

Synthesis, properties and fluorescence quenching in a polycation based on polyetherurethane with pyrene fluorophore

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Abstract

A soft polyurethane based on poly(tetramethylene oxide) diol, 4,4'-diphenylmethane diisocyanate (MDI) and *N*-methyldiethanol amine partially quaternized with 4-chloromethylphenylcarbamoyl-1-oxymethylpyrene was prepared and characterized using spectral and thermal methods. The content of pyrene attached to the polyurethane backbone is of 10.9 wt.% polymer. The structure of the nanophase separated domains in the corresponding polymeric film was visualized using topographical information from atomic force microscope (AFM) image. The solution properties of this polymer have been studied by fluorescence spectroscopy in tandem with the quenching of fluorescence in the pyrene–polyurethane by nitrobenzene used as efficient quencher under a concentration of about 9.65×10^{-4} M. Even more interestingly, a substantial quenching was observed for such polymer in the thin film exposed to the saturated vapors of nitrobenzene as result of the formation of complex between the excited pyrene molecule (electron donor) and nitrobenzene (electron acceptor). Moreover, the fluorescence recovery from the polymeric film occurred after 80 min of standing in a clean atmosphere. Because these films may be readily over coated with other films of varying thickness and composition, it should be possible to develop a variety of vapor-based “chemical” sensors for the detection of chemical analytcs.

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1. Introduction

Synthesis and properties of photosensitive materials containing a highly sensitive aromatic fluorophore to external stimulus have attracted increasing interest in the recent years, not only for their optical and physical properties, but also for specialized applications as chemosensing, optical switching and molecular computation and so on [1,2]. Among these ones, choosing of the pyrene as sensing probe in various polymers is mainly motivated of its advantageous features such as high fluorescence emission quantum yield and a rather long excited state lifetime. The most studies have been reported on the photophysical properties of the (non)-covalently bound pyrene in light-sensitive molecular structures [3–5], pyrene polymers [6,7], amphiphilic copolymers [8] or polyelectrolytes [9,10], in which pyrene is used in order to characterize the structure, conformational properties and more specifically that of the polymer micellization

[12]. The qualities of the pyrene as free fluorescent probe in some polyurethanes were also successfully exploited for evaluation of the polarity of cellular membranes [13], hydrophobicity of the polyurethane foams [14] or interactions in the solution of model polyurethane ionomers [15]. Of interest, there are the results obtained on acrylic and Nafion membranes with pyrene rings which led to understanding self-assembly of the ionomeric chains, deduced earlier from complementary methods [16–18].

As a continuation of our work on the photoionomers with fluorescent, photochromic or UV/laser ablative properties generated of stilbene [19,20], azoaromatic [21–23], triazine moieties [24–26] incorporated in the hard or soft segments of the polyurethane backbone, we reported how one could use a pyrene polymer to detect the onset of association in single or mixed solvents, where the spectra of environmentally sensitive probes respond to perturbations in the local environment [27]. For example, changes in solvation that occur because of the polyethylene oxide sequences into the polymeric chains can evoke changes in the fluorescence properties of these polymers.

In this paper, we present the synthesis, structure and fluorescence properties of a flexible polyetherurethane (65% soft

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segment) containing a small amount of pendant pyrene located on the quaternary ammonium groups as well as the fluorescence quenching in the solution and film state by nitrobenzene to evaluate sensing ability.

2. Experimental

2.1. Materials

Poly(tetramethylene oxide) diol (PTMG, $M_n=2000$, Aldrich) was dried and degassed at 100–110 °C and 1–2 mmHg for 2 h before utilization. 4,4'-Diphenylmethane diisocyanate (MDI, Aldrich) and *N*-methyldiethanolamine (Aldrich) was used as received. Dimethylformamide (DMF) was dried over 5 Å molecular sieves.

