydrogen bonding alone would be expected to cause the contrary effect to that exhibited by the copolymer series. In point of fact, the copolymers show what might be termed “normal” behavior in that juxtaposition of structurally dissimilar repeat units usually precludes efficient chain packing, bringing about a consequent reduction in intermolecular restrictions to cooperative chain motion. One might additionally argue that intrinsic rotation barriers are also eased as the relatively bulky acetate side groups are replaced by hydroxyls. The concomitant increase in hydrogen bonding in the copolymer series is observably unable to counter such changes in chain rigidity in this case.

Blend compatibility is somewhat different since this requires the formation of favorable heterocontacts between the components. Induced heterocontacts are indeed evidenced by infrared spectroscopy, and these, adopting the conformational entropy view of polymer miscibility,[23] must be accompanied by local interchain ordering and restricted mobility. This is then reflected by an increase of the blend $T_g$ above that predicted by additivity to an extent consequent on the nature and strength of the interaction energy. From the hydroxyl and the pyrrolidone carbonyl band shifts, the overall hydrogen-bonding interactions in the blend system are certainly stronger than those of the copolymers, and these undoubtedly drive the system to miscibility and result in the observed $T_g$ behavior.

Similar behavior has been observed in other polymer blend systems[24–26] where there are strong hydrogen bond interactions between the components. In the case of the blends studied here, the decisive contribution to the changing glass transition is the decreased chain mobility caused by the increasing H-bond cross-linking.

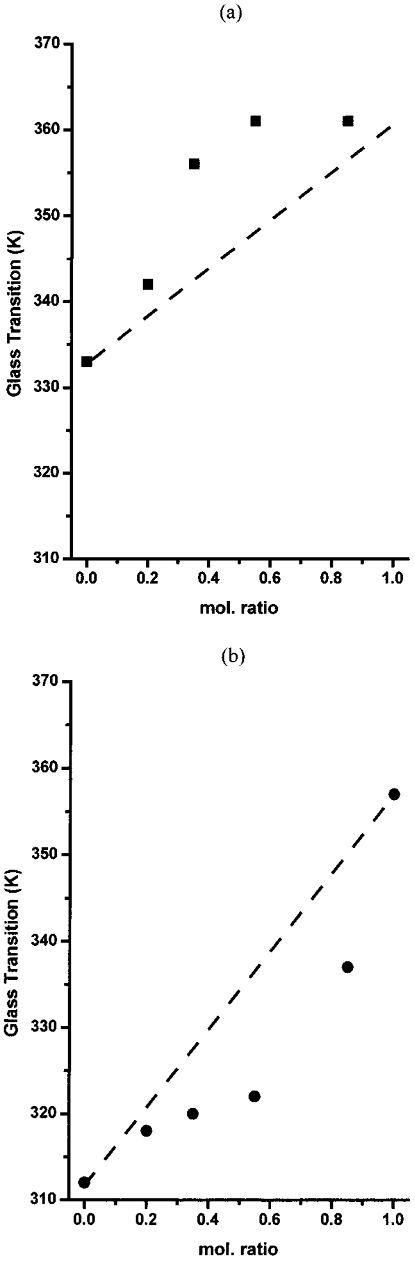

**Figure 3.** Glass transition temperatures for (a) polymer blends and (b) VAc/VA copolymers plotted against copolymer composition. The basis for the linear interpolation lines is given in the text.

The changes in free volume that can be detected by PALS are of lesser importance than the changes in mobility and are not reflected in the observed monotonic increase in $T_g$.

Related mixtures of vinyl acetate–vinyl alcohol copolymers with poly(*N*-vinylpyridine),[27] poly(*N*,*N*-dimethylacrylamide),[28] and poly(ethyoxazoline)[29] are also miscible, whereas those with with PVAc and PVA homopolymers are not. Here hydrogen bonding is also proposed as the driving force for single-phase behavior. In our system, PVAc is miscible with PVP “as-prepared” but was noted to undergo phase separation over a period of a few days thereafter. One can interpet this observation in terms of a critical demixing temperature located close to the $T_g$ of the PVAc component and that the system, in the absence of hydrogen bonding, is at best marginally compatible. No such problems were encountered when blends of PVP and the copolymers were examined, emphasizing that hydrogen bonding stabilizes these systems.

