Relaxations in Poly(vinyl alcohol) and in Poly(vinyl acetate) Detected by Fluorescence Emission of 4-Aminophthalimide and Prodan

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Received: February 17, 2005; In Final Form: May 11, 2005

Steady-state and time-resolved emission spectroscopy (TRES) of the medium-sensitive probes 4-aminophthalimide (4-AP) and 6-propionyl-2-(dimethylamino)naphthalene (Prodan) were performed at 77 and 298 K in vacuum-sealed thin films of poly(vinyl alcohol) (PVA) and poly(vinyl acetate) (PVAc). The two probes show similar red-edge effect in steady state emission and a red shift with time in TRES in PVA. In PVAc the red shifts are much smaller and the spectral shift for 4-AP is slower. 4-AP locates in highly polar environments in PVA, where H-bond interaction with the polymer is important. Prodan locates in less polar environments, as evidenced by the position of the emission maximum with respect to reference solvents. Consequently, the observed monoexponential spectral red shift with time of 4-AP in PVA and in PVAc is attributed to relaxation of the interaction of the probe with the hydroxy and acetate moieties, respectively. The more intense interaction of the lighter −OH moiety with the probes explains the greater and faster spectral shift observed in PVA compared to PVAc. The lifetime of this monoexponential spectral shift is independent of temperature in PVA and takes place with a highly negative activation entropy. This fact is attributed to a collective rearrangement of −OH groups to better interact with the excited state. This relaxation nevertheless does not account for the complete accommodation of the excited state. Prodan shows a linear variation of the spectral shift with time that can be explained by microheterogeneity. In PVA, the width at half-maximum of the emission spectra does not change with time for Prodan and it decays with a lifetime similar to the lifetime of the spectral shift in the case of 4-AP. The differences in the behavior of the probes are attributed to their different average location in the polymer matrix.

Introduction

Interaction of excited states of dyes with polymer matrixes is important in applications such as displays,[1] memories and switches,[2] sensors,[3] and photochromic materials.[4] On the other hand, the use of fluorescent probes has proven to be useful for diverse studies in polymer science, such as diffusion and swelling,[5,6] characterization of the heterogeneity of environments,[7−9] phase segregation,[10−12] thermal transitions,[13,14] detection of free volume,[15−17] and the study of curing processes.[18−21] Excited states can be used to monitor fast dynamics in these media, when time-resolved fluorescence spectroscopy can be used,[22,23] or long-term relaxations such as those involved in polymer curing can be monitored by steady-state emission spectroscopy. The production of the excited state involves a very fast and great energy input into the system. This shift from local equilibrium triggers relaxation motions in the probe and the matrix. This can be monitored by time-resolved emission spectroscopy (TRES).

Relaxations in polymers spread a broad frequency spectrum[24] from very fast reorientation of lateral moieties in the nanosecond time scale to reorganizations responsible for the aging of the polymer in the thousands of seconds domain. Almost all of them can be monitored by emission spectroscopy because of its sensitivity and the selectivity provided by the adequate choice of a medium-sensitive probe.[15,19,25−27] Solid matrixes such as glassy polymers and gels are heterogeneous at a molecular level and have much lower fluctuation rate than fluid samples. As a consequence, dynamic processes in glassy polymers often show a dispersive kinetic behavior.[28]

Poly(vinyl alcohol) (PVA) is a polymer with broad applications that is produced by hydrolysis of poly(vinyl acetate) (PVAc). It is environmentally degradable. The high concentration of OH− moieties provides hydrophilic environments compatible with water and living tissues. The hydroxyl group plays a key role in the structure of PVA.[10] These moieties associate in pools controlling the folding of the polymer carbon backbone. On the other hand, the polymer chains are maintained together by H-bonding, and this fact is responsible for the relatively high glass transition temperature of PVA, which lays in the vicinity of 350 K.[11,13] The structure and the extension of the H-bond interactions can be conveniently studied by IR absorption spectroscopy.[13,29] Nevertheless, this technique cannot render information on the heterogeneity and on the dynamics of these interactions. On the other hand, TRES of suitable fluorescent probes can be an adequate technique to obtain this later information.

Among several molecular probes, some aminophthalimides show a very efficient fluorescence emission, with a large Stokes shift that is very sensitive to medium polarity and to the

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10.1021/jp050844a CCC: $30.25 © 2005 American Chemical Society
Published on Web 07/28/2005

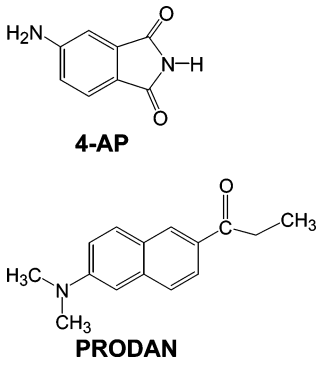

Figure 1. Structure of 4-aminophthalimide (4-AP) and 6-propionyl-2-(dimethylamino)naphthalene (Prodan).

