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*Short communication*

# Fluorescence studies of the self- organization phenomena in film state and solutions of some polyurethanes

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The fluorescence properties of stilbene- polyurethane were studied by means of trans-cis photo isomerism and fluorescent emission of the stilbene in polycation and compared with urethane-stilbene derivative and with another cationomer with fluorophore introduced via quaternization of the same precursor with urethane- stilbene halide. In the case of pyrene-polyurethane the process of excimer formation between the pyrene molecules attached to the ionic polyurethane was investigated in tetrahydrofuran (THF), dimethylformamide (DMF) and film state. The formation of aggregates or core–shell micelles was sustained by the fluorescence data, which indicated the existence of pyrene units in the ground state of the molecule, giving rise thus to an explanation for the high excimer-to monomer intensity ratio.

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## 1. Introduction

The incorporating of a trans-stilbene chromophore in a ffaty acid and phospholipids chains have been found to exhibit sharp changes in absorption and fluorescence spectra upon self-assembly in Langmuir-Blodgett films and aqueous dispersion. The spectral changes are readily associated with aggregates in which there is a strong noncovalent interaction between trans-stilbene chromophore [1].

The objective of this work is to characterize the phase behavior of some polyurethane cationomers by use of stilbene and pyrene as fluorescence label. The phase behavior of these polymers was studied in tetrahydrofuran, nitrobenzene and thin film.

Fluorescence label technique provides a particularly useful tool for studies of microscopic dynamics and conformations of polymers.

## 2. Experimental

The synthesis of the stilbene monomer and of the polyurethane with anchored stilbene chromophore was given in [2].

The synthesis of the pyrene derivative and pyrene polyurethanes was given in [3]. 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 microstructure determination of the photopolymers and the presence of micro/nanostructured aggregates in thin films were evidenced by fluorescent spectroscopy and AFM technique. The polymer film was prepared by the casting of the polymer solution in DMF (dimethylformamide) 1% onto quartz plates and than was allowed to dry at 50-55 $^0$C under reduced pressure. The fluorescence spectra were obtained at room temperature (without corrections) with an 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 ±40cm$^{-1}$. To obtain the fluorescence electronic spectra of the stilbene derivatives in the crystalline states as powder, we fixed the compounds between two quartz plates. The wavelength of the excitation radiation for the monomer and polymer was 360nm. Integration of the peak area gave the relative fluorescence intensity (arbitrary units).

## 3. Results and discussion

To investigate the photoinduced properties in our system, the fluorescence spectra for irradiated samples with UV light were compared to the corresponding absorption spectra. The next figures depict the absorption and emission spectra of some polyurethane polymers in solution and thin films. For example, UV spectroscopy confirmed the absorbance peaks for stilbene-Cl in the region $\lambda_A$= 286-328 nm in DMF which emits a violet blue fluorescence at $\lambda_F$ = 416 nm, whereas in the solid state two maxima at 444 nm and 470 nm were registered (Fig. 1) (Fig. 2). This finding suggests formation of a excimer of stilbene- Cl, originating from the attractive interaction of an excited stilbene group with another stilbene group in the ground state.The red shifted relative to that of dissolved derivative in DMF owing to the formation of aggregation between fluorophores.This photoselection of the monomer fluorescence may be 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 with the excitation wavelength region of the fluorescence spectrum provided evidence for the presence of more stable aggregates.

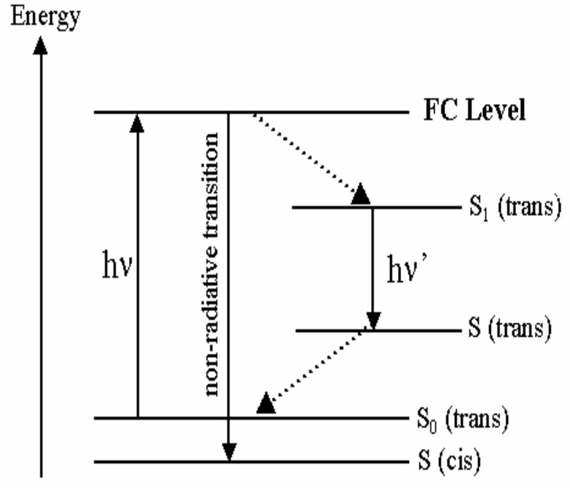

*Fig. 1. The scheme of electronic transitions for stilbene molecule.*

On the basis of the observed excimer emission in stilbene- polyurethane most importantly, is that the anchoring of stilbene onto the ammonium quaternary structure caused a red shift of the excimer (Fig. 3) [4]. This shift appear because of modification of the polymer conformation due to specific interactions generated by the physical crosslinking between polymer chains with effect on increasing of stability of the aggregates.

