Phosphorescence and Fluorescence of Poly(vinyl Alcohol) Films

JANUARY MIELOSZYK, REGINA DRABENT, and JÓZEF SIÓDMIAK, *Institute of Physics and Food Chemistry, Academy of Agriculture and Technology, 10-957 Olsztyn, Poland*

Synopsis

Luminescence properties of poly(vinyl alcohol) (PVA) films were investigated at room and low (103 K) temperatures. It was estimated that the PVA films can be regarded as luminescentless matrices when excited by radiation of wavelengths greater than 420 nm ($\lambda_{exc} \geq 420$ nm).

INTRODUCTION

Isotopic and anisotropic poly(vinyl alcohol) (PVA) films are often used as a matrix for spectral investigation of dyes and pigments.[1-7] PVA films as rigid matrices are mainly used to study the fluorescence properties of the dyes. Much information about dyes and pigments can be outlined during the investigation of phosphorescence properties at room and low temperatures.

If absorption spectra of a dye and that of a PVA film overlap then the excitation of the dye can be connected with emission of the matrix. The greater the share of the emission of a matrix in the total emission, the less the yield of dye luminescence and concentration.

The aim of this paper was to study the phosphorescence and fluorescence of the PVA films at room and low temperatures. It was also necessary to determine the spectral range of excitation in which the PVA matrix does not exhibit the emission.

EXPERIMENTAL

Coarse-grained PVA powder from Loba-Chemie Wien-Fischamend was used for experiments. The PVA macromolecules are built up from two types of monomers; vinyl alcohol CH_2=CHOH and vinyl acetate CH_2=$CHOOCCH_3$. The PVA used in our experiment contained much vinyl acetate, but not more than 50%.[1]

The PVA was mixed with redestilled water in a weight ratio 1:6 and maintained for 24 h at room temperature to swell. The mixture was warmed up in thermostatic condition (353 K) during 12 h and was allowed to cool down for next 12 h. This solution was poured on level glass plates and dried at room temperature for some days to obtain rigid and transparent films.

The Opton PMQ MM12Q spectrophotometer equipped with cryostat was used to record the absorption spectra. The fluorescence spectra, phosphorescence spectra, and polarized phosphorescence spectra were measured using a

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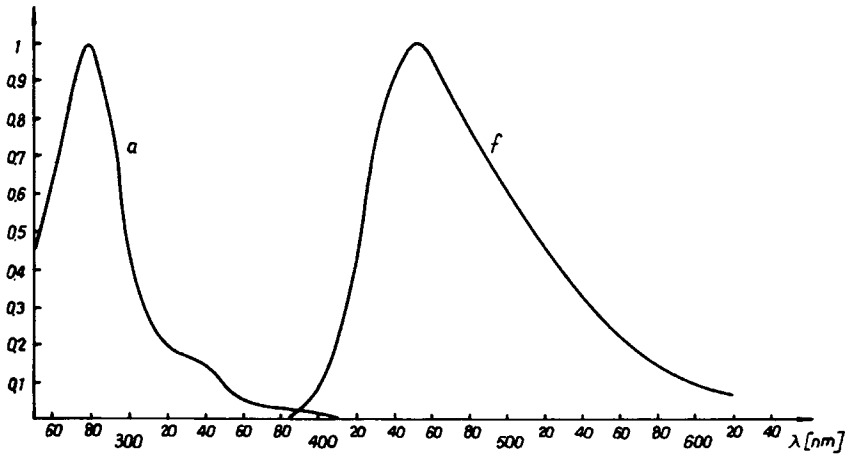

Fig. 1. Absorption spectrum (a) and fluorescence spectrum (f) of the PVA films normalized to 1 in. maximum.

set designed by us.[8] All spectra were studied at room temperature (293 K) and low temperature (103 K).

The apparatus correction and correction with regard to reabsorption were accomplished for all measurements. All spectra were normalized to 1 in. maximum to compare band positions.

RESULTS AND DISCUSSION

The absorption spectra of the PVA films at low temperature (103 K) were measured to determine the excitation range of the PVA emission. It was found that the absorption spectrum at low temperature was similar to that at room temperature. So the spectral range of excitation was the same at low and room temperatures. To estimate the wave range in which the PVA films can be regarded as luminescentless matrix the measurements were performed from 240 to 450 nm. It was found that the emission properties of the PVA films depended on the method of preparation of films (especially on the degree of dryness and the time of storage). Therefore the typical results for all investigated samples are discussed in this paper.

The PVA films exhibited a relatively weak fluorescence in the excitation region from 260 nm to about 410 nm at both room and low temperatures. The fluorescence band appeared at about 450 nm (Fig. 1).

The PVA matrices demonstrate the phosphorescence at low and room temperatures. The intensity of phosphorescence at low temperature is about five times greater than that at room temperature. And there occurs characteristic dependence between the position of phosphorescence maximum and the wavelength of exciting light. The measurements of phosphorescence were performed for three wavelengths of exciting radiation (λ_{exc} = 280 nm, 340 nm, and 400 nm). Those wavelengths lie in three exciting regions to which three different phosphorescence bands can be attributed. Figure 2 shows that there are three phosphorescence bands of maxima at about 490 nm, 540 nm, and 580 nm at room temperature (solid line) and of maxima at about 460 nm, 520 nm, and 565 nm at 103 K (dotted line).

