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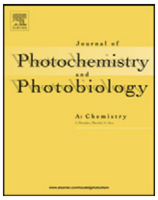

Fluorescence properties of 4-amino salicylic acid in polymers

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ABSTRACT

In this manuscript we report spectral and photophysical parameters of 4-amino salicylic acid in protic polar and less polar aprotic polymer matrices. Dual emission is observed in both the polymers. The band appearing at longer wavelengths (B band) is attributed to excited state intramolecular proton transfer (ESIPT) whereas the band around 330 nm (U band) is due to those conformers, which fail to undergo ESIPT. We attribute the difference in spectral behaviour in these polymers to the simultaneous presence of different neutral/ionic species, free volume and polarity effects.

1. Introduction

Excited state intramolecular proton transfer (ESIPT) is one of the most studied excited state chemical reactions, which, in general, is thought to be extremely fast (taking place in tens or hundreds of femtoseconds) [1–3]. In general, a large Stokes shifted emission band is a signature of ESIPT reaction [4–11], which controls the functioning of various biological systems [7–10]. Recently, the role of dyes showing ESIPT has been demonstrated in some polymers for their use as polymer host lasers [12,13], photostabilizers [14], photochromic materials [15,16] and luminescent solar collectors [17,18]. Moreover, these systems have also been projected to be useful in developing sensors for temperature [19] and humidity [20] and xerographic toners [21].

Since Weller's discovery of ESIPT in these molecules [22–24], salicylic acid (SA) and its derivatives have attracted considerable interest in the past [25–50] due to their various projected applications in the applied field. In the ground state, SA and its derivatives are present as two rotamers P and R (Scheme 1) [25,26]. Rotamer P is more stable than R [25] due to stronger intramolecular hydrogen bond. Excitation of rotamer P in the gas phase and in non-polar solvents gives rise to an ultrafast excited state intramolecular proton transfer (ESIPT) from the hydroxyl to the carboxyl group resulting in the formation of the tautomeric (T*) form (~60 fs in case of methyl salicylate (MS) [1]). This accounts for the large Stokes shift of SA fluorescence and its derivatives ($\lambda_{em} \approx 440$ nm) [25–35]. Rotamer R cannot undergo ESIPT and has normal fluorescence band with maximum at ~330 nm [25,26].

In protic polar solvents, such as water and ethanol, the fluorescence band maximum of SA and its derivatives moves to shorter wavelengths (~410 nm). This is accompanied by an increase in lifetime (1 to 6–8 ns) and fluorescence quantum yield [33,35]. Various neutral and ionic species have been identified in solutions [35].

Though SA and MS have been investigated extensively, the photophysics/photochemistry of substituted derivatives have been studied to somewhat lesser extent [37–50]. Particularly the study of 4-amino salicylic acid (4-ASA) and its esters has been confined mainly to solvents [41–45] and appears quite interesting. Kim and Yoon [44] observed that the fluorescence characteristics of 4-ASA are affected by varying the concentration of the solute molecule. Further, they observed dual emission at 330 nm and 440 nm in nonpolar aprotic solvents and have attributed it to the emission from the locally excited (LE) molecule and ESIPT states of the normal molecule. In nonpolar aprotic solvents, ESIPT as demonstrated by the large Stokes shift results in emission around 440 nm. However in aprotic polar solvents the large Stokes shifted emission band becomes broadened, indicating existence of another emission band probably originated from intramolecular charge transfer (ICT) [42,44]. These results are interpreted in terms of normal, twisted intramolecular charge transfer (TICT) and ESIPT fluorescence in aminosalicylates [42] and ESIPT coupled with charge transfer in 4-ASA [44]. In methanol it was suggested [44] that with increase in concentration an open intermolecularly hydrogen bonded conformer is formed which fails to undergo ESIPT.

Recently, study regarding the effect of amino group (–NH_2) substitution at 4th and 5th position on photophysical/photochemical properties of salicylic acid was done [45] and it was observed that

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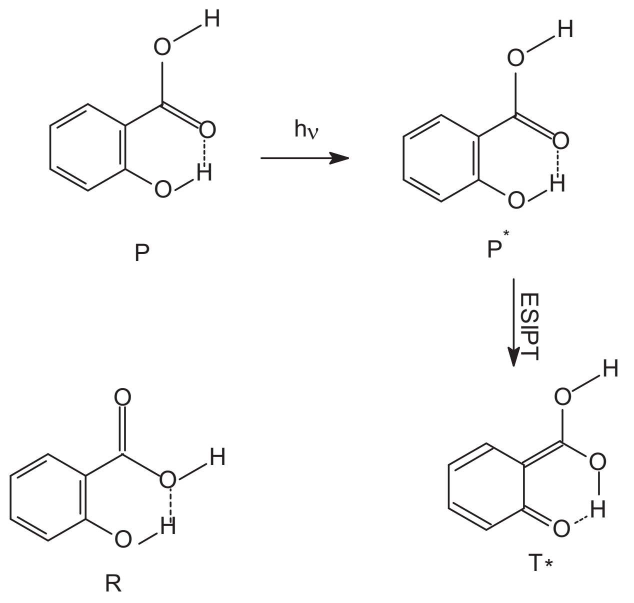


Scheme 1.

in aqueous solution, amino substitution at 4th-position does not lead to dual emission, unlike 5-ASA. However, normal and large Stokes shifted emission bands in 5-ASA are attributed to emission from the excited state tautomers of ground state zwitterion and anion, respectively.

It is evident from the above discussions that most of the fluorescence studies of 4-ASA undertaken so far are focused on the solution phase. The photo-induced excited-state relaxation processes in various polymers are useful for studying different specific interactions between solute and host polymers as it has been found that the photophysics and photochemistry of excited molecules are affected due to various polymer microenvironmental effects [51–55]. In fluid media, the fluorescence occurs at the same wavelength irrespective of the excitation frequency because of the fast relaxation time (τ_r) in comparison with the excited state lifetime (τ_f), and a dynamic equilibrium exists among these solvation sites. In rigid media, however, the dynamic equilibrium among different solvation sites is lost and emission occurs from the Frank Condon (FC) state that corresponds to the specifically excited solvation site, because the relaxation rate constants of different solvation sites are different. This leads to excitation wavelength dependence of fluorescence parameters [54]. Fluorescent probes have been used to observe orientation, rotational motion, conformational changes, diffusion of polymers, micro-polarity, micro-viscosity, free-volume, Young's modulus, hydrophobicity, etc. [53–59].

In view of the above we undertook a systematic study of the fluorescence 4-amino salicylic acid (4-ASA) in polar protic polymer poly vinyl alcohol (PVA) and less polar aprotic polymers poly methyl methacrylate (PMMA) and cellulose acetate (CA) and have explored the presence of various species/phenomena that contribute to the observed spectral features.

2. Experimental

2.1. Materials and polymer film preparation

4-ASA (obtained from Aldrich) of 98% purity was tested for its fluorescence purity and used as such. All the polymers were purchased from Sigma–Aldrich, India. All the solvents used were either of spectroscopic grade or were checked for their fluorescence purity. 4-ASA doped CA films were prepared by dissolving CA (average molecular weight 30,000) powder in acetone and mixing it with the desired concentration of 4-ASA in acetone. The resultant mass was spread in polypropylene dish to obtain the film. 4-ASA doped PMMA films were prepared by dissolving PMMA (average molecular weight 2,00,000) grains in ethyl acetate (EA) and mixing it with desired concentration of 4-ASA in EA. The films were again obtained by drying the mass in polypropylene dish. 4-ASA doped PVA films were prepared by mixing PVA (average molecular weight 1,25,000) grains with desired amount of 4-ASA in water. This mass was spread in polypropylene dish and was dried in an incubator. All the films were prepared for four concentrations, i.e., 0.01 wt%, 0.025 wt%, 0.05 wt% and 0.1 wt%. The average thicknesses of the polymer films were around 0.2 mm. The molecular structural formulae of different polymer matrices viz. PVA, PMMA and CA are shown below as Scheme 2.

2.2. Instrumentation

Steady state absorption spectra, at room temperature were recorded by dual beam JASCO V-550 spectrophotometer. The excitation and emission spectra were recorded by using JASCO FP–777 spectrofluorometer and data were analyzed by related software. Fluorescence decay curves were obtained by using time-correlated, single-photon counting (TCSPC) setup, coupled to a micro-channel plate photomultiplier (Hamamatsu, R3809U). Tsunami mode locked picosecond laser was used as the excitation source. Pulse width of the mode locked Tsunami laser is <2 ps which operates at 82 MHz, and the time per channel was 0.049 ns. The samples were excited at 295 nm and the fluorescence decay emission was collected by a monochromator at respective wavelengths with a collection bandwidth of 10 nm. A cut-off filter was used to prevent scattering of the excitation beam from the samples. The number of counts in the peak channel was at least 10,000.

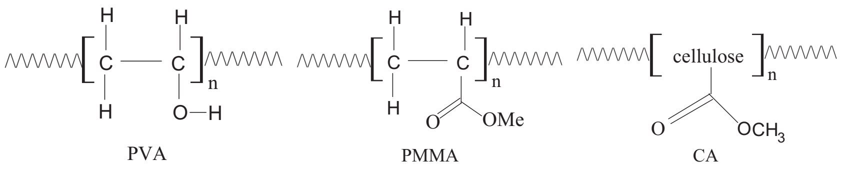
Time-resolved fluorescence decay curves were analyzed by deconvoluting the observed decay with the instrument response function (IRF) to obtain the intensity decay function represented as a sum of discrete exponentials:

$$I(\tau, t) = \sum_i \alpha_i \, e^{-t/\tau_i}$$

where $I(t)$ is the fluorescence intensity at time t and α_i is the amplitude of the ith lifetime such that $\sum_i \alpha_i = 1$.

3. Results and discussion

The steady state and time domain parameters of 4-ASA in different polymers are given in Tables 1 and 2, respectively.



Scheme 2.

Table 1
Spectral parameters of 4-ASA in protic and aprotic polymers for different concentrations.

Polymer	Conc. (wt%)	O.D.	λ_{ab} (nm)	λ_{em} (nm) (λ_{ex} = 300 nm)	Stokes shift (cm^{-1})
PVA	0.05	0.628, 0.445	271, 302	330, 410	2900, 8800
	0.025	0.528, 0.354	271, 301	330, 410	2900, 8800
	0.01	0.016, 0.014	269, 301	330, 410	2900, 8800
PMMA	0.05	0.642, 0.617	282, 305	331, 440	2600, 10059
	0.025	0.492, 0.481	282, 304	331, 440	2700, 10167
	0.01	0.018, 0.015	282, 305	331, 440	2600, 10059
CA	0.05	0.672, 0.696	282, 305	337, 435	3100, 9798
	0.025	0.522, 0.562	282, 305	337, 435	3100, 9798
	0.01	0.024, 0.022	282, 304	337, 435	3200, 9905

Table 2
Decay data of 4-ASA (0.25 wt%) in protic and aprotic polymers at λ_{ex} = 295 nm.

Polymer	λ_{em}	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	χ_2^2	χ_3^2
PMMA	340	7.8 (6.2)	1.1 (63.2)	0.16 (30.6)	5.40	1.11
	400	3.0 (11.0)	1.1 (53.8)	0.47 (35.2)	2.71	1.01
	500	–	1.5 (33.4)	0.59 (66.6)	1.02	–
CA	340	11.3 (7.7)	1.1 (58.5)	0.38 (33.8)	6.32	1.07
	400	4.9 (17.0)	1.4 (41.5)	0.54 (41.5)	3.91	1.02
	500	–	1.4 (49.4)	0.50 (50.6)	1.04	–
PVA	340	2.8 (14.6)	1.4 (51.2)	0.58 (34.2)	2.31	1.13
	400	2.6 (15.0)	1.4 (40.3)	0.70 (44.7)	1.87	1.15
	500	7.9 (24.4)	2.8 (38.3)	0.99 (37.3)	3.20	1.21

Corresponding amplitudes are given in parentheses. χ_2^2 and χ_3^2 are for two and three exponential fits, respectively.

3.1. Protic polar polymer

In PVA, 4-ASA (0.025 wt%) shows two absorption bands at ~270 nm and ~301 nm (Fig. 1). Within our experimental limits, absorption spectrum (as shown in Table 1) does not significantly change upon changing the solute concentration, unlike in polar solvents, e.g., methanol [41]. It can be mentioned here that in the concentration range (0.01–0.1%), taken in the present study, there is no evidence of dimers in the steady state spectra of 4-ASA. On excitation with λ_{ex} = 300 nm, dual emission (Fig. 1) with a large Stokes shifted emission (Blue, B band) at 410 nm is observed along with a normal emission band at 330 nm (ultraviolet, U band). The Stokes shifts for U and B bands with respect to the longer wavelength absorption band are 2900 cm^{-1} and 8800 cm^{-1}, respectively (Table 1). However, the B band has a maximum at significantly longer wavelengths as compared to that observed in basic methanol, at low concentrations in methanol/ethanol and water [43–45].

The excitation spectra monitored at different emission wavelengths are given in Fig. 2. When excitation spectrum is monitored at λ_{em} = 330 nm, only a single excitation band appears at 290 nm (Fig. 2b). While at λ_{em} = 412 nm, two bands appear at 273 nm and 305 nm (Fig. 2a), and excitation spectrum begins to look like absorption spectrum beyond this emission wavelength.

It can be noted here that in methanol, its parent molecule SA has been found to be present in the form of monoanion as well neutral species [35]. Moreover, the polarity of PVA ($E_T(30)$ is 51.9) is comparable to that of methanol ($E_T(30)$ = 55.5) [57]. In analogy with SA we can expect that in PVA also both neutral and anionic species should be present. To confirm this we checked the spectra in basic as well as acidic PVA by adding a few drops of NaOH and H_2SO_4 (Figs. 1 and 3).

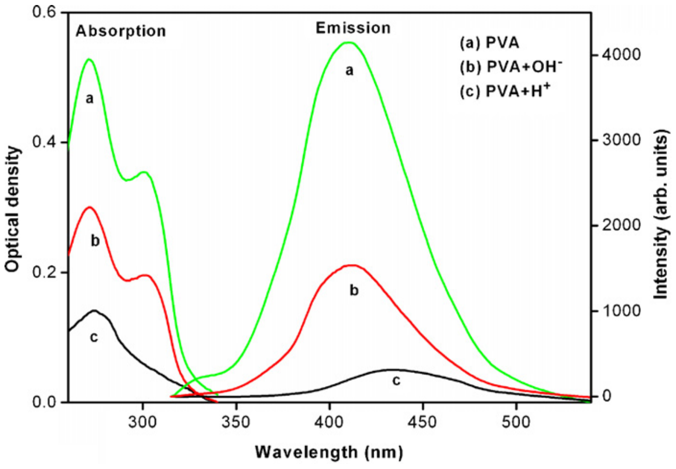


Fig. 1. Absorption and emission spectra of 4-ASA (0.25 wt%) in neat (a), basic (b) and acidic (c) PVA.

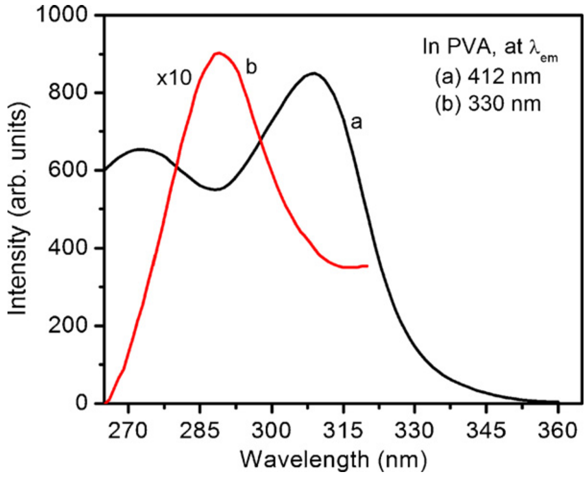


Fig. 2. Excitation spectra of 4-ASA (0.25 wt%) for (a) B band (412 nm) and (b) U band (330 nm).

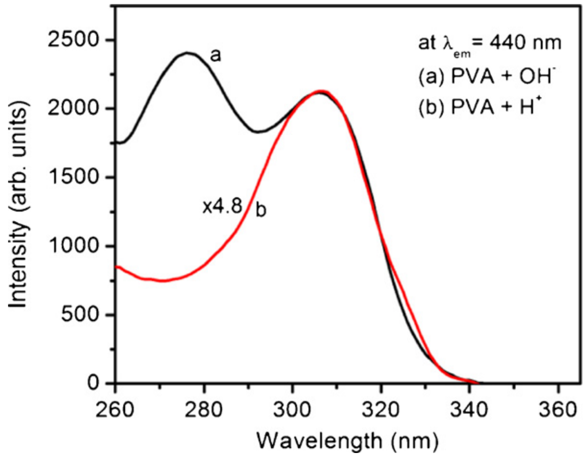


Fig. 3. Excitation spectra of 4-ASA (0.25 wt%) for B band (440 nm) in basic (a) and acidic (b) PVA.

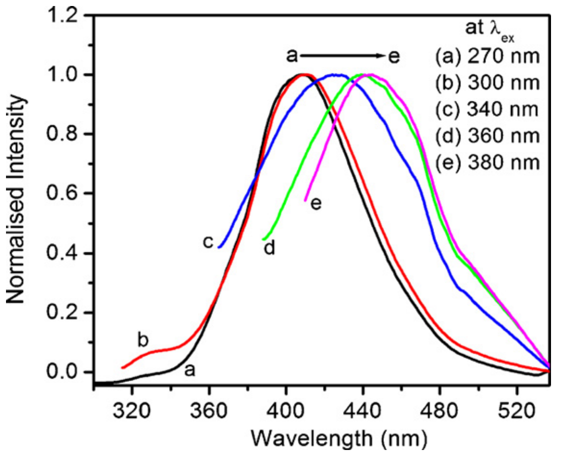


Fig. 4. Emission spectra of 4-ASA (0.25 wt%) in PVA at different excitation wavelengths.

It can be seen that in the presence of OH^-, the absorption spectrum remains almost unchanged (Fig. 1b) and the emission (Fig. 1b) shows a single band at 410 nm with structure around 390 nm. In acidic PVA, on the other hand, the absorption spectrum is different from neat as well as basic PVA as only a single absorption band (Fig. 1c) appears at 270 nm only, while the emission (Fig. 1c) is observed at ~440 nm (B band) and U emission is not observed. It can be suggested here that the B band observed at 410 nm in neat PVA should be because of overlapped emissions from neutrals (probably hydrogen bonded rotamers (P)) and anions [35] contrary to the suggestion of Kim and Yoon [44] that it originates only in neutrals. Interestingly in the presence of base, appearance of a pronounced shoulder around 390 nm shows that more anions should be present. However, unlike in case of aqueous solution [45], both neutrals and anions are present in PVA even in the presence of base, which indicates that all the 4-ASA molecules may not be exposed to the base in this matrix. The absence of 340 nm band in basic as well as acidic PVA points that the R type of conformers may be less in number in these environments.

The excitation spectra (Fig. 2) suggest that U band should originate from R type of conformers, which do not have appropriate hydrogen bond for undergoing ESIPT and hence show normal Stokes shift. Emitting species (ionic and neutral) present in protic PVA polymer are shown in Scheme 3.

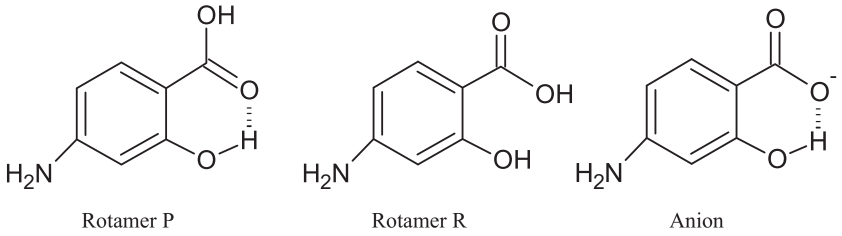
The B band at 440 nm (observed in acidic PVA, Fig. 1c), of course, should come from fast ESIPT reaction in P type of conformers. However, the band at 410 nm in neat and basic PVA can be attributed to the overlapped emission from anion and neutral species (rotamer P), which undergo ESIPT. This is evident from the excitation spectra also (Fig. 3). Thus, the U emission unambiguously can be attributed to R type of conformers. This also is in disagreement with the suggestion of Kim and Yoon [44] that the UV band is due to the LE state of the P type of conformer. Had it been from LE state of P, the excitation spectra would have been identical for both UV and B emissions.

Moreover, the excitation spectra are quite different for acidic/basic PVA (Fig. 3). For acidic PVA, the spectrum shows only band around 305 nm unlike for basic PVA where two bands are evident. Again this behaviour can be due to increased neutrals in presence of acid.

Interestingly emission spectra are also found to be dependent on excitation wavelength. Fig. 4 shows the emission spectra of 4-ASA monitored at different excitation wavelengths. On excitation at the red edge of the first absorption band, emission maximum of the B band shifts to the longer wavelength side. This phenomenon is termed as red edge excitation (REE) or edge excitation red shift (EERS).

EERS observed for 4-ASA can be interpreted due to different conformers trapped in different geometries. In a fluid medium these conformers interchange rapidly, however, in rigid medium the conformers are trapped in certain geometric configurations. The viscosity required to trap different conformers depends on the structure of the molecule and the amount of free volume in the matrix [54,55]. As PVA has less free volume [55], one can expect EERS effect in this matrix.

The time domain measurements (Table 2, Fig. 5) show that the decay fits with a triple exponential function throughout the emission profile. At λ_{em} = 340 nm, recovered decay times are τ_1 = 2.8 ns, τ_2 = 1.4 ns and τ_3 = 0.58 ns (Table 2) whereas at the extreme red edge of the emission spectra (at λ_{em} = 500 nm), the decay components are τ_1 = 7.9 ns, τ_2 = 2.8 ns and τ_3 = 0.99 ns. At λ_{em} = 340 nm, the presence of these components can be attributed to the presence of two neutral (P and R) and ionic species (A) in the overlapped emission spectrum whereas at λ_{em} = 500 nm, only P type of neutrals are expected to be present (emission from ions may not contribute at this wavelength). As we did not see any rise time even at 500 nm



Scheme 3.