The pyrene-polyuretane cationomer series was studied in solvents of different quality (DMF and THF) and in a thin film for one of them for at least two reasons. First, DMF is a good solvent for polyurethanes, including the pyrene moieties, and so a reduced number of ground-state pyrene associations could exist in this medium in which excimer formation occurs predominantly by diffusion. Second, the THF quality is not so good for polymers, but it is good for pyrene, and in a such solvent, just a few pyrene–pyrene interactions between the pyrene rings seem to be favored. Relative intensities of the vibronic bands of pyrene fluorescence are known to show a significant dependence on the micro environmental polarity around pyrene. The ratio of the third to the first vibronic bands ($I_3/I_1$) in fluorescence spectra of pyrene reflects the polarity in local media where pyrene exists, i.e., $I_3/I_1$ ratio being larger in less polar media (Fig. 4) [3].

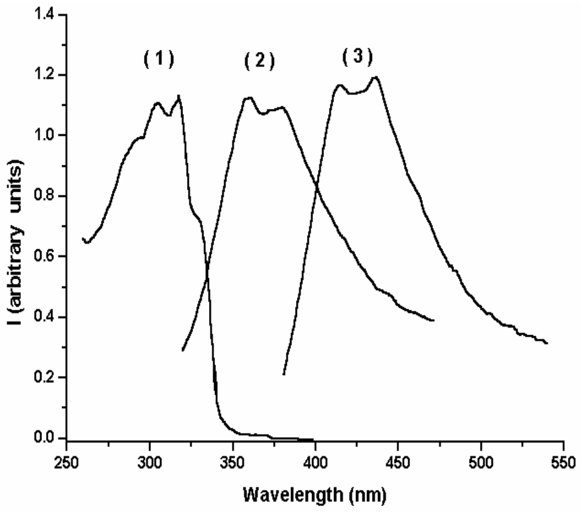

*Fig. 2. (1) Absorption spectrum of the stilbene diol in DMF and its fluorescence spectra (2) in DMF and (3) in the solid state*

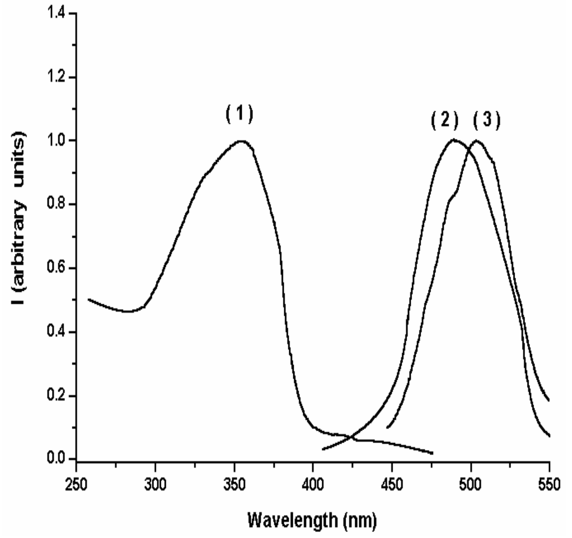

*Fig. 3. (1) Absorption spectrum of Polyurethane Stilbene in DMF and its fluorescence spectra (2) in DMF and (3) in film state.*

Therefore, the $I_3/I_1$ for the pyrenil monomer can be used to discuss environmental effects on pyrene fluorescence. In general, when the content of pyrene labels in a copolymer is ≥ 1 mol %, interaction between covalently bound pyrene chromophores may lead to excimer formation. The emission bands of the excimer are centered on 480 nm in THF. To obtain further information about the microenvironment around the pyrene groups, the fluorescence quenching was compared between the copolymers and the pyrenil monomer by use of nitrobenzene as quencher (Fig. 5).