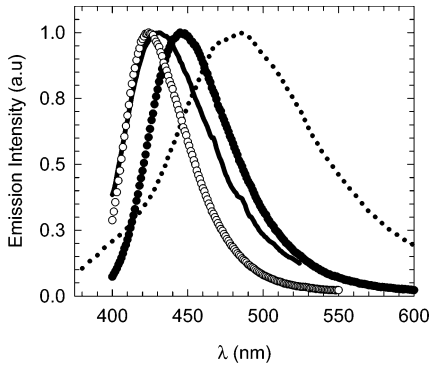

Figure 2. Steady-state emission spectra at 298 K of 4-AP ($\lambda_{exc} = 340$ nm) in PVA (dotted line) and in PVAc (solid line) and of Prodan ($\lambda_{exc} = 370$ nm) in PVA (black circles) and in PVAc (white circles).

hydrogen-bond-donating capability (HBD) of the environment:[30−33] for example, the emission maximum of 4-aminophthalimide (4-AP) shifts from 430 nm in toluene to 550 nm in water.[34] Additionally, the excited state of this probe has a relatively long lifetime of ca. 15 ns, which has small variations in a variety of solvents from toluene to acetonitrile.[35] The excited state lifetime as well as the emission quantum yield drop very much in protic solvents, such as alcohols and especially in water.[31,34,35] Due to its long excited state lifetime and its high solvatochromism, 4-AP is an ideal probe for monitoring medium relaxation, especially where H-bonds are involved.[32,33] It was extensively used to monitor microenvironments and solvation in a great variety of media, including micelles,[35] cyclodextrins,[31] hydrogels,[8] and ionic liquids.[36]

Prodan (6-propionyl-2-(dimethylamino)naphthalene) is a well-known polarity-sensitive fluorescent probe used to study the dipolar relaxation processes in proteins, lipids, and gels.[19,20,26,32,37−42] It possesses a dipole moment much larger in the excited-state than in the ground state, but contrary to 4-AP, its lifetime is of only ca. 3−4 ns in a variety of solvents and is shorter (ca. 2 ns) either in nonpolar media such as hydrocarbons or in water.[32,37]

In this work, we study the dynamics of H-bond interactions in PVA by steady-state and time-resolved fluorescence emission of 4-AP and Prodan (see Figure 1 for their structure). By using these two probes of similar excited-state sensitivity, the dynamics of the relaxation process can be probed in the nanosecond time window. We compare the results with those in PVAc, a parent polymer that cannot H-bond with the dyes.

Experimental Section

Chemicals. 4-Aminophthalimide (4-AP, 97% purity, Acros Organics) was recrystalized from ethanol. 6-Propionyl-2-(dimethylamino)naphthalene (Prodan, Molecular Probes) was used as received.

Dichloromethane (Merck, UVASOL) was distilled and stored on molecular sieves (4 Å), absolute ethanol (Merck) was used as received, and water was from a Milli-Q system. Poly(vinyl alcohol) (PVA, Fluka, average molecular weigth $M_w = 72\,000$, 97.5−99.5 mol % hydrolysis) and poly(vinyl acetate) (PVAc, Aldrich, $M_w = 83\,000$) were used as received.

Sample Preparation. PVA (0.5 g) was dissolved in hot water and the solution was left at room temperature. Drops of an ethanolic solution of the dye were incorporated to the polymer in a $1{:}10^{-5}$ polymer:probe ratio, and the polymer was stirred. The final solution was poured into silanized Petri dishes, and the liquid films were allowed to dry slowly with the lids on at room temperature. Finally, the films were kept at 40 °C in a vacuum stove for 24 hs and removed from the molds to be placed into NMR tubes that were immediately sealed under vacuum. TGA analysis under nitrogen showed a water content of 2.5 ± 1.0% w/w.

For PVAc, the preparation of the samples was similar to that of PVA, but replacing the water and ethanol by dichloromethane. These samples were processed at room temperature.

Steady-State Emission Spectra. The corrected steady-state emission spectra were recorded on a PTI QuantaMaster QM-1 luminescence spectrometer. The emission was collected from the back face in a front-face arrangement and right angle excitation-detection geometry. Measurements at 77 K were performed by placing the NMR tube containing the film in a Dewar containing liquid nitrogen. For measurements at room temperature, the NMR tube was placed in the empty Dewar.

Time-Resolved Fluorescence. Fluorescence decays were measured with time-correlated single-photon-counting equipment (Edinburgh Series 9000) provided with PMT tubes and excitation and emission monochromators. Excitation was achieved with a medium-pressure hydrogen discharge lamp. The instrument response function had a fwhm around 1.5 ns. With deconvolution it is possible to reliably measure lifetimes down to 0.5 ns. The samples were placed and measured under identical conditions as in the steady-state experiments. The time-resolved spectra were reconstructed from the decay curves registered at different emission wavelengths. For each sample, 11 wavelengths were measured. Samples with 4-AP were excited at 340 nm, and Prodan-containing films were excited at 370 nm.

Results

The steady-state emission spectra of 4-AP and Prodan in both polymers are shown in Figure 2. Fluorescence in the protic polymer (PVA) is red-shifted and broader for both dyes compared to the nonprotic polymer (PVAc).

Figure 3 shows the dependence of the wavelength of the maximum of these spectra on the excitation wavelength and temperature for both polymer films and probes. The position of the emission maximum displays the red-edge effect in emission, typical of media with relaxation times comparable to or much longer than the excited-state lifetime.[25,43−46] This results in heterogeneity of environments for the locations of the probe.