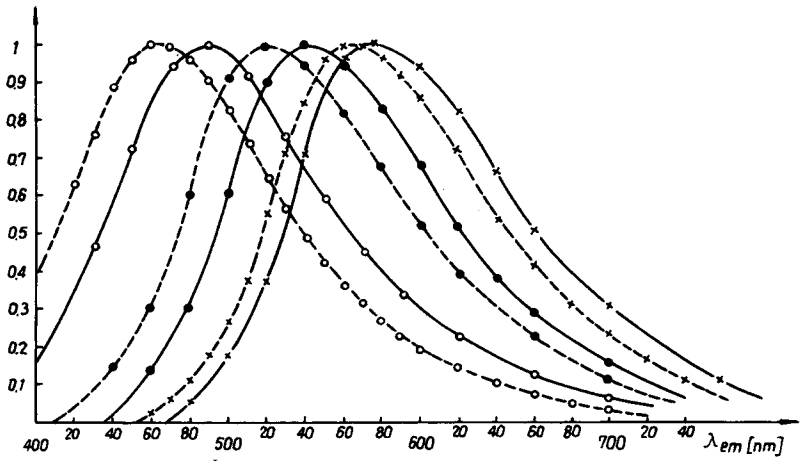

Fig. 2. Phosphorescence spectra of the PVA films at room temperature (293 K solid line) and low temperature (103 K, dotted line), normalized to maximum. (○○) λ_{exc} = 280 nm, (●●) λ_{exc} = 340 nm, (××) λ_{exc} = 400 nm.

Polarized excitation spectra are shown on Figure 3. It is possible to conclude that in the PVA matrices three exciting ranges (R_1, R_2, R_v) can be distinguished at room and low temperatures. The R_1, R_2, R_v have different value of phosphorescence anisotropy. Our previous investigation[1] proved that electronic absorption spectrum of the PVA consists of two bands (band 1, λ_{max} = 332 nm and band 2, λ_{max} = 278 nm). Range of excitation applied in experiments is due to those absorption bands (λ_{exc} = 280 nm and 340 nm) and it contains the long-wave edge of spectrum (λ_{exc} = 400 nm). It can be considered that the phosphorescence was excited in the range of three electron transitions (excitation regions R_1, R_2, R_v) for two reasons. (1) The dependence the phosphorescence spectra on exciting wavelength (Fig. 2) and (2) the character of polarized excitation spectrum (Fig. 3). It seems that three different chromophore groups of PVA chains contribute to the absorption spectra.

Lloyd[9] proved that the chromophores with empiric formula —(CH=CH)$_n$—CO— for n between 1 and 3 are responsible for absorption in the ultraviolet (UV) region and for $n > 3$ in the visible region. Character and quantity of

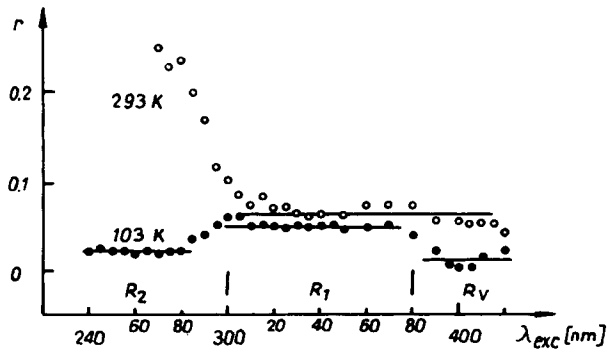

Fig. 3. Polarized excitation spectra of the PVA films in room (293 K) and low (103 K) temperature. r— anisotropy of phosphorescence.

those chromophore groups are connected with conditions of polymerization of PVA. It suggests that it is possible to attribute the three different electron transitions postulated above to three different chromophore groups.

The position of phosphorescence spectra depends distinctly on temperature. At a given exciting wavelength the phosphorescence spectrum shifts toward longer waves with increase of temperature (on Fig. 2, dotted and solid curves). It is possible to explain this shift of phosphorescence spectrum with relaxation effects in individual structures of the PVA chain. It was found by Smit et al.[10] that hydroxyl groups of PVA chains can rotate (at temperature 210 K) and the relaxation time is about 30 ms. The order of magnitude of this time is the same as the lifetime of phosphorescence. Hence we can conclude that the relaxation of polymer microstructure is able to influence the energy transfer of triple exciting level and it can be liable for the batochromic shift of the phosphorescence spectrum with increase of temperature.

It is necessary to emphasize that the relaxation of component parts of the PVA chain should be taken into consideration when the PVA film is applied as matrices to investigate energy states of dyes. It is important when the lifetime of a dye is less than 100 ms.

In conclusion, the PVA films exhibit phosphorescence which depend on the exciting wavelength at low temperature (103 K). If the range of light emission is determined by half-width of bands, then the phosphorescence of the PVA films encloses a range of wavelengths from 410 nm to about 660 nm. Phosphorescence at room temperature is about five times weaker than that at low temperature. It is possible to observe weak prompt fluorescence in the range from 400 to 510 nm at both room and low temperatures. Relaxation effects influence emission properties of the PVA films very much. The PVA films can be regarded as luminescentless matrix only when the exciting wavelength $\lambda_{exc} \geq 420$ nm.

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