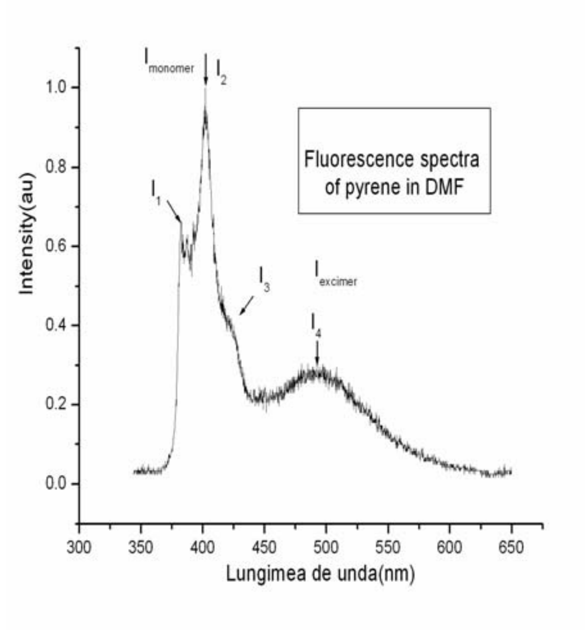

*Fig. 4. Fluorescence spectra of pyrene in solution.*

Fig. 5 illustrates the fluorescence spectra for Py–PUC1 in THF. The spectra are identical to those of the pyrene derivative, except for the maximum of the blue monomer fluorescence which are shifted in the polymer by about 2–4 nm. In such a case, the vibrational fine structure undergoes changes with the transfer of pyrene from a polar environment to a nonpolar one, suppressing thus the allowed and forbidden vibrations including the 0–0 band. At a first approximation, the observed shifts can be attributed to the formation of hydrophobic associates, which increase with decreasing solvent polarity. This is a result of the high concentration of pyrene located on the polymeric chain when the probability of two pyrene molecules meeting increases. Therefore, in a low-polarity solvent such as THF, the aggregation of cationic groups containing hydrophobic pyrene in their structure leads to the formation of hydrophobic aggregates with a hydrophilic interior, whereas in DMF, single polyions coexist as well as free aggregates with polyions and counterions, manipulated tightly by electrostatic forces. The influence of the small accounts of nitrobenzene on the pyrene- polyurethane solved in DMF, was studied by means of fluorescence technique, the fluorescence decays of the pyrene rings from pyrene polyurethane cationomer. The effect of quencher concentration on the fluorescence decay of the pyrene molecule observed at room temperature is shown in Fig. 5. These results provide support for the existence of specific interactions between quencher as electron acceptor and singlet-excited pyrene located in the vicinity of the hydrophilic group into polycation, as electron donor.

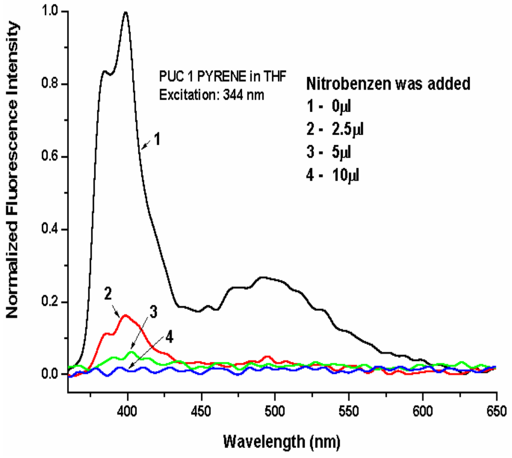

*Fig. 5. Fluorescence quenching of pyrene polyurethanes with quencher as nitrobenzene type.*

## 4. Conclusions

The fluorescence measurements in solutions and film state permit us the following conclusions.

1. The synthesized polymers had fluorescence properties, and their fluorescence decay acquired in the THF and DMF solutions indicated the presence of a certain level of association between the pyrene moieties attached to the ionic group.
2. The existence of the aggregates or dimerized probe in the ground state of the molecule was indicated by the high excimer- ionomer intensity ratio.
3. The solvent dependence of the fluorescence suggested a hydrophilic environment for pyrene in the polyurethane cationomer, where an increased excimer emission was observed.
4. The fluorescence study of the stilbene polyurethanes showed different properties in solution and film state. Especially, aggregation produces strong effects on the photophysics of stilbene chromophores. Thus, a red shift of emission band in film state occurs and formation of excimers in both state was observed.

## References

[1] Shinichi Yusa, Mikiharu Kamachi, Yotaro Morishima Journal of Polymer Science. Part A. Polymer Chemistry **37**, 47-58 (1999).

[2] E. Buruiana, Tinca Buruiana, Georgeta Strat, M. Strat, J. Photochemistry and Photobiology A: Chemistry, **162**(1), 23-31 (2004).

[3] Emil C. Buruiana, Tinca Buruiana, Georgeta Strat, M. Strat, J. Polym. Sci. Part A: Polym. Chem. **43**, 3945-3968 (2005).

[4] Grabchev, J. Photochem. Photobiol. A. Chem. **41**, 135 (2000).

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