2.2. Synthesis

4-Chloromethylphenylcarbamoyl-1-oxymethylpyrene was prepared according to our previously data [27]. A polyurethane precursor (PR) was synthesized by a two-step condensation reaction from poly(tetramethylene oxide) diol (PTMG, $M_n=2000$, 0.01 mol), 4,4'-diphenylmethane diisocyanate (MDI, 0.03 mol) and *N*-methyldiethanolamine (NMDA, 0.02 mol). The NCO-terminated prepolymer was prepared by the reaction of MDI with PTMG under dry argon atmosphere at 65 °C for 6 h. After the prepolymer was degassed under vacuum and its temperature was reduced at 50 °C, NMDA in anhydrous acetone was added. The reaction was carried out at 55–60 °C for 4 h. The pyrene rings were introduced by a quaternization of the above polyurethane (1 g PR) with 0.11 g pyrene derivative in anhydrous DMF ($c=20\text{ g dL}^{-1}$), according to the procedure described previously [27]. The resulting polymer (Py-PUC) was precipitated in diethyl ether, collected by filtration and then dried under reduced pressure.

2.3. Characterization

The structure of polymers was verified by ^1H NMR and IR/UV–vis spectroscopy using a Bruker 400 MHz spectrometer and Specord M80/Specord M42 spectrophotometers, respectively. Molecular weight distribution of the precursor (PR) was measured by a PLEMD 950 apparatus equipped with two PL gel mixed columns at 120 °C. The thermal transitions were measured on a Perkin-Elmer differential scanning calorimeter by cooling of the polymer to –130 °C and heating at a rate of 20 °C min^{-1} up to 230 °C. Reduced viscosity of PR ($\eta_{\text{red}} 0.32\text{ dL g}^{-1}$) was determined to 25 ± 0.2 °C in a DMF solution ($c 0.4\text{ g dL}^{-1}$) with an Ubbelohde viscometer having a 0 Å capillary. The polymer film was prepared by casting of the polymer solution in DMF ($c 1\text{ wt.}\%$) onto quartz plates and then was allowed to dry at 50–55 °C under reduced pressure. An atomic force microscope (AFM; Model DI 5000) was used to probe the surface morphology of the prepared film. For fluorescence studies, it was necessary to remove the unattached pyrene present in the polymer by successive precipitation into diethyl ether, followed by drying under vacuum. The fluo-

rescence spectra were obtained at room temperature (without corrections) with a SLM 8000 spectrofluorimeter (Japan) 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, as presented earlier [19]. For quenching, was used a desiccator of 25 l in which is placed a Petri dish which contains 5 ml nitrobenzene. The polymer film was introduced in desiccator after a preliminary saturation in vapors (about 30 min).

3. Results and discussion

To develop fluorescent ionic polyurethanes with good film forming properties, a conventional precursor (PR) based on poly(tetramethylene oxide) diol of 2000 average molecular weight (PTMG), 4,4'-MDI and *N*-methyldiethanolamine (NMDA) was prepared to be used further in the quaternization of the tertiary amine functionality with 4-chloromethylphenylcarbamoyl-1-oxymethylpyrene. The structure of the polymers was confirmed with ^1H NMR and IR spectroscopy, GPC and elemental analysis. For polyurethane precursor, a molecular weight of 29,200 determined by GPC sustains the formation of a block copolymer with alternating flexible segments (65%) characterized of a low glass-transition temperature (T_g , soft segments) and polar hard blocks, including urethane structures and a minor component of cationic groups with pyrene pendant.

Fig. 1 shows the schematic representation of the structure of pyrene–polyurethane (Py–PUC) used in our study. The pyrene functionality attached to the polymeric backbone was determined from the ^1H NMR spectrum taking in consideration the peak intensity ratio of the aromatic protons for the pyrene moiety ($\delta = 8.0\text{--}8.6\text{ ppm}$) to the aromatic protons of the methylene bis-phenylurethane structure ($\delta = 7.0\text{--}7.35\text{ ppm}$) formed in the latter. As seen in Fig. 2, effective labeling was thus confirmed by ^1H NMR, for which quantification of the process from the evolution of integrated areas indicated around 10.9 wt.% pyrene in Py–PUC. This allows appreciating the concentration of ammonium quaternary groups at 27.2 mequiv. ionic groups/100 g polymer. Another signals are positioned at 9.5 ppm (protons of the urethane structure), 7.33 ppm (aromatic