The apparent free volume as a function of composition of the copolymers (Figure 2) behaves in a rather unexpected manner. There is an initial increase in $\tau_3$ with an increase of the alcohol units up to 35 mol %, followed by a pronounced decrease at 55 mol %. A problem that can arise when comparing data from systems with differing chemical composition is a change in the annihilation mechanism. However, there is no evidence to suggest that there are unusual annihilation mechanisms in either of the pure components and therefore reasonable to assume that there are no changes in mechanism when the blends are investigated. Consequently, it is tempting to suggest that the extending network attains a critical value that “collapses” the matrix and reduces the available free volume. Since there appears to be no evidence of crystalline ordering in the copolymers at the higher degrees of hydrolysis (an understandable source of densification), one must then postulate that this arises from an amorphous restructuring. As a trigger for such an event, we suggest that a change in the balance of the type of hydrogen bond contact occurs above a specific concentration of hydroxyl functions, such as a switch in the relative amounts of intra- and intermolecular bonds. Unfortunately, the hydroxyl infrared bands contain no resolvable components that can be assigned to either of these types and that might be used to quantify such a change. Alternatively, and we believe more likely, the structure may be responsive to the relative concentration of acceptor types, either carbonyl oxygen or hydroxy oxygen. Since the hydrogen bond length lies in the narrow range 2.6−3.1 Å, any cross-linked network must accommodate this steric restriction, especially at high hydrogen-bonding levels. However, intramolecular (and indeed intermolecular) bonds to carbonyls as acceptors will still allow a more “open” structure to form initially, having a carboxy unit interposed between main chain and hydrogen bond site. At the higher degrees of hydrolysis the predominant acceptor in the system is the hydroxyl function, which enforces a structurally “tighter” link. Once a critical value of H-bonding is reached, there a cooperative “zipping up” effect as other sites, not previously in the correct steric format for bond formation, are drawn into closer contact and so leading to the experimentally observed collapse in free volume. Since there is no corresponding discontinuity in the $T_g$ behavior obvious from our data, we are led to the conjectural conclusion that the thermally activated cooperative molecular motion occurring at $T_g$ is not simply controlled by matrix free volume effects and, following the arguments in regard to $T_g$ vs composition behavior, that intrinsic chain stiffness is the more important controlling factor. Expressed another way, as long as there is sufficient free volume for a chain segment to relax it does so, and any changes in free volume above this minimum requirement will not affect $T_g$ behavior. The PALS data in Figure 2 quantify relative free volume changes and not absolute changes.

The FTIR shifts in the polymer blends imply that PVP does compete successfully with the inter- and intramolecular hydrogen bonding in the copolymer and has been able to form a new hydrogen-bonded network between the two components of the blends. Nevertheless, the positron lifetime data for the blends (Figure 2a) follow the same pattern as the copolymer components; there is an increase up to 35 mol % vinyl alcohol, after which there is a significant reduction of the measured positron lifetime. Another, more direct, comparison is given by the positron lifetime data at a fixed 10 K below the $T_g$ of each sample, and this is shown in Figure 4 with the values listed Table 1; again the same trend is observed as for the fixed temperature data. Table 1 also indicates the free volumes of the PVP/PVAc blend (no hydrogen bonding), and the blends with the 55% and 85% copolymers, to be close to an average of their respective components, indicating additivity of free volume. In contrast, the 20% and 35% blend free volumes are significantly greater than their corresponding averages. The incorporation of PVP as a blend component thus appears to have had little effect on the free volume trend exhibited by the vinyl acetate−vinyl alcohol copolymers, i.e., an more “open” structure which then changes to a one with much less free volume. Why the free volume pattern of one component should be preserved in this way cannot at the present time be fully explained. An extension of the carbonyl acceptor vs hydroxyl acceptor argument to the blend situation is certainly valid given the structure of PVP, but it is surprising that the composition at which “collapse” occurs remains apparently unaltered. More likely, as in the majority of polymer blends, there is some level of heterogeneity at the segmental level at which pure component properties can be expressed. In this regard a somewhat similar argument has been previously expressed by ourselves[30,31] to explain aspects of free volume-related relaxation behavior in blends.