For both probes, the magnitude of the red shift with either excitation wavelength or temperature is greater in PVA than in PVAc. Figure 3 also shows the wavelength of the maximum of the emission of 4-AP and Prodan in 2-propanol (for PVA curves) and in ethyl acetate (for PVAc curves) at room temperature. These solvents are taken as reference media for PVA and PVAc, respectively, because of the similarity in their chemical struc-

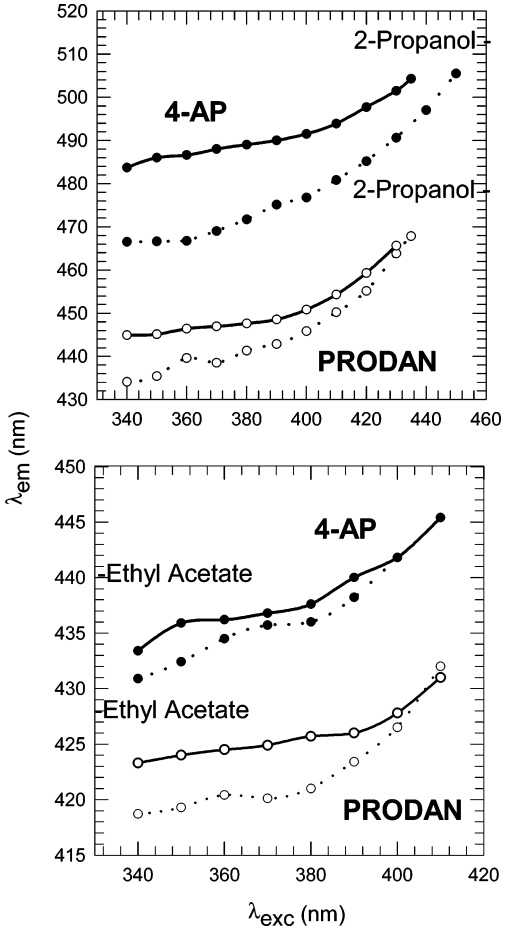

Figure 3. Wavelength of the emission maximum (λ_{em}) as a function of excitation wavelength (λ_{exc}) for 4-AP and Prodan in PVA (upper panel) and in PVAc (lower panel), at 77 K (dotted lines) and 298 K (solid lines). The ticks at the right/left of the upper/lower panel indicate the emission maxima in 2-propanol and in ethyl acetate for 4-AP and Prodan at room temperature.

tures. The values of the wavelength of the maximum of emission of both probes in PVA tend to approach the corresponding maximum of emission in 2-propanol, indicating the ability of 4-AP and Prodan to sense the more polar environments. 4-AP approaches better than Prodan the value of its emission maximum in 2-propanol. In PVAc, the value of the emission maximum in ethyl acetate is surpassed by both probes upon excitation in the extreme red edge. Here also 4-AP can sense more polar environments than Prodan.

It can be also seen from Figure 3 that a constant value, i.e. a plateau, is not achieved for the value of the maximum of emission, not even if excitation takes place at the longest possible red edge of the excitation spectrum. This indicates that some relaxations of the probe−polymer interactions take longer than the excited-state lifetime to be completed.

Considering the red edge excitation shift results, we chose 340 and 370 nm as excitation wavelength for TRES for 4-AP and Prodan, respectively. Under these conditions, emission spectral shifts are greater as a function of temperature, and the ensemble of excited molecules has the greatest difference with respect to the totally relaxed emission.

4-AP. Figure 4 shows the TRES of 4-AP in PVA at 77 and 298 K and the corresponding one in PVAc at 298 K. Samples were excited in the blue edge of the absorption spectrum (λ_{exc} = 340 nm), where the steady-state emission is practically wavelength independent (see Figure 3). The spectra at every selected time were fitted to a Gaussian distribution function of

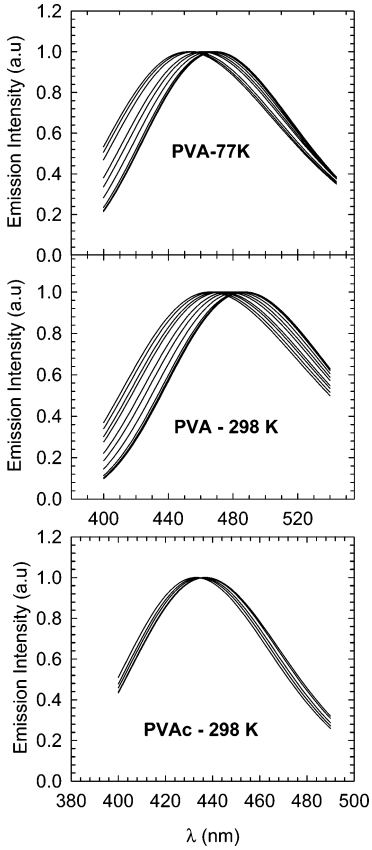

Figure 4. Time-resolved emission spectra (TRES) of 4-AP in PVA at 77 K (upmost panel) and 298 K (middle panel) and in PVAc at 298 K (lowest panel). From left to right, the times for the TRES are 0, 1, 2, 3, 5, 7, 10, 15, 20, and 30 ns for PVA (upmost and middle panel). For the lowest panel, times are 0, 5, 10, 20, and 30 ns.

energy that reproduces the emission profile with less than a 2% deviation.[47] The corrected steady-state emission, obtained for the same sample under identical conditions used for TRES experiments, was used to normalize the time-integrated emission at every wavelength. From these spectra, the energy of the emission maximum (ν_{max}, in cm^{-1}), the total emission intensity (I_{tot}), as well as the full spectral bandwidth at half-maximum (fwhm) of the emission spectrum were obtained.

As we can see from Figure 4, in both polymers, 4-AP has a time-dependent emission spectrum in the temperature range studied. The initial emission shifts to the red with time in all cases.

Figure 5 represents the time dependence of ν_{max} and I_{tot} of 4-AP in PVA at 77 and 298 K and in PVAc at 298 K. The maximum of the emission shifts monoexponentially in both polymers in all cases. The lifetime for the decay of the spectral shift ($\tau_{\nu max}$) and for the decay of I_{tot} (τ_{Itot}), the extrapolated maximum of emission of the initially excited molecules ($\nu_{max,in}$), and the maximum of emission when the observed spectral shift is completed ($\nu_{max,fin}$) are summarized in Table 1.