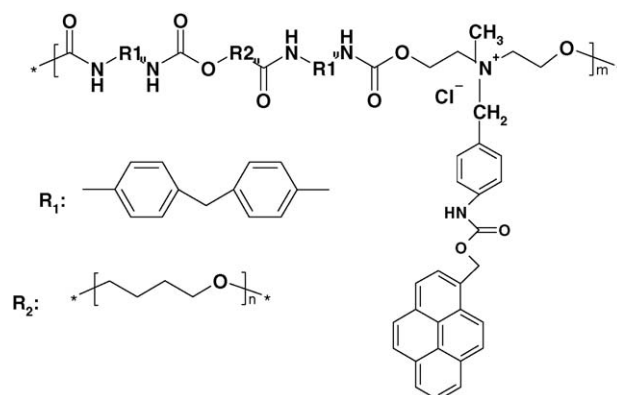


Fig. 1. Structure of pyrene–polyurethane (Py–PUC).

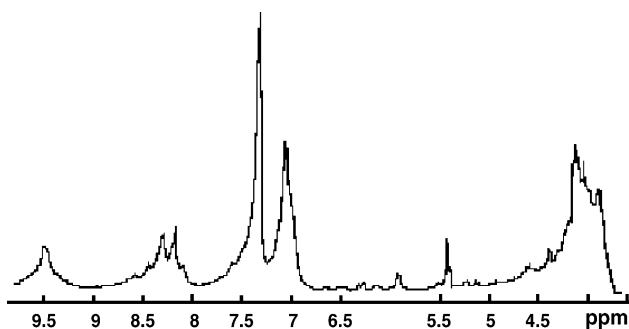


Fig. 2. ^1H NMR spectrum of pyrene-polyurethane (Py-PUC) in DMSO-d_6 .

protons belong to the phenylene from pyrene derivative overlapped with those in *ortho* to urethane group from MDI and at 7.07 ppm (aromatic protons in meta position to urethane group), 5.4 ppm (methylene protons from esterurethane pyrene derivative), 4.0–4.13 ppm (methylene protons from esterurethane groups), 3.3 and 1.47 ppm (methylene protons from PTMG). Py-PUC is soluble in *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and less soluble in tetrahydrofuran (THF). Additionally, a soft film of elastomeric type can be obtained by solution casting on various substrates, like ionomer polyurethane structures.

In the IR spectrum (not shown) of Py-PUC, the absorption band positioned at 3350 cm^{-1} is assigned to the stretching vibrations of the NH urethane groups. Absorption bands near 1740 cm^{-1} owing to the free CO stretching vibrations, at 1710 cm^{-1} from hydrogen-bonded CO and at $2890\text{--}2990\text{ cm}^{-1}$ corresponding to CH_2 units can be also noticed. The same splitting of the carbonyl peak of the urethane moieties due to the

free and hydrogen-bonded groups was observed for the cationic polymer, as result of the presence of hydrogen bonding after quaternization with pyrene derivative. Absorption bands at 1100 and 1200 cm^{-1} are attributed to the polyether structure.

As the physical properties of the polyurethanes are primarily related to the degree of phase separation between the two constituent segments forming microdomains, DSC analysis was carried out with only for the precursor. In this polymer, just a single-glass transition ($T_g -36.5^\circ\text{C}$) assigned to the soft segment was registered. Compared to the T_g of pure PTMG ($T_g -84^\circ\text{C}$) it could deduce that an increase in the degree of the hard-soft segment mixing in the polyurethane matrix is promoted by the shorter length of chain extender [28].

