Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 116 (2013) 13–16

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Fluorescent polymer coatings with tuneable sensitive range for remote temperature sensing

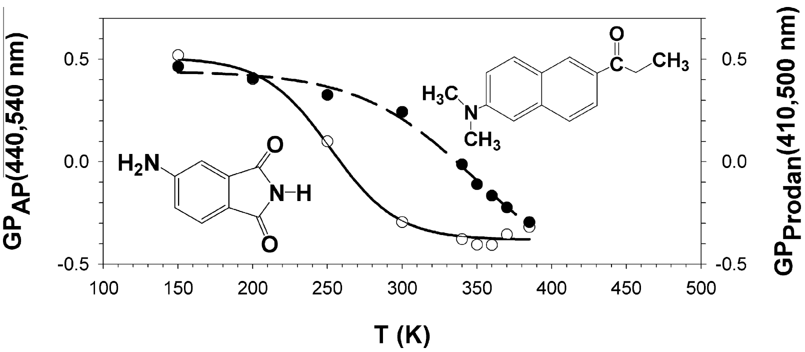
Beatriz C. Barja [a], Carlos A. Chesta [b], Teresa D.Z. Atvars [c,*], Pedro F. Aramendía [a,*,1]

[a] *INQUIMAE and Dept. Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón 2, C1428EHA Buenos Aires, Argentina*
[b] *Departamento de Química y Física, Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Río Cuarto, 5800 Río Cuarto, Córdoba, Argentina*
[c] *Chemistry Institute, State University of Campinas, PO Box 6154, Campinas 13083-970, SP, Brazil*

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.

Introduction

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

---

* Corresponding authors. Tel.: +55 19 3521 3078; fax: +55 19 3521 3023 (T.D.Z. Atvars), tel.: +54 11 4576 3378; fax: +54 11 4576 3341 (P.F. Aramendía).

E-mail addresses: barja@qi.fcen.uba.ar (B.C. Barja), cchesta@exa.unrc.edu.ar (C.A. Chesta), tatvars@iqm.unicamp.br (T.D.Z. Atvars), pedro@qi.fcen.uba.ar (P.F. Aramendía).

[1] Present address: Centro de Investigaciones en Bionanociencias (CIBION)-CONICET, Godoy Cruz 2390, 1425 Buenos Aires, Argentina.

1386-1425/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.saa.2013.07.003

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, Tg, 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 (λ_{exc}) at 150 K. The inset shows the plots of the emission maxima as a function of λ_{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.

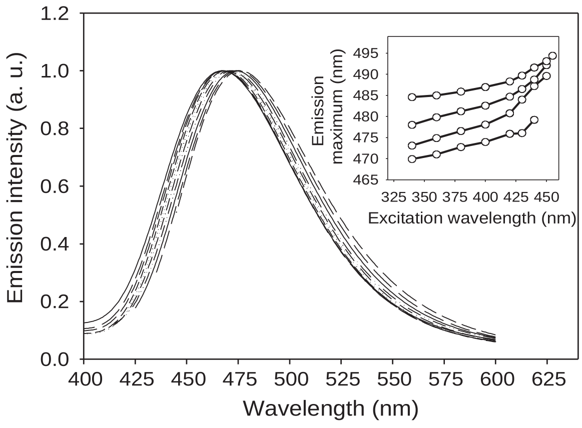


Fig. 1. Emission spectra of AP in PVA at 150 K excited at 340, 360, 380, 400, 420, 430, 440, 450, and 460 nm (curves from left to right). Inset: emission maximum as a function of excitation wavelength for the same system. Curves from bottom to top correspond to 150, 200, 250, and 360 K, respectively.