The amplitude of the spectral shift of 4-AP with time (Figure 5 and Table 1) is larger in PVA ($\Delta\nu_{max}$ = 1000 cm^{-1} at 298 K) than in PVAc ($\Delta\nu_{max}$ = 260 cm^{-1} at 298 K). This is due to the greater interaction of the probe with the −OH groups of PVA. In addition, the spectral shift is faster in PVA ($\tau_{\nu max}$ = 6.2 ns at 298 K) than in PVAc ($\tau_{\nu max}$ = 13.5 ns at 298 K). The results also show that $\tau_{\nu max}$ is temperature-independent between 77 and 298 K, indicating a very low activation energy (<0.1 kJ/mol). The full spectral bandwidth at half-maximum decreases with time in PVA with a lifetime of τ_{fwhm} = 7 ns at both temperatures,

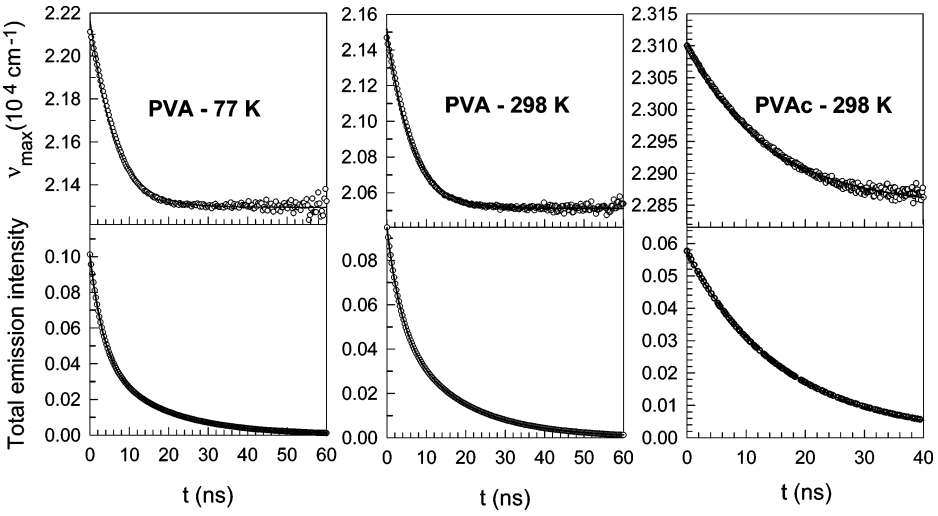

Figure 5. Time dependence of the maximum of emission (ν_{max}) and of the total emission intensity for 4-AP in PVA (at 77 and 298 K) and PVAc at 298 K. Deconvoluted decays are shown.

TABLE 1: Spectroscopic and Kinetic Data Derived from TRES of 4-AP and of Prodan in PVA and in PVAc

probe	polymer	T (K)	$\nu_{max,in}$ (cm^{-1})[a]	$\nu_{max,fin}$ (cm^{-1})[a]	$(\nu_{max,in} - \nu_{max,fin})$[a] (cm^{-1})	$\tau_{\nu max}$ (ns)	τ_{Itot1} (ns)	τ_{Itot2} (ns)	τ_{fwhm} (ns)
4-AP	PVA	77	22 170	21 300	870	6.2	3.6 (50%)[b]	16.2	7.1
	PVA	298	21 500	20 510	1000	6.2	3.8 (60%)[b]	16.1	7.3
	PVAc	298	23 100	22 850	260	13.5	16.7	−	const.[c]
Prodan	PVA	77	22 360	21 860[d]	500	−[e]	3.9	−	const.[c]
	PVA	298	22 120	21 630[d]	490	−[e]	3.6	−	const.[c]
	PVAc	298	23 530	23 530[d]	<50	−	3.5	−	const.[c]

[a] Uncertainties are ±50 cm^{-1}. [b] The value in parentheses is the percentage of the amplitude of this lifetime component of the decay. [c] No appreciable change in the spectral bandwidth. [d] Values at 20 ns. [e] No kinetic analysis of these data was performed.

very similar to the value of $\tau_{\nu max}$. This can be related to the decrease in the inhomogeneity of the excited-state population caused by relaxation. Almost no change in the spectral bandwidth with time is observed in PVAc. All these data can be explained by the greater interaction of the probe with the −OH groups of PVA.

The decay of I_{tot} is single exponential in PVAc for 4-AP, indicating that the emission efficiency is not affected by the spectral shift. In PVA the total emission decay is not single exponential. It can be very well fitted by a sum of two exponential terms with one decay time shorter than and one longer than $\tau_{\nu max}$ (Table 1).

Prodan. Figure 6 shows the TRES of Prodan in PVA at room temperature. The inset of the figure shows the dependence of ν_{max} with time. Prodan has an excited-state lifetime (ca. 3.4 ns) shorter than the characteristic time of the spectral shift of the maximum of the emission observed for 4-AP (6.2 ns). From the inset of Figure 6, we can see, on one hand, that the spectral shift does not reach a constant value during the excited-state lifetime of Prodan and, on the other hand, that the spectral shift observed for Prodan is slower than the one observed for 4-AP. The kinetics of the spectral shift shows a linear dependence of ν_{max} with time, and consequently, no kinetic analysis was performed with these data. This behavior can be explained by considering a microheterogeneous distribution of Prodan in the polymer as discussed below (see Discussion). To estimate the spectral shift with time, the value of $\Delta\nu_{max}$ was obtained from the difference of ν_{max} between 0 and 20 ns (when the emission intensity of Prodan is negligible).