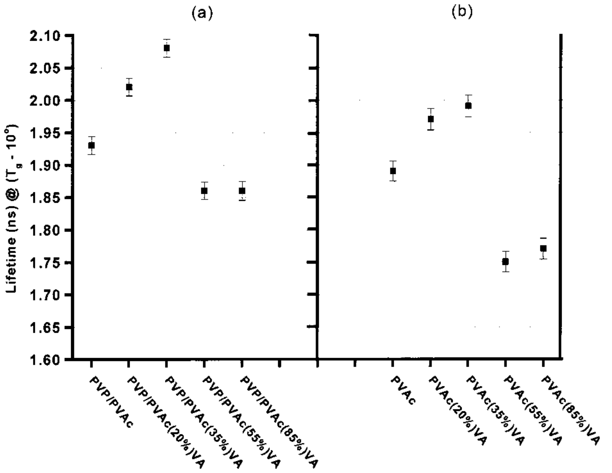

**Figure 4.** Positron annihilation lifetimes ($\tau_3$) for (a) polymer blends and (b) VAc/VA copolymers at 10 K below the glass transition temperatures.

Finally, the product $(\tau_3)^3 I_3$ can be considered; this parameter is regarded by some workers[11] to provide the best indicator of free volume characteristics in polymer systems and is shown in Figure 5 where it may be seen that the previously observed trends are confirmed, with the “collapse” between PVAc(35%)VA and PVAc(55%)-VA being, if anything, more pronounced.

## Conclusions

This is the first study of the effect of hydrogen bonding on the internal structure of a binary polymer blend using using positron annihilation spectroscopy. The results indicate that, at low levels of hydrogen bonding, these secondary bonding interactions tend to lead to a

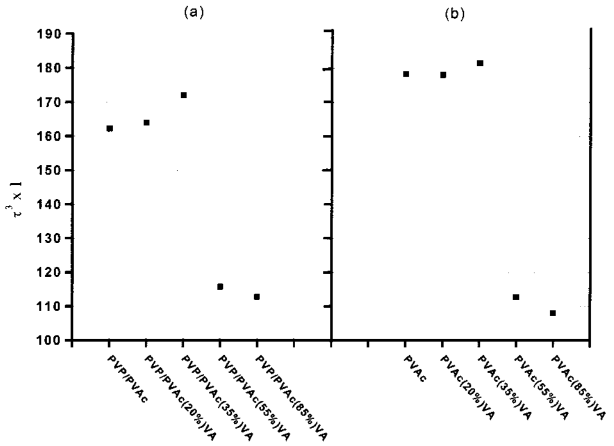

**Figure 5.** Positron results expressed as $(\tau_3)^3 I_3$ for (a) polymer blends and (b) VAc/VA copolymers at 10 K below the glass transition temperatures.

more open structure with an increase in the free volume of the system over that expected by additivity. The suprising outcome of the study is, as the number of hydrogen bonds increases, that there appears to be a critical level of hydrogen bonding above which a rapid decrease in the free volume of the system occurs. This is proposed to be caused by a cooperative extension of the three-dimensional hydrogen-bonded network as the number of hydrogen-bonding sites in the blend increases, along with a relative decrease in the proportion of carbonyl group hydrogen bond acceptors which favor a more open hydrogen-bonded structure. Why the transition from open to dense structure should take place over such a narrow range remains unanswered, but this problem will be addressed in future studies.

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