Atomic force microscopy being a microscopic technique which allows the imaging of surface morphology on a nanometer scale resolution, the surface topography of the Py-PUC deposited on quartz was examined and some different positions per substrate were taken. Fig. 3 shows the AFM image of the polymer film with thickness of $1.5\ \mu\text{m}$. Although Py-PUC had a good-quality film its surface is not flat and clean resulting in numerous hills and valleys placed into a very smooth structure. This provides direct evidence for the presence of a relatively high nanophase separation within polyurethane film, where a spherulitic morphology of the hard domains that percolated randomly through the matrix of the soft segments seems to be suggested. The dimensional distribution of the multichain aggregates arranged in a quasi-linear mode can be observed in the profilometric curve attached to this figure. Therefore, this polymeric fluorophore is phase separated on a length scale of a few nanometers, typical to the segmented polyurethanes [29,30] but other details on the ionomer chain aggregation is underway in our laboratory.

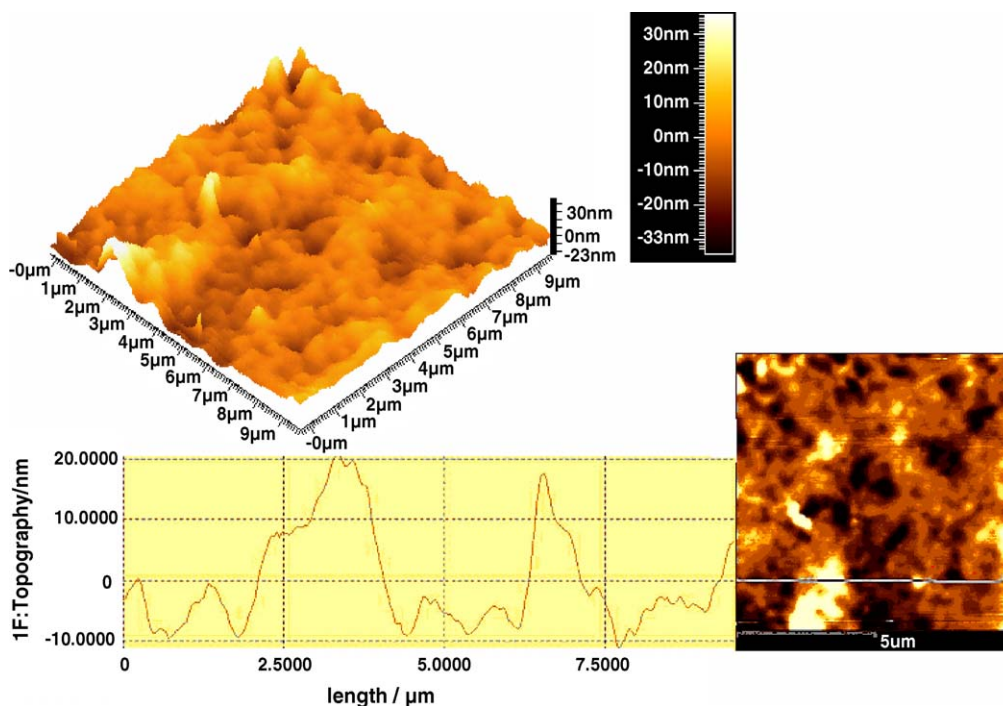


Fig. 3. AFM images for a pyrene-polyurethane film (Py-PUC).

Table 1
Vibronic bands and the intensity ratio in pyrene fluorescence spectra (I_1/I_3 , I_E/I_M) for the pyrene polycation

Polymer	λ_{exc} (nm)	λ_F (nm)				I_1/I_3	I_E/I_M
		I_1^a	I_2^a	I_3^a	I_4^b		
Py-PUC (DMF)	344	381.13	398.11	419.43	486.76	1.41	1.12
	365	386	399	417	487.6	0.8	1.07
Py-PUC (THF)	344	377	396	412	482	0.6	0.45
Py-PUC (film)	344	382.7	398.7	419.3	483.7	1.866	1.345

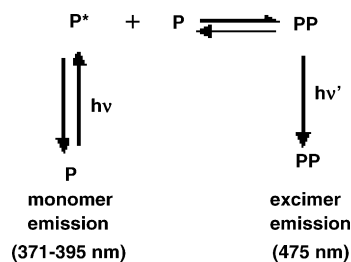
^a Monomer fluorescence.

