

FLUORESCENCE PROPERTIES OF THE POLYURETHANE WITH ANCHORED STILBENE CHROMOPHORE

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Some aspects of the *trans-cis* photoisomerism and fluorescent emission of the stilbene chromophore in polyurethane cationomers were studied comparatively with the urethane-stilbene diol. The stilbene polycations absorbed at $\lambda_A = 316$ nm and emitted violet-blue light with emission maxima at $\lambda_F = 444$ nm (dimethylformamide solution) and $\lambda_F = 465$ nm (solid state). The redshift of the fluorescent band of the polyurethane stilbene is obvious and suggests that in thin films there are small aggregates of stilbene molecules.

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1. Introduction

Polyurethane polymers, particularly functionalised stilbene polymers, have attracted a great deal of interest in the last years due to their unusual properties and optoelectronic applications [1-2].

The photophysics properties, non-linear optical characteristics and electroluminescent properties, have been studied. [3]. The effect of stilbene in biophysical labelling methods has been also used to investigate the processes affecting the fluctuation and dynamics of the biological membranes [4].

Despite of research effort focused on such polymers, there are no examples in literature describing ionic polyurethanes containing stilbene or pyrene chromophores, considered more interesting than non-ionic ones due to the effects of ionic sites. These photosensitive polymers have unique properties of forming aqueous dispersions and high quality films at room temperature, and, by this reason, have made them suitable for applications in the field of modern ionomer adhesives and coating materials, including textiles and synthetic leather [5].

2. Experimental

The synthesis of the stilbene monomer and of the polyurethane polymer with anchored stilbene chromophore was given in [6]. The studied compounds have been obtained at the "Petru Poni" Institute of Macromolecular Chemistry, Romanian Academy of Iasi.

The structure of the ionic diol with a stilbene group and polyurethane with a stilbene chromophore was verified by NMR, FTIR and UV spectroscopy on JEOL-60 MHz, SPECORD M-80 and SPECORD UV-VIS spectrophotometers.

The polymer film was prepared by the casting of the polymer solution in DMF (dimethylformamide) 1% onto quartz plates and then was allowed to dry at 50-55 °C under reduced pressure.

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For fluorescence measurements, the electronic absorption spectra of the solutions of stilbene derivatives were recorded with SPECORD UV-VIS Carl Zeiss Jena spectrophotometer. All emissions spectra were obtained without corrections. The concentration of the solution range between 10^{-1} and 10^{-3} mol/l and the thickness of the absorbing layer changed between 2 and 10 mm. The fluorescence spectra were obtained at room temperature with equipment containing a double monochromator with a diffraction network of the GDM-1000 type, a compensatory printer of the K-201 type and a selective amplifier. The accuracy of the determination of the positions of absorption and fluorescence electronic bands was 40 cm^{-1} . To obtain the fluorescence electronic spectra of the stilbene derivatives in the powder crystalline states the compounds were ixed between two quartz plates. The excitation wavelength for the monomer and polymer was 360 nm. Integration of the peak area gave the relative fluorescence intensity (arbitrary units).

3. Results

The fluorescence of the stilbene group of the monomer diol and the fluorescence of the polyurethane stilbene appear because of the singlet excited state of the *trans*-stilbene molecule is capable of returning to the initial *trans* form accompanied by a well pronounce radiative emission (fluorescence) according to the following scheme:

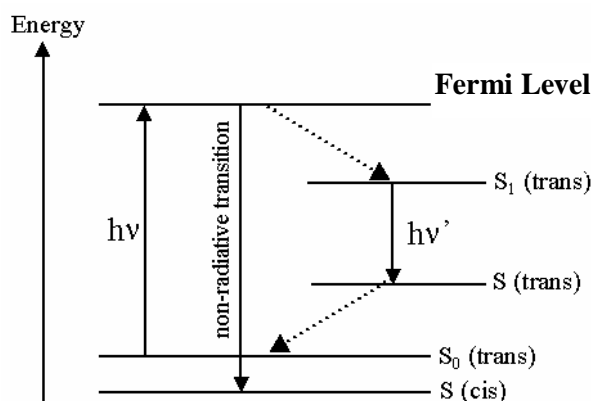


Fig. 1. Scheme of the energy levels for the *trans* and *cis* stilbene.

The electronic emission and absorption spectra of the stilbene diol in the DMF and in the crystalline state are given in the Fig. 2.