From the amplitude of the spectral shift, Prodan stabilizes better in PVA ($\Delta\nu_{max} = 490$ cm^{-1}) than in PVAc (where no spectral shift takes place, $\Delta\nu_{max} \approx 0$, see Table 1). This is in agreement with the results obtained for 4-AP.

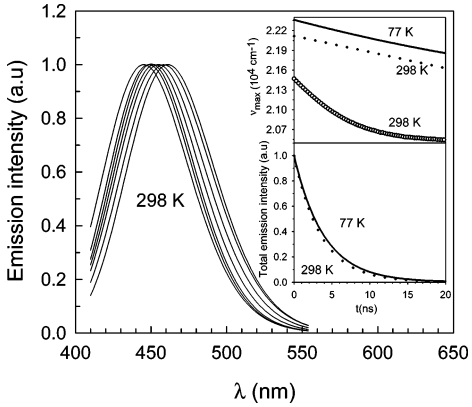

Figure 6. Time-resolved emission spectra of Prodan in PVA at 298 K. Upper inset: Time dependence of the maximum of the emission at 77 K (solid line) and 298 K (dotted line) for Prodan and for 4-AP at 298 K (hollow circles). Lower inset: Decay curves of the total emission intensity of Prodan at 77 K (solid line) and 298 K (dotted line). Deconvoluted decays are shown in both insets.

The TRES of Prodan also shows that the time evolution of the spectral shift is temperature-independent in the range studied (see the inset of Figure 6). Contrary to the behavior of 4-AP, the spectral bandwidth (fwhm) of Prodan emission does not change appreciably with time.

The decay of the total emission intensity is monoexponential with lifetimes of 3.4−4.0 ns (see Table 1). These values are very similar to the excited-state lifetime of Prodan in most solvents.

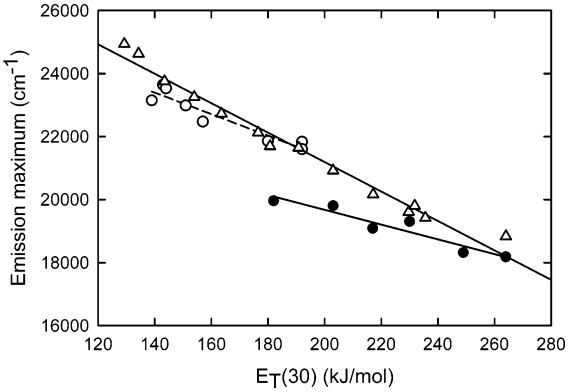

Figure 7. Correlation of the emission maximum of 4-AP and Prodan in neat solvents with the medium parameter $E_T(30)$. Triangles: Prodan in cyclohexane, benzene, triethylamine, chlorobenzene, chloroform, acetone, dimethylformamide, acetonitrile, 2-propanol, ethanol, methanol, propylene glycol, ethylene glycol, and water [solvents listed by increasing value of $E_T(30)$].[37,41,42] Hollow circles: 4-AP in aprotic solvents triethylamine, toluene, diethyl ether, dioxane, tetrahydrofuran, acetone, acetonitrile.[31,47,48] Full circles: 4-AP in protic solvents *tert*-butyl alcohol, 2-propanol, ethanol, methanol, trifluoroethanol, water.[31,47,48] The lines represent the linear correlations given by eqs 1−3 in the text, respectively.

Discussion

There are similarities and differences between the behavior of the two probes in PVA and in PVAc. The two probes show similar red-edge effect, red shift in TRES with $\tau_{\nu max}$ independent of temperature in PVA, slower relaxation in PVAc, and a smaller amplitude than in PVA. This was expected due to the similar medium sensitivity of 4-AP and Prodan.[30,32,33,37,41,42] The differences in behavior are a higher interaction of 4-AP with the polymers compared to Prodan, as evidenced by the position of the emission maximum with respect to the reference solvents (Figure 3); a different kinetics for the spectral shift; and a different behavior of the fwhm of the emission spectra with time. This later parameter does not change for Prodan and it decays with a lifetime similar to the lifetime of the spectral shift in the case of 4-AP.

Figure 7 shows the position of the emission maximum of the probes in different solvents. For Prodan, there is a good correlation between this parameter ($\nu_{max,PR}$) in pure solvents and the medium parameter $E_T(30)$ for a great variety of solvents, including protic and aprotic ones (cyclohexane, benzene, triethylamine, chlorobenzene, chloroform, acetone, dimethylformamide, acetonitrile, 2-propanol, ethanol, methanol, propylene glycol, ethylene glycol, and water).[37,41,42] The linear correlation of these parameters can be represented by

$$\nu_{max,PR}(cm^{-1}) = 30540 - 46.75E_T(30)(kJ/mol) \quad (1)$$

The emission maximum of 4-AP shows distinct correlations with $E_T(30)$ for protic and for aprotic media.[35] In aprotic solvents (triethylamine, toluene, diethyl ether, dioxane, tetrahydrofurane, acetone, acetonitrile),[31,47,48] the linear correlation is

$$\nu_{max,4-AP}{}^{aprotic}(cm^{-1}) = 28185 - 34.22E_T(30)(kJ/mol) \quad (2)$$

while for the protic ones (*tert*-butyl alcohol, 2-propanol, ethanol, methanol, trifluoroethanol, water)[31,47,48] it is

$$\nu_{max,4-AP}{}^{protic}(cm^{-1}) = 24365 - 23.45E_T(30)(kJ/mol) \quad (3)$$

The complete relaxation of the excited states of 4-AP involves intramolecular rearrangements (amino planarization and internal charge transfer (ICT)[30,32,47]) and reorientation of neighbor molecules for optimum solvation. The different behavior of the emission of 4-AP in protic and aprotic media evidences the importance of H-bond interactions in the relaxation of 4-AP and, consequently, the special ability of this probe to sense them.[32] For Prodan, two emitting states were found: a locally excited (LE) state with a blue emission and an ICT state with a red-shifted emission that is sensitive to environment relaxation and is highly temperature dependent.[37,42] We do not observe emission from the LE state of Prodan but only what corresponds to ICT emission.

