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FