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## Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: [www.elsevier.com/locate/saa](http://www.elsevier.com/locate/saa)

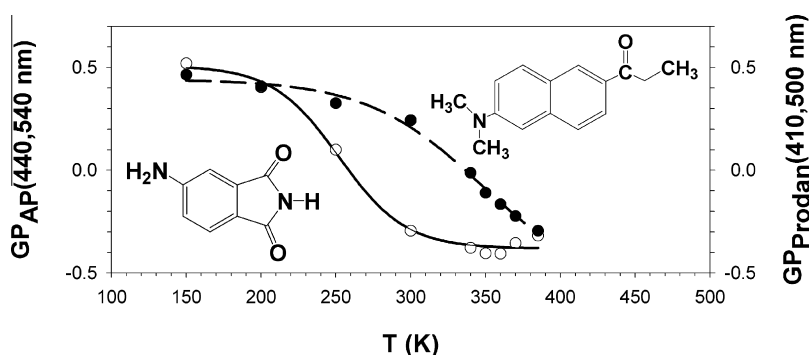
## Fluorescent polymer coatings with tuneable sensitive range for remote temperature sensing

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## HIGHLIGHTS

- Coatings of poly(vinylalcohol) – fluorescent dyes are adequate temperature sensors.
- Red edge excitation shift of emission is the working principle.
- The sensitivity range is greater than 100 K.
- The useful temperature range can be tuned by the dye–polymer interactions.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Article history:

Received 13 February 2013

Received in revised form 25 June 2013

Accepted 1 July 2013

Available online 10 July 2013

## Keywords:

Temperature sensor

Remote sensing

Polymer coatings

Temperature sensitive paints

Fluorescence

## ABSTRACT

Polymer films of poly(vinyl alcohol) containing the fluorescent dyes 4-aminophthalimide (AP) or 6-propionyl-2-dimethylamino-naphthalene (Prodan) are used as temperature-sensitive fluorescent coatings for remote temperature sensing. Temperature can be obtained by a two-wavelength ratiometric-based emission intensity measurement. The coatings are sensitive in a 100 K temperature range that can be tuned by polymer–solute interactions. The usable range is 200–300 K for AP and 280–380 K for Prodan.

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## Introduction

Optical molecular sensing is a matter of intense research because it offers the possibility of easy and inexpensive detection

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while providing a very high sensitivity and low detection limit, especially when emission spectroscopy can be used [1]. Luminescent sensors are commercially available for different cations and anions [2–4]. Detection of physical parameters by molecular sensors has been much less explored [5–7]. Though there are quite well known luminescent sensors for polarity [8–13], the literature has much less examples of temperature sensitive luminescent systems [4,14–16]. Due to enhanced nonradiative deactivation with temperature, almost all fluorophore has a negative emission intensity coefficient. But normally this variation is small. Ruthenium(III) polypyridines display temperature sensitive emission

intensity due to the presence of emission quenching excited states that can be populated by thermal activation [17]. Poly(N-isopropylacrylamide) and polymers of related monomers have been copolymerized with acrylate labeled with a polarity-responsive fluorescent benzoxadiazole to render nanometric sized beads with extraordinary temperature sensitivity of a factor of 2 per each Celsius degree. The sensitivity range of 3–9 K is tunable by the polymer nature [18].

For applications such as remote sensing of two dimension temperature mapping, as in aerodynamic wind tunnel tests, the temperature sensitive material must be dosified as paint and its luminescence should fall in the visible range of the spectrum. The studies using temperature sensitive paints provide valuable information on aerodynamic performance and on heat transfer in structures [19]. A luminophore is included in a polymer matrix and the temperature dependent intensity is collected. Porphyrin and perylene derivatives as well as Ru or Eu complexes or Eu doped lanthanide oxides are used as active material.

In contrast to direct luminescence intensity, ratiometric measurements are able to compensate light source fluctuations in time and space and the uneven distribution of luminophore in the coating and the coating thickness variations. Ratiometric luminescent systems proposed for temperature sensors include high spin-low spin switchable quenching of an organic luminophore linked to a Ni(II) macrocyclic complex [14], the monomer exciplex emission of perylene and N-allyl-N-methylaniline [15], and the state switching of Ru(II) complexes [16]. Of all these systems, the second is the only one used in a polymer matrix: a polystyrene matrix used to build a ratiometric sensor with Arrhenius type response in the 300–360 K range.

In this work, we report on the characteristics of the temperature sensitivity of poly(vinylalcohol) (PVA) films containing 4-aminophthalimide (AP) or 6-propionyl-2-dimethylamino-naphthalene (Prodan), considering their application as temperature sensitive coatings. These systems seem quite promising because the temperature sensitive range can be tuned by choosing the probe-polymer pair. Probe location in the polymer, as well as the nature and strength of probe polymer interactions are the key to the appropriate material performance.

Molecular movements such as diffusion and molecular reorientation are highly restricted in inorganic solids but they are less confined in polymer systems [20,21]. These movements influence emission very much through excited state reactions (excimer or exciplex formation or quenching), and through the medium contribution to the Stokes shift, respectively. The contribution of local reorientation motions is particularly important in fluorophores that have a great difference in molecular interactions with the medium between the ground and the excited states. This is the characteristic of typical medium sensitive probes for polarity and medium relaxation [8,22].

AP and Prodan are highly fluorescent molecules with similar medium sensitivity of their luminescent characteristics [23–25]. In particular, they are sensitive to the polarity as well as to the hydrogen bond donating (HBD) capability of the medium. The temperature dependent emission spectrum of AP was first reported by Ware [23]. Prodan was extensively used to measure fluidity changes in membranes and lipid bilayer induced by temperature [26]. The incomplete medium relaxation in polymers gives rise to what is called red edge excitation shift (REES) [27–29]. This effect is evidenced as a red shift in the emission spectrum as the excitation wavelength of the fluorophore is increased in the red edge of the absorption band. The magnitude of the shift depends on the difference of interaction between ground and excited states of the fluorophore with the medium, and on the relative values of the excited state lifetime and the characteristic time of the relevant medium relaxations. REES persists in a very broad temperature

range from cryogenic temperatures to some degrees above the glass transition temperature,  $T_g$ , of the polymer. AP and Prodan in PVA meet all the requirements to perform as excellent systems for the planned experiments [30].

## Experimental section

### Chemicals

4-aminophthalimide, AP, was purchased from Aldrich and recrystallized from ethanol. 6-Propionyl-2-(dimethylamino)naphthalene, Prodan, was from Molecular Probes and was used as received. Poly(vinylalcohol), PVA, was from Fluka and poly(vinylacetate), PVAc, was from Polysciences.

### Sample preparation

Polymer films were casted from an aqueous solution (for PVA) or from a dichloromethane solution (for PVAc) of the polymer and dye, allowed to dry under air and finally dried under vacuum at 40 °C overnight. The films were placed in a quartz tube and sealed under vacuum.

### Temperature dependent emission spectra

Were recorded in a SLM steady state spectrofluorimeter with an APD Cryogenics cryostat for temperature variation and control. Spectra were corrected for the wavelength dependent sensitivity of the emission channel of the spectrofluorimeter.

## Results and discussion

Fig. 1 shows the REES of AP in PVA. Emission spectra are shown for different excitation wavelengths ( $\lambda_{exc}$ ) at 150 K. The inset shows the plots of the emission maxima as a function of  $\lambda_{exc}$  in a very broad temperature range. From this latter plot it is evident that the broadest spectral shift with temperature is attained in the blue edge of the excitation spectrum. Therefore 340 nm was chosen as the most suitable excitation wavelength for AP. Similar analysis was applied to spectra excited at 370 nm to see the behavior of the system at a wavelength nearer to the Hg line of 366 nm (results not shown). With a 10% smaller spectral shift with temperature, all the main features remain unchanged under these conditions compared to 340 nm excitation.

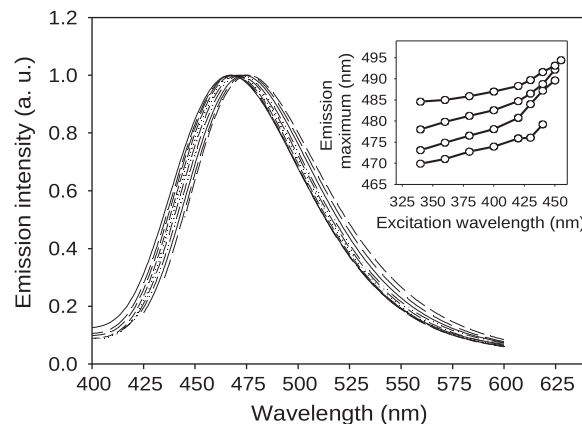
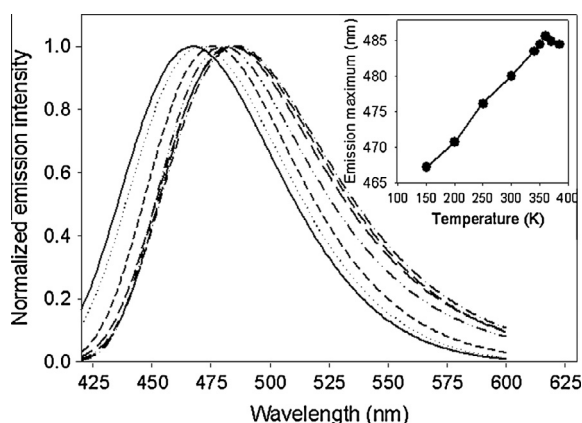


Fig. 1. Emission spectra of AP in PVA at 150 K excited at 340, 360, 380, 400, 420, 430, 440, 450, and 460 nm (curves from left to right). Inset: emission maximum as a function of excitation wavelength for the same system. Curves from bottom to top correspond to 150, 200, 250, and 360 K, respectively.



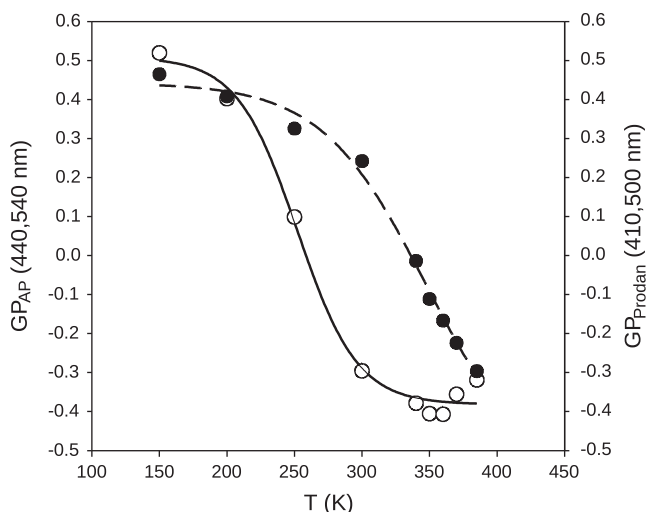
**Fig. 2.** Emission spectra of AP in PVA, excited at 340 nm, as a function of temperature (from left to right: 150 K, 200 K, 250 K, 300 K, 340 K, 360 K, 385 K). The inset shows the temperature dependence of the emission maximum.

**Fig. 2** plots the emission spectra of AP in PVA as a function of temperature when the sample is excited at 340 nm. The inset shows the temperature dependence of the emission maximum under these conditions. The shift is 20 nm to the red upon temperature increase from 150 to 360 K. This shift is due to the molecular interactions with the hydroxyl groups of the polymer. For comparison, in poly(vinylacetate) (PVAc) the red shift is only 5 nm. Similar results are obtained for Prodan in PVA and PVAc. For this sample, the shift amounts to 18 nm in PVA between 150 and 385 K and 5 nm in PVAc in the same temperature range [30].

The temperature response of these fluorescent coatings can be best displayed as a ratiometric function. The best choice is a pair of wavelengths, one in the blue and one in the red edge of the emission spectrum. We prefer to express this function as the generalized polarization (GP) [31], as expressed in the following equation.

$$GP_{\lambda_1, \lambda_2} = \frac{I_{em}(\lambda_1) - I_{em}(\lambda_2)}{I_{em}(\lambda_1) + I_{em}(\lambda_2)} \quad (1)$$

The choice of the appropriate emission wavelengths ( $\lambda_1$  and  $\lambda_2$ ) is particular for each compound and polymer matrix. **Fig. 3** displays the GP as a function of temperature for PVA films containing AP or Prodan. The two fluorophores exhibit their steepest temperature response in different ranges: 200–300 K for AP films, and 300–385 K



**Fig. 3.** Generalized polarization plots for AP (hollow circles) and Prodan (filled circles) in PVA films as a function of temperature.

for Prodan containing films. This difference has various origins. On one side, Prodan displays a shorter excited state lifetime compared to AP. The single wavelength emission decays are not single exponential, so the excited state lifetime is characterized by its average decay time. These values are 3 ns for Prodan and 15 ns for AP [30]. The longer excited state lifetime favors polymer relaxation prior to emission at a lower temperature and this effect can tune the range of the steepest temperature sensitivity of the film. Another factor that governs the temperature range of maximum sensitivity is the location of the probe in the polymer environment. Optimum solvation of the excited state requires the movement of polymer moieties to accommodate an excited state with appreciably different interactions with the environment than the ground state. PVA chains pack in environments with concentrated hydroxyl moieties highly polar and hydrogen bonding to the probe and other environments more apolar with a higher concentration of hydrocarbon chains. In another work [30] we showed by solvatochromic plots that AP is able to penetrate the OH rich pockets of the polymer and locate in environments with polarity similar to *tert*-butyl alcohol or 2-propanol. In the diversity of environments where AP might locate there is always a great contribution of hydrogen bonding interactions. Prodan locates in environments similar to acetone or acetonitrile, not evidencing the participation of hydrogen bond interactions. The complete relaxation of the excited state requires therefore higher temperature to be achieved. Therefore probe location contributes in the same direction to the difference in sensitivity range of AP and Prodan.

All measurements reported in this work were performed under vacuum in a sealed tube. Moisture content affects PVA relaxations because water is a plasticizer of PVA, and therefore results in variable humidity environments may differ broadly from those under dry conditions. Though this is a disadvantage of the polymer matrix chosen, it does not invalidate the principle of sensing and displaying the temperature sensitivity. The drawback can be overcome by an appropriate change in the polymer matrix, or alternatively it could be advantageous to tune the temperature response range.

The method overcomes many drawbacks of polymer films for temperature sensitive applications such as extremely slow diffusion that prevents bimolecular reactions and takes advantage of this restriction in mobility of the polymer chains by using a one component sensor. It has the advantage over liquid crystalline cholesteric coatings, in that it has a broader temperature response range. Finally, the possibility of tuning the most sensitive temperature range with the excited state lifetime of the fluorophore and with polymer probe interactions is an attractive feature of this approach.

## Conclusions

We propose a simple to use and inexpensive temperature sensitive coating. The temperature dependent signal is originated on the spectral shift of a fluorescent dye embedded in a polymer matrix. In this matrix, the shift, which is known as red edge excitation shift, is caused by incomplete relaxation of the polymer environment. Understanding the molecular basis of the working signal allows optimizing and extending the usable systems and conditions. AP and Prodan are examples of fluorescent dyes with a great change in interactions with the environment between the ground and the emissive electronic states: electric dipolar moment, hydrogen bonding interactions, relaxed geometry in each state. On the other side, PVA is a suitable polymer to enhance these differences. The same rationale can be used to propose other combinations to tune the temperature range for maximum sensitivity or the spectral range for excitation and emission.

## Acknowledgments

BCB, CAC, and PFA are members of Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET, Argentina). The work was performed under financial support from ANPCyT, UBA, and CONICET (Argentina), and FAPESP, CNPq/INEO (Brazil).

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