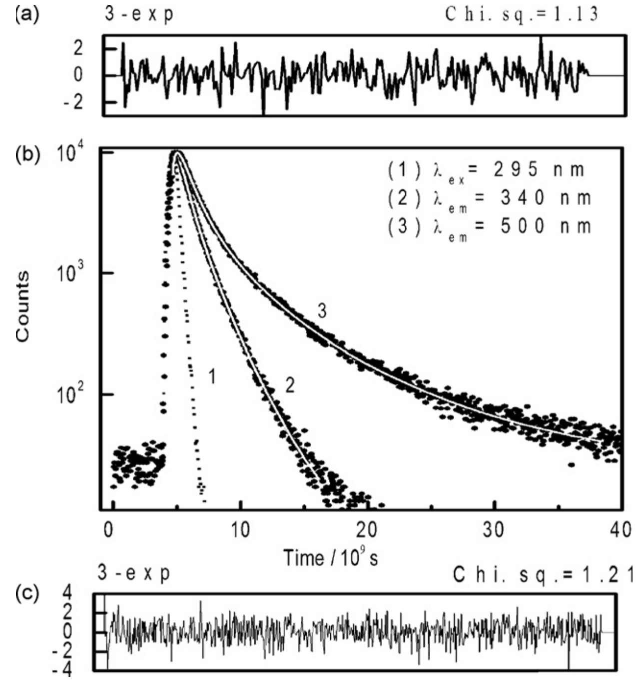


Fig. 5. Decay curves of 4-ASA (0.25 wt%) in neat PVA (1) instrumental profile and decay curves with λ_{ex} = 295 nm at λ_{em} = 340 nm (2) and 500 nm (3). Residuals and the χ^2 values for λ_{em} = 340 nm (a) and for λ_{em} = 500 nm (c).

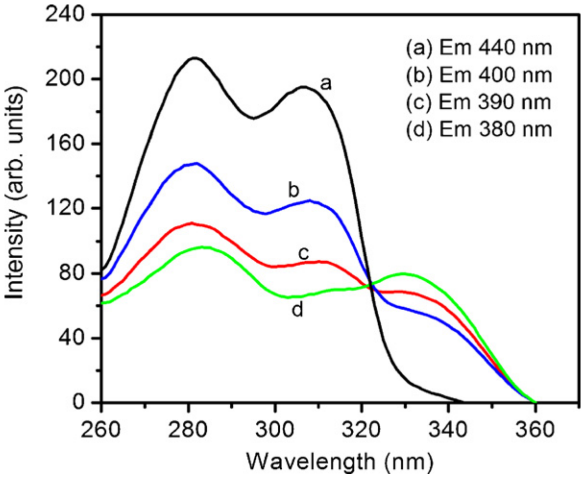


Fig. 7. Excitation spectra of 4-ASA (0.25 wt%) for different emission wavelengths in PMMA.

(tail part of the spectra), an excited state reaction appears to be unlikely. Of course, a longer decay component (7.9 ns) may originate from those neutrals, which are linked with hydrogen bonding to the polymer. At the same time we would also like to mention that the presence of three components indicates that data may get somewhat complicated because of the trapping of neutrals in various geometries as well as due to the presence of various species in the polymer. This fact is also corroborated by the fact that EERS is observed in the emission.

3.2. Aprotic polymers

Absorption spectra of 4-ASA (0.025 wt%) show two absorption bands at 280 nm and 305 nm in both CA and PMMA polymers (Fig. 6) and the absorption appears independent of concentration of solute.

In PMMA, on excitation at λ_{ex} = 300 nm, again dual emission (Fig. 6) with a large Stokes shifted emission band at 440 nm (B band) is observed along with normal emission band at 334 nm (U band) whereas in CA, the B band shows maximum around 435 nm (Fig. 6). The Stokes shifts of U and B bands corresponding to their longer wavelength absorption band in PMMA are 2600 cm^{-1} and 10059 cm^{-1} and for CA are 3100 cm^{-1} and 9798 cm^{-1}, respectively (Table 1). A small shift in the emission maxima on these two aprotic matrices may be due to difference in the respective hydrogen boding ability of the polymers. It can be noted that unlike PVA, the B emission is considerably red shifted in these matrices.

In the excitation spectra of 4-ASA in aprotic polymers (Fig. 7), one can notice two excitation bands (Fig. 7) identical to the absorption spectrum (Fig. 6) for λ_{em} = 440 nm. Akin to PVA, the U and B bands can be assigned to R and P type of conformers.