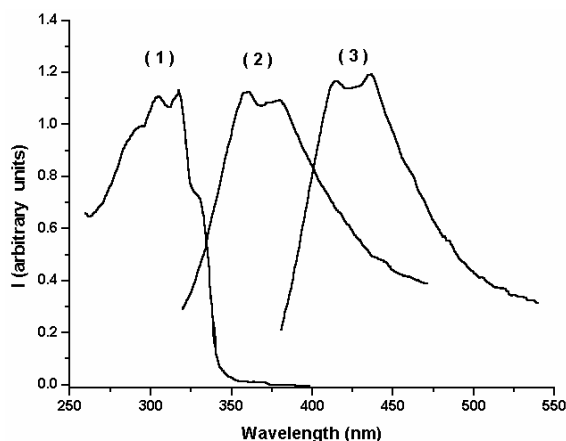


Fig. 2. (1) Absorption spectrum of the stilbene diol in DMF and its fluorescence spectra (2) in DMF and (3) in the solid state.

To assess the effect of a stilbene fragment on the fluorescence properties of the polycations, we have compared the photobehaviour of the diol with that of the solid state (Table 1).

Table 1. Fluorescence data for the stilbene monomer and cationic polyurethane in solution and solid state; a – Quantum fluorescence yield; b – Stokes shift.

Sample	λ_{abs} (nm)	λ_{fluo} (nm)	Φ_F^a	$\Delta\nu^b$ (cm^{-1})
Stilbene diol				
DMF	303	416	0.16	8965
Solid	-	433	0.18	9909
CPU – S ₁				
DMF	316	444	0.16	9238
Film	316	465	0.16	10140

Compared with the previously measured fluorescence wavelength of the stilbene molecule, the fluorescence spectra of the monomer in the solid state showed a strong bathochromic shift of the corresponding peak to $\lambda_{\text{fluo}} = 430, 449$ and 512 nm, with maxima at 433 nm. A reasonable explanation of this redshift can be given through excimer association of stilbene units statistically distributed in the layer. Therefore, the maximum fluorescence wavelength of the stilbene chromophore incorporated into the ionic vicinity was sensitive to the medium (solution or solid state) because the processes occurring with excited stilbene molecule are dependent on the intramolecular effects (interactions) of the substituent and the existence of the nanometer scale aggregates.

Under the same conditions, a similar trend was also obtained for excited trans-stilbene in polymer solutions and films. Figure 3 shows the absorption peak of cationic polyurethane CPU-S₁ (Fig. 3 (1)) and the dependence of the fluorescence emissions of trans-stilbene in a DMF polymer solution (Fig. 3 (2)) and in a film (Fig. 3 (3)). A correlation of the film and solution fluorescence spectra indicated a monotone redshift of the emission maximum to 465 nm in the polymer film, as compared to the value of 444 nm measured in the DMF solution. Even though the polycation film is chemically homogeneous, this redshift is obvious and suggests that in the thin films there are small aggregates of stilbene molecules.

To clarify the ability of the stilbene unit to emit the absorbed light energy, we calculated the quantum fluorescent yield with the Parker method [7] and with anthracene as a standard.

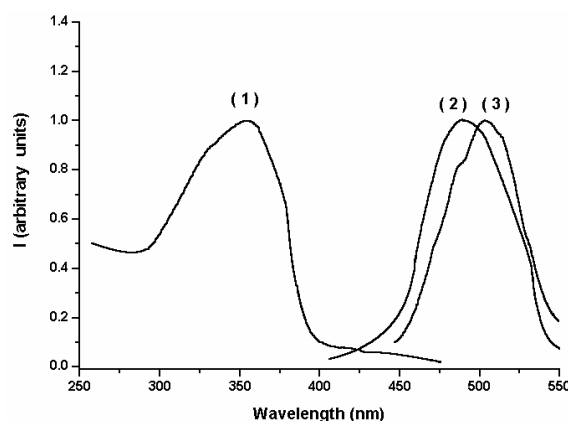


Fig. 3. (1) Absorption spectrum of Poliuurethane Stilbene in DMF and its fluorescence spectra (2) in DMF and (3) in a polymer film.

From these results, it can be observed that in the studied derivatives, notable steric effects are responsible for the significant decrease in the fluorescent yield in comparison with that of stilbene (quantum fluorescent yield = 0.75). The fact that in solution the quantum fluorescent yield is very similar to the quantum fluorescent yield in the solid state suggests the relative importance of the interaction between the excited state and solvent in the non-radiative process.

Moreover, exciting stilben diol in solution or in crystal with $\lambda_{ex}=328$ nm a shift of excimer fluorescence was not recorded. This clearly indicates that in the stilbene derivatives a hydrophobic aggregation takes place. This photoselection of the monomer fluorescence may be the result of structural reorganization of the ionic associates into polar solvent which facilitates the dissociation process to form isolated salt groups. The fact that in solid state the emission maximum of stilbene remains unmodified within the excitation wavelength region of the fluorescence spectrum puts in evidence the presence of more stable aggregates.

4. Conclusions

The presence of the fluorescent stilbene in the ionomeric chains results in poly (ether urethane) cationomers with fluorescent properties.

The redshift of the fluorescent band of the polyurethane stilbene is obvious and suggest that in thin films there are small aggregates of stilbene molecules.

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