^b Excimer fluorescence.

3.1. Fluorescence spectra of pyrene-PUC

In order to make this study feasible, we first need to understand the intrinsic properties of this polymer in solvents like DMF, THF and additionally, the dependence of its dynamical behavior on its local environment. Therefore, Py-PUC was studied in solvents of different qualities, since DMF is a good solvent for polymer as well as for the pyrene moieties, while the THF is not so good for polyurethane but is good for pyrene. If in the former a reduced number of ground-state pyrene associations could exist in this media in which the excimer formation occurs predominantly by diffusion, in THF just few pyrene-pyrene interactions between the pyrene rings seem to be favored [11].

Table 1 summarizes the relative positions of the main vibronic bands in the pyrene-polyurethane fluorescence together with a tentative of peaks assignment. In Fig. 4a and b, the fluorescence spectrum is shown for Py-PUC in DMF measured at an excitation wavelength of 344 and at 365 nm. As shown in this figure, the spectra are typical of pyrene fluorescence and exhibit a well-resolved vibronic fine structure and much better structured at excitation of 344 nm. In the first case, the first peak (I_1) arises from the (0, 0) transition from the lowest excited electronic state



Scheme 1. Mechanism for monomer and excimer emission of the pyrene molecule (P).

being a “symmetry-forbidden” transition that can be enhanced by the distortion of the π electron cloud. As result, I_1 displayed at 381.13 nm can give improved values of the fluorescence intensity in polar solvents or environments. The third maxima (I_3 peak) appeared at about 419.43 nm corresponds to allowed transitions and is no sensitive to the solvent polarity. Consequently, the fluorescence intensities at 381.13, 398.11 and 419.43 nm are assigned to single-fluorophore molecular emission, whereas the intensity at 486.76 nm is attributed to excimer emission. This situation for pyrene fluorophore is briefly illustrated in Scheme 1. The analysis of spectrum indicates that the maximum in the monomer emission (I_1 – I_3) is blue shifted by 2–3 nm relative to that of pyrene derivative [27].

As described in the literature [31], the ratio of the first-to-third vibronic bands in the fluorescence spectrum of pyrene is often a useful indicator of the polarity in local media where pyrene exists. In order to determine the I_1 – I_4 areas the spectrum was deconvoluted into four Gaussian curves (Table 2). Thus, the (0, 0) transition being favored in DMF, the I_1/I_3 ratio expresses the environmental effects on pyrene fluorescence in the polymeric backbone. Particularly, the value estimated to 1.48 for Py-PUC indicates clearly that even in very dilute solution, there is a hydrophilic environment for pyrene in the above polycation. Such result is surprising for a hydrophobic fluorophore

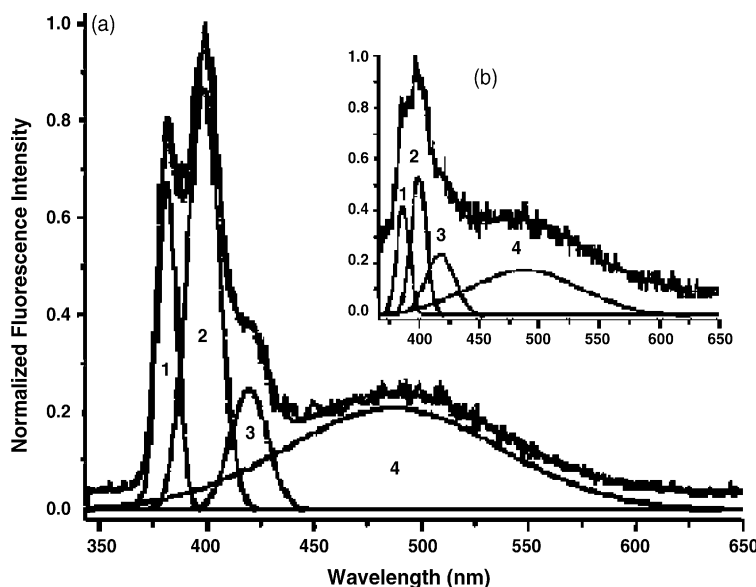


Fig. 4. Fluorescence spectra monitored at $\lambda_{\text{exc}} = 344$ nm (a) and $\lambda_{\text{exc}} = 365$ nm (b) for pyrene-polyurethane (Py-PUC) in DMF; monomer fluorescence (1–3) and excimer fluorescence (4).