In comparing steady-state emission maxima in different media, one should take into account the existence of a time-dependent emission spectrum. In neat solvents near room temperature, the emission maxima adequately characterize the relaxed excited state, so strictly speaking, one should compare them with the relaxed emission spectrum in constrained media such as polymers (i.e., with the fitted infinite time emission spectrum). If the time-dependent emission spectrum arises from the contribution of different environments that differ in emission and lifetime (microheterogeneity), then one can, as a first approach, use the neat solvents as references for the variety of environments (assuming that each environment does not relax during excited-state lifetime).

Prodan and 4-AP display the normal red edge excitation shift effect in both polymers. At a given temperature, assuming that relaxation proceeds with the same dynamics in all locations, the red shift in emission with excitation wavelength reflects the heterogeneity of the microenvironments of the polymer matrix, indicating that relaxation of the medium is slower than excited-state lifetime.[43−46]

Because of the greater amplitude of the red-edge effect in PVA, we can conclude that heterogeneity in this polymer is greater than in PVAc. This is also in agreement with the larger fwhm of the steady-state fluorescence emission spectra in PVA compared to PVAc (Figure 2).

In PVA, the range covered by the emission maximum of 4-AP at room temperature indicates protic environments with values of $E_T(30)$ from 180 to 200 kJ/mol. This means solvating power between that of *tert*-butyl alcohol and 2-propanol, which is in agreement with the structural similarity of these media to PVA. As shown in Figure 3, the value of λ_{max} in 2-propanol seems to be an asymptote at high temperature or at excitation in the extreme red edge of the absorption. At 298 K, the initial emission of 4-AP has a maximum at 465 nm (Table 1), beyond the relaxed emission in acetonitrile (463 nm), the most polar non-HBD solvent measured. At the end of the emission, the maximum shifts to 488 nm, a wavelength range that is only attained in HBD environments. All these considerations indicate that 4-AP locates in a variety of environments but that in all of them there is a great contribution from H-bond interaction.

The environments sensed by Prodan in PVA are less polar, ranging from acetone [λ_{max} = 452 nm, $E_T(30)$ = 180 kJ/mol] to an environment more polar than acetonitrile (λ_{max} = 462 nm). This indicates a lower capability of Prodan to enter the −OH pockets and might explain the lower sensitivity of this probe to sense the relaxation (see below). This observation is similar to conclusions derived from experiences of Prodan emission in poly(methyl methacrylate) (PMMA)−silica sol−gel mixed glasses.[41] In these media, Prodan locates preferentially in PMMA environments but is substantially influenced by the more polar silica skeleton. In line with these observations, the red shift of the emission maximum with temperature is smaller for Prodan than for 4-AP.

The emission maximum in ethanol (524 nm for 4-AP, 496 nm for Prodan), perhaps a better reference solvent for PVA, seems difficult to attain by either probe. This indicates that the inter- and intrachain hydrogen bonds are more effective than those involving polymer/probe, and thus, they are not available to accommodate all the necessary hydroxyl groups of the polymer for an optimum interaction with the probes. The proportion of water remnant in PVA after drying ($2.5 \pm 1.0\%$) is not enough to plasticize the polymer. Furthermore, emission spectra do not show any evidence of the interaction of the probes with water taking into account that the emission maxima in this solvent are at 550 nm for 4-AP and at 532 nm for Prodan.

In PVAc, much smaller variations in the emission maximum with excitation wavelength are observed and easily explained by the lower polarity and nonprotic character of this medium [$E_T(30) = 168$ kJ/mol[49]]. Both probes sense environments similar to ethyl acetate [$E_T(30) = 159$ kJ/mol], which is the expected reference solvent for PVAc: values of λ_{max} between 435 and 445 nm for 4-AP and between 423 and 432 nm for Prodan represent an $E_T(30)$ between 152 and 165 kJ/mol for 4-AP and between 148 and 158 kJ/mol for Prodan. In PVAc also, Prodan locates in less polar environments than 4-AP. This fact can be rationalized by comparing the structure of the probes: the dimethyl substitution in the amino group of Prodan, as well as the second benzene ring with a propionyl substituent, are less hydrophilic than the primary amine and the imide moiety of 4-AP. The greater ground-state dipole moment of 4-AP compared to Prodan[32] also contributes in the same direction.

TRES shows clearly that spectral shift takes place with a faster kinetics in PVA than in PVAc for 4-AP (see Figure 5 and Table 1). The spectral shift is completed within the excited-state lifetime of this probe. TRES shows that the excited ensemble changes with time. This change can be a consequence of microheterogeneity, which selects the longer living locations, a consequence of excited-state stabilization due to local relaxation of probe−polymer environments, or a consequence of both effects. In what follows, we will discuss the influence of relaxation and microheterogeneity to explain the results for both probes.