Interestingly for λ_{em} = 380 nm, a new excitation band appears around 330 nm in the excitation spectrum (Fig. 7). Moreover, at 320 nm, an isobestic point is observed in the excitation spectra.

The emission spectra corresponding to various excitation wavelengths are shown in Fig. 8. At longer wavelengths of excitation, 380 nm band is quite prominent. We have also noticed that the intensity of the 380 nm band is relatively increased with concentration (not shown). The appearance of the red shifted band in excitation spectra for 380 nm together with its increase with concentration suggests the presence of aggregates although they are not evident in the absorption (probably because of their

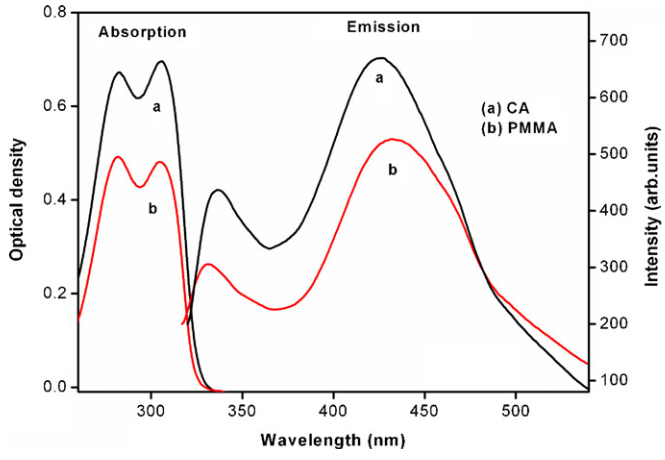


Fig. 6. Absorption and emission spectra of 4-ASA (0.25 wt%) in CA (a) and PMMA (b) at λ_{em} = 300 nm.

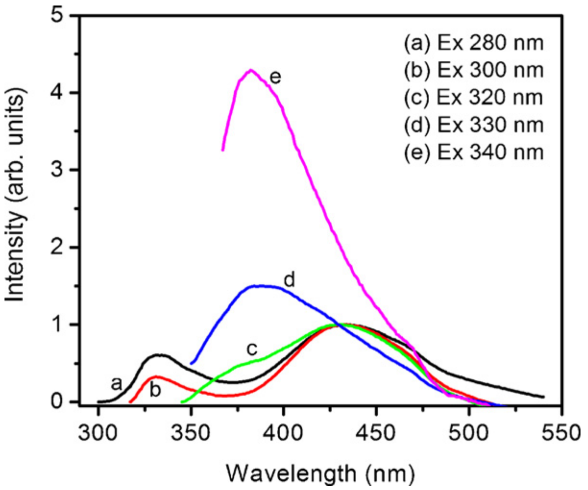


Fig. 8. Emission spectra of 4-ASA (0.25 wt%) in PMMA for different excitation wavelengths.

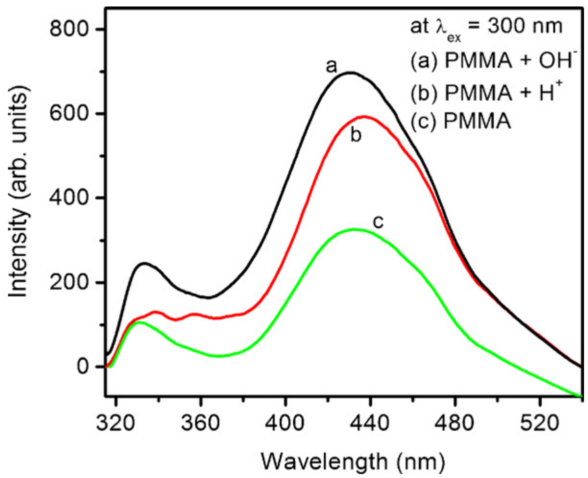


Fig. 9. Emission spectra of 4-ASA (0.25 wt%) in neat (a), acidic (b) and basic (c) PMMA at λ_{em} = 300 nm.

less number). In analogy with earlier reports for SA in nonpolar matrices [27] this band can be attributed to aggregates although PMMA is somewhat polar in nature. It is noteworthy that in polar PVA we did not see this emission, which rules out the presence of aggregates in polar matrices. However, unlike PVA, EERS is not noticed in this matrix. This can be attributed to less free volume in case of PVA as compared to PMMA [55]. It is well known that smaller the free volume, the more will be the EERS [55].