Table 2
Parameters of the Gaussian curves resulting from fluorescence spectral deconvolution for the pyrene polycation

Polymer	λ_{exc} (nm)	Relative peak intensities (λ_{F})			
		I_1	I_2	I_3	I_4
Py-PUC (DMF)	344	7.869	16.215	5.318	26.233
	365	5.740	8.545	7.165	19.937
Py-PUC (THF)	344	5.240	7.837	8.733	10.039
Py-PUC (film)	344	2.490	5.121	1.335	12.037

introduced into polyurethane containing a reduced number of cationic groups of ammonium type. A similar conclusion was drawn from the data for pyrene resulted from the study of perfluorinated ionomers (PFI) having sulfonic groups [12].

Compared to a hydrophilic ionic polyurethane [27] discussed earlier ($I_1/I_3 = 0.64$), where predominate hydrophobic microdomains, contribution the soft segment nature (PEG, PTMG) besides that of cationic groups appears to be important for the synthesized polycations, which give rise to a subtle difference between the environment afforded to a pyrene group. Moreover, the effect of solvent on the association between the pyrene pendants in such polymers could be interpreted by a combination of factors including hydrophobic/hydrophilic and electrostatic forces.

Monitoring carefully the process of excimer formation, the intensity ratio of excimer to monomer (I_E/I_M) was calculated by taking the ratio of intensity for the excimer formation (peak area 486.76 nm) and the peaks area for the pyrene monomer (381.13, 398.11 and 419.43 nm). According to this ratio ($I_E/I_M = 0.89$), the emission of Py-PUC in DMF is characterized by an increased excimer emission (excited dimer), which evidently, can occurs when pyrene molecules are in close proximity. This is a consequence of the relatively high concentration of pyrene incorporated on the polymer chain, where the probability of two pyrene molecules to encounter increases.

On the other hand, exciting at the red edge of the absorption maximum with 365 nm in DMF (Fig. 4b), a marked decreasing of the first vibronic band ($I_1/I_3 = 0.80$) was observed concomitantly with a slight increasing of the excimer ($I_E/I_M = 0.93$). The major contribution to the changing of excitation wavelength is the shift in the excitation spectra of the pyrene towards red with about 4 nm (I_1, I_2), whereas the third peak I_3 is blue shifted with 2 nm. By comparing the fluorescence spectra acquired in nonpolar solvents like THF, was clearly that Py-PUC showed characteristic structureless emission. Whether in DMF solution is promoted the formation of excimers, in THF less excimer is formed (Table 1). This observation suggests that in THF pyrene moieties are located into a polar environment in polymer, and consequently, the interaction between pyrene groups may be restricted. As result, the polymer adopts a more collapsed conformation in non-polar solvent than in DMF.

In film state, the emission spectrum of Py-PUC presents four peaks centered between 377 and 425 nm, corresponding to probe monomer emission and another band assigned to excimer emission at about 437–600 nm (Table 1). The I_1/I_3 ratio for poly-

mer film ($I_1/I_3 = 1.86$) determined from deconvolution results (Fig. 6b) is also sensitive to the polarity of its environment suggesting that the probe is into hydrophilic microdomains. From the ratio of the intensity of the excimer peak (I_E) to that of the monomer (I_M), displaying maxima centered at 483.7 and 400 nm, respectively, it was found a value I_E/I_M of 1.345. Such finding suggests that there is a significant increasing in the excimer formation for Py-PUC in thin film due to the formation of aggregates. Again, this fitting seems to be a measure of the hydrophilic character of the pyrene residues and its ability to form a higher amount of excimer in film state relative to the monomer emission.