A red shift with time can be explained by microheterogeneity if the lifetime is longer for the most red-emitting sites. This can be the case for Prodan, but not for 4-AP, as explained below. On the other hand, relaxation always shifts the spectrum to the red through local stabilization of the excited state. Pure homogeneous relaxation (with the same kinetics in all environments) is accompanied by a rise time in the red edge of the emission with a lifetime equal to the faster decay lifetime in the blue edge. We do not observe a rise time component in the decay of either of the probes in the red edge of the emission spectrum. This lack does not exclude the participation of relaxation in the spectral shift, because a combination of microheterogeneity and relaxation can also render the observed behavior, as discussed below. Though we cannot exclude that a raise time can be present in the red emission edge at times shorter than the time resolution of the experiment (faster than 0.5 ns), such a raise component is not necessarily present in microheterogeneous relaxation.

As pointed out previously, 4-AP locates in a variety of environments with characteristics ranging from those of *tert*-butyl alcohol to 2-propanol. These solvents define an interval where the lifetime of 4-AP is practically constant: 13.0 ns in 2-propanol[30] and 13.4 ns in *tert*-butyl alcohol. The lifetime of 4-AP is smaller in the most protic solvents (8 ns in ethanol, 7 ns in methanol, and 1.2 ns in water)[34,35] as compared to polar nonprotic and apolar environments (14 ns in acetonitrile, 13 ns in toluene, and 15 ns in dioxane).[35,47] Also, the emission efficiency drops in protic solvents (ϕ_f of ca. 0.1) compared to aprotic media (ϕ_f of ca. 0.65).[31]

Decay simulations were carried out for Prodan using a very simple microheterogeneous model. The proposed values of the parameters of the simulations described below are similar to and consistent with those obtained from experimental data. The model for Prodan assumes three different sites with Gaussian emission spectra with maxima at 24 500, 23 500, and 22 500 cm^{-1}, $\nu_{max,1}$, $\nu_{max,2}$ and $\nu_{max,3}$, respectively, and equal Gaussian standard deviation of 1500 cm^{-1} (equivalent to a fwhm of 2940 cm^{-1}). Their lifetimes were assumed to be 3.4, 3.7, and 4.0 ns, τ_1, τ_2, and τ_3, respectively. Equal population and emission efficiency was assumed for each site. No exchange between sites or local relaxation was considered. This situation can be depicted by the following scheme:

$$\begin{aligned} Pr_1^* &\xrightarrow{k_1} Pr_1 + I_f(\nu_{max,1}) \\ Pr_2^* &\xrightarrow{k_2} Pr_2 + I_f(\nu_{max,2}) \\ Pr_3^* &\xrightarrow{k_3} Pr_3 + I_f(\nu_{max,3}) \end{aligned} \tag{4}$$

The results show that the shift in the emission maximum is practically a straight line decaying from 23 500 to 23 200 cm^{-1} in 20 ns. The fwhm of the emission spectrum is constant at 3370 ± 40 cm^{-1} (this variation is smaller than our experimental uncertainty in this parameter), whereas the total emission intensity follows with very good precision a monoexponential decay with a lifetime of 3.7 ns. In other words, the spectral shift takes place with a rate constant equal to $(1/\tau_1 - 1/\tau_3)^{-1}$ [equal to $(23\ ns)^{-1}$ in the example], while the total emission intensity decays with an effective first-order rate constant similar to the average rate constant, $(3.7\ ns)^{-1}$ in the example. This simple microheterogeneous model adequately describes the situation for Prodan, without need of postulating relaxation (see the Supporting Information for details).

For 4-AP in PVA the situation is different. The decay of the total emission is double exponential with lifetimes of ca. 4 and 16 ns, and there is a single-exponential spectral shift with a lifetime of ca. 6 ns and a spectral fwhm decay with a lifetime of 7 ns. The record of a complete decay of the spectral shift for 4-AP in contrast to Prodan is not a consequence of a longer observation window for the former probe but of a faster decay, as the inset in Figure 6 shows. In the microheterogeneous picture, the observed spectral shift requires a greater spread in the values of the local rate constants than for Prodan, and this is indeed observed for 4-AP: lifetimes between 2 and 17 ns are fitted in the double exponential single wavelength decays. The same model of eq 4 was applied to 4-AP with the parameters 22 500, 21 500, and 20 500 cm^{-1} for $\nu_{max,1}$, $\nu_{max,2}$, and $\nu_{max,3}$, respectively, and 0.43, 0.17, and 0.06 ns^{-1} for the corresponding rate constants. The Gaussian dispersion was set to 1500 cm^{-1} for all positions. Very good agreement with the experimental results is obtained under these conditions (see the Supporting Information for details). There is, nevertheless, a contradiction with the behavior observed for 4-AP in most media. Short lifetimes on the order of 6 ns were measured for 4-AP either in low-density apolar media, such as near supercritical CO_2,[50,51] with emission maximum around 405 nm, or in ethanol or methanol, with emission maxima around 520 nm. Lifetimes as short as 2 ns are only observed for 4-AP in water, where the emission maximum is at ca. 550 nm (18 200 cm^{-1}),

a value never attained in PVA. The expected behavior upon polarity increase for 4-AP would be a decrease in lifetime and in quantum yield. Both of these trends would cause a blue shift with time in a microheterogeneous model, as the red edge of the emission would decay faster.