In acidic or basic PMMA, steady state spectrum more or less remains unaltered (Fig. 9). A notable point is that in acidic medium U band in the emission spectrum (Fig. 9b) becomes structured. It is likely that some cationic species may also be present in PMMA in the presence of acid. However, we did not observe emission due to anion even in basic PMMA (Fig. 9a). This may probably be due to less number of anions in this matrix.

Decay curves for 4-ASA in PMMA are shown in Fig. 10 and the results are summarized in Table 2. The fluorescence decay for 340 nm fits with a triple exponential function with decay times as τ_1 = 7.8 ns, τ_2 = 1.10 ns and τ_3 = 0.16 ns, respectively (Table 2). At the extreme red edge of the emission spectra (at λ_{em} = 500 nm) the decay fits to bi-exponential function. The decay component (τ_2) remains almost constant in the entire profile. Again at 340 nm (for λ_{ex} = 295 nm) the presence of R and P species can be invoked to explain the decay data. However, the presence of third component in PMMA is somewhat intriguing. It is less polar than PVA [57,59] and hence presence of anion can be ruled out. The presence of various trapped species can also be ruled out as EERS is not observed. The contribution from aggregates is also not possible because these have considerable red shifted excitation. In view of this we feel presence of free as well as hydrogen-bonded conformers in this matrix may be responsible for the third component as it has a hydrogen bond accepting nature.

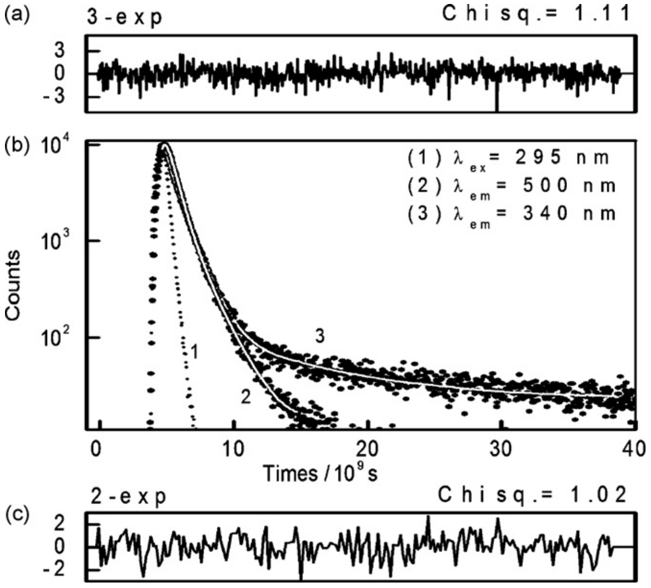


Fig. 10. Decay curves of 4-ASA (0.25 wt%) in neat PMMA (i) instrumental profile and decay curves with λ_{ex} = 295 nm at λ_{em} = 500 nm (2) and 340 nm (3). Residuals and the χ^2 values for λ_{em} = 340 nm (a) and for λ_{em} = 500 nm (c).

Increase in the decay time in these polymers as compared to the fluid solutions [42] indicates that the rigidity of the matrix decreases the nonradiative transition as in case of salicylic acid (SA) [35].

Similar trend in decay time results was obtained for another aprotic polymer CA (Table 2). However, the fluorescence intensity and magnitude of decay times decrease in the order of CA > PMMA. The difference in fluorescence parameters probably should be due to difference in the free volume as well as the binding nature of the polymer.

However, it is not possible to directly correlate the changes in spectral as well as decay time behaviour to free volume/glass transition temperature (T_g) as CA, PVA and PMMA have glass transition temperatures of 65–68 °C, 85 °C and 105–114 °C, respectively [60–62]. As the spectral as well decay parameters are not only dependent on free volume but on the polarity and binding ability of the polymer also, it is not possible to correlate these feature with free volume in the case of present study. At the same time we would like to mention that it will be interesting to see the effect with polymer having same polarity/binding character but different glass transition temperatures (by changing pendant groups), e.g., PMMA, polyethyl methaacrylate (PEMA) and polypropyl methacrylate (PPMA) [60,61].

4. Conclusion

The steady state and time resolved spectra of 4-ASA in polymer matrices reveal some new interesting features. In polar protic PVA, anion and neutral species (rotamer R and P) are identified. It has also been demonstrated that the different emission bands originate from different conformers contrary to earlier suggestions that these emissions come from the same conformer. In PMMA neutral species (rotamer R and P) are present, which partly convert to cations in the presence of acid. Moreover, presence of aggregates is also noticed in less polar polymers. We feel that present study will have implications in the study of probes for polymers.

Acknowledgements

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