3.2. Fluorescence quenching experiments

To probe the internal motions of macromolecules by fluorescence technique, the fluorescence decays of the pyrene rings from Py-PUC was acquired in DMF with various amount of nitrobenzene added as an efficient quencher of pyrene to a polymer solution of very low concentration. The effect of quencher concentration on the fluorescence decay of the pyrene molecule observed at room temperature is shown in Fig. 5. Depending on the concentration of nitrobenzene, the quenching of the excited pyrene resulted in a significant reducing of the fluorescence intensities from Py-PUC, as the concentration of nitrobenzene increased (9.65×10^{-4} to $2.4 \times 10^{-2} \text{ mol L}^{-1}$). The quencher dependence of the total area for monomer and excimer fluorescence was followed up to concentrations of nitrobenzene of about $2.4 \times 10^{-2} \text{ mol L}^{-1}$, when the quenching is completely. 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. Although by adding of quencher to the polymer solution only the diffusional process of excimer formation would be affected, we find in the fluorescence spectra (unshown) that the monomer emission is equal quenched as that for excimer form.

Returning to the polymeric film (Fig. 6a) exposed to the saturated vapors of nitrobenzene and measuring the pyrene

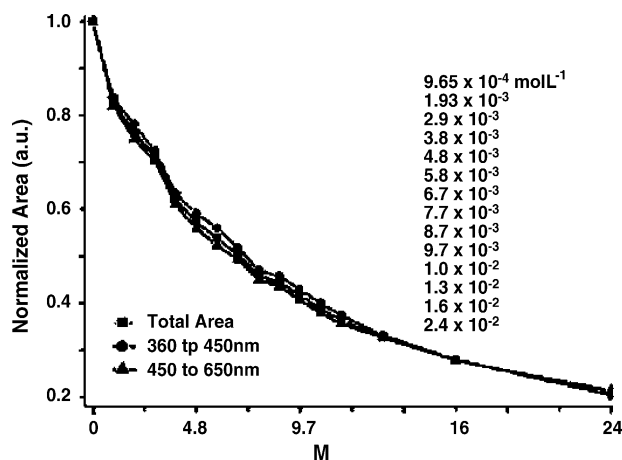


Fig. 5. Nitrobenzene effect at different concentration on the fluorescence decay for Py-PUC in DMF at $\lambda_{\text{exc}} = 344 \text{ nm}$.

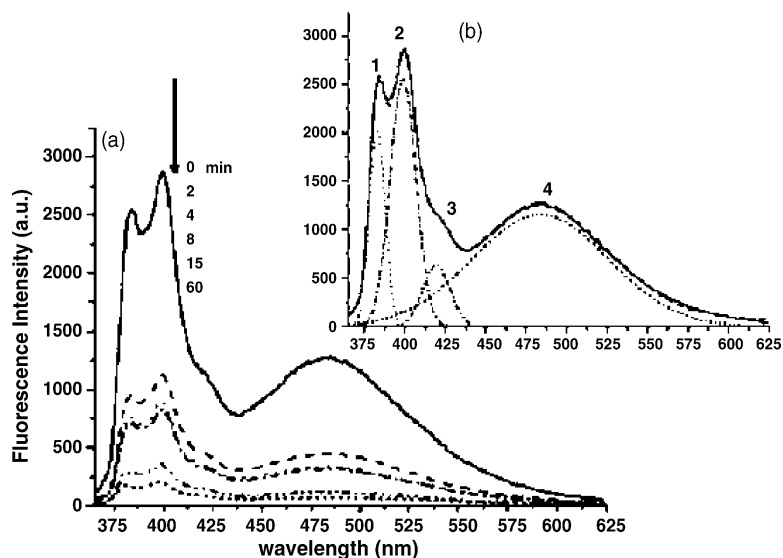


Fig. 6. Fluorescence decay profiles for Py-PUC in film state (a) in the absence of nitrobenzene vapors (0 min) and after different exposure times at nitrobenzene saturated vapors at $\lambda_{\text{exc}} = 344$ nm and (b) deconvolution.