In view of the later discussion and taking into account that we have already excluded a pure relaxation picture, we considered a simple relaxation model in a microheterogeneous ensemble. Local relaxation affects local decay rate constant, $k(t)$, and emission energy, $\nu_{max}(t)$, both of which become time-dependent. We will assume that both obey a simple relaxation law with equal relaxation time, as given by[52]

$$k(t) = k_\infty + (k_0 - k_\infty) \exp(-k_r t) \quad (5)$$

$$\nu_{max}(t) = \nu_\infty + (\nu_0 - \nu_\infty) \exp(-k_r t) \quad (6)$$

All locations have equal decay rate constants but different emission energy. This is a reasonable assumption for 4-AP, in view of the independence of the emission lifetime between *tert*-butyl alcohol and 2-propanol. In line with the assumptions of the microheterogeneous model presented above, we assume three different types of locations with equal emission efficiency and relative population. In this picture, spectral shift arises on the time dependence of $\nu_{max}(t)$, so it takes place with a rate given by k_r. Consequently, this parameter should be equal to ca. $(6\ ns)^{-1}$. On the other hand, the deviation of the total emission decay from a single exponential reflects the local kinetic behavior; therefore, k_0 and k_∞ can be set equal to the two rate constants observed for the decay of I_{tot}, $(3.6\ ns)^{-1}$ and $(16\ ns)^{-1}$, respectively. The same values for $\nu_{max,1}$, $\nu_{max,2}$, and $\nu_{max,3}$ are assumed, which in this model are set equal to ν_0, and finally the spectral shift $(\nu_0 - \nu_\infty)$ is set to 1000 cm^{-1}. The time-dependent monochromatic emission intensity can be obtained by multiplying the time-dependent spectra and populations and adding over all locations. With this procedure, under the above conditions, no rise time is observed in the red edge of the emission spectrum, in agreement with the experimental facts (see the Supporting Information for details).

In view of the previous discussions, we conclude that relaxation contributes to the TRES observed for 4-AP.

The zero-time-extrapolated λ_{max} values of 4-AP in PVA (451 nm at 77 K and 465 nm at 298 K) are similar to the initial emission λ_{max} at 203 K in 1-propanol (ca. 450 nm). The magnitude of the spectral shift in PVA at 298 K (23 nm) is much smaller than in 1-propanol at 203 K (ca. 50 nm).[30] These facts indicate that the environment in which 4-AP is located is not necessarily less polar than 1-propanol but that the rearrangement of the polymeric environment is not complete for optimum solvation. In summary, we can describe the relaxation in PVA as a complete relaxation of some rearrangements involving the −OH moiety and its HBD capability but not a full accommodation for optimum solvation of the excited state. There are presumably relaxations in the subnanosecond time scale that are not observed, but the existence of a red edge excitation shift indicates a broad spectrum of relaxation times that includes times comparable to or longer than the excited-state lifetime. In the nanosecond time range the relaxations relevant to accommodate the excited state of 4-AP are well-represented by a single lifetime that is temperature independent.

If we accept the relaxation explanation for Prodan, the slower relaxation observed for this probe can be explained if we consider that in PVA a less polar environment means a smaller density of −OH groups. This lower density can be the responsible for the lower probability of attaining the transition state for relaxation.

Figures 5 and 6 show the most striking observation of this work, namely, that the kinetics of the spectral shift is temperature-independent in PVA, both for 4-AP and for Prodan. This fact points to a negligible or nonexistent activation energy for $k = 1/\tau_{\nu max}$. From the kinetic point of view, the rate constant can be described by the Eyring equation:

$$k = \frac{k_B T}{h} \exp(\Delta S^\ddagger/R) \exp(-\Delta H^\ddagger/RT) = \frac{\exp(k_B T)}{h} \exp(\Delta S^\ddagger/R) \exp(-E_a/RT) \quad (7)$$

Considering the results for 4-AP and setting $E_a = 0$, we obtain an activation entropy, $\Delta S^\ddagger = -92$ J/K mol for $k = 1.6 \times 10^8\ s^{-1} = (6.2\ ns)^{-1}$. This negative value of the entropy indicates an isoenergetic but highly improbable conformation of the polymer environment in the transition state that leads to relaxation. This relaxation involves the −OH moiety. A collective quasivibrational reorganization of −OH moieties in the vicinity of the probe has a low probability and consequently a highly negative activation entropy but can be isoenergetic if it only involves torsional vibrational energy. This picture has a similarity with the solvent relaxation in simple alcohols. In these media, the ultrafast component of the solvation dynamics originates on fast libration and intermolecular vibration modes involving the −OH moiety. It accounts for 60−70% of the total solvation energy.[53] These movements are more restricted in the solid PVA. In PVAc, the acetate moiety is the most interacting with the probes, due to its polarity. This portion, in turn, interacts with a smaller energy with the probes. This explains the different characteristics of the dynamics observed in both media.

In summary, the experiments show that 4-AP and Prodan are suitable probes to sense the microheterogeneity and relaxation in PVA. The difference in the behavior of the two probes originates in their location in the polymer network. 4-AP is able to locate in the highly hydrophilic environments, while Prodan, with a more hydrophobic structure, is not able to penetrate the locations with higher −OH density. As a consequence, while TRES experiments of Prodan can be explained exclusively by the heterogeneity of the probe locations, similar experiments with 4-AP show that both heterogeneity and relaxation of −OH moieties contribute to the spectral shift.

Acknowledgment. P.F.A. and C.C. are members of Carrera del Investigador Científico from CONICET (National Research Council of Argentina). The work was performed with financial support from Fundación Antorchas (Argentina) and grants PICT06-4438 (ANPCyT, Argentina) and PIP 0388 (CONICET, Argentina). B.C.B. thanks FCEN (UBA) and CAPES (Brazil) for travel grants.

Supporting Information Available: Simulation of TRES by a microheterogeneous scheme and by a microheterogeneous plus relaxation kinetic scheme. This material is available free of charge via the Internet at http://pubs.acs.org.

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