fluorescence it was noticed that after 2 min of exposure the fluorescence intensity decreased with about 60%. Practically, after about 15 min of exposure under nitroaromatic vapors, the excimer fluorescence disappeared completely from the spectrum of Py-PUC film and that monomer is quenched around 95%. It is important to conclude that after 1 h of standing in an atmosphere free of nitrobenzene vapors, the fluorescence spectrum of the polymeric film is identical with the initial one.

To sustain the above results, another experiment on a film completely quenched with saturated nitrobenzene vapors was performed examining the evolution of the monomer fluorescence (397 nm) with time. A plot of the data purchased even at short time intervals (5 s) after excitation at 340 nm, indicates a marked increase of the monomer fluorescence in the measured range, when a plateau is attained in about 80 min (Fig. 7). This behavior anticipates that the quenching process of the pyrene located in a more hydrophilic environment occurs via reversible local polymer motions. Taken together, the above results suggest

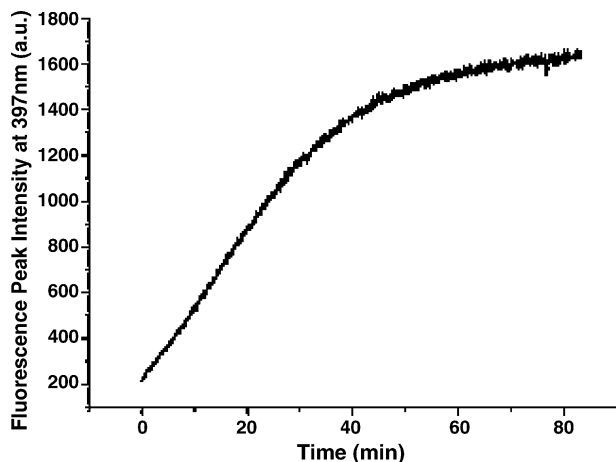


Fig. 7. Fluorescence recovery for Py-PUC film fully quenched with nitrobenzene vapors on the times.

an attractive way for a potential sensor based on fluorescence recovery from an elastomeric film of pyrene polycation.

A last remark must be made concerning the fluorescence quenching in solution which normally follows Stern–Volmer kinetics [7]. According to the Stern–Volmer equation the data calculated for Py-PUC in DMF fit on nearly perfect straight line. This linearity of the Stern–Volmer plots for the pyrene fluorescence quenching by nitrobenzene up to concentrations of 7.7×10^{-3} M indicates the dynamic nature of the quenching process controlled by diffusion. Over this concentration of nitrobenzene, the fluorescence quenching of the pyrene signifies a straight line but there is an upswing in the curve. Future studies will include fluorescence quenching experiments with other quenchers and optimizing the sensitivities for the detection of a variety of analytes in both liquid and vapor phases.

4. Conclusions

A new segmented polyurethane fluorophore of soft elastomer type containing pyrene incorporated in the quaternary ammonium groups was synthesized and characterized in comparison with a hydrophilic polycation. From the fluorescence measurements in solution and film state, the following results were obtained:

- (1) the nature of the polyol (PTMG, PEG) has a greater effect on the properties of cationic polyurethanes compared with the polymers containing ionic groups;
- (2) solvent dependence of the fluorescence suggested a hydrophilic environment for pyrene in the polycation based on PTMG in DMF, where an increased excimer emission was evidenced;
- (3) deconvolution results sustain the formation of hydrophilic microdomains in which pyrene emits a higher quantity of excimer compared to the monomer emission both in DMF and film state;

- (4) quenching kinetics in DMF solution indicate that for concentrations of nitrobenzene in the range 9.65×10^{-4} and $2.4 \times 10^{-2} \text{ mol L}^{-1}$, the reaction may operate equally for both the monomer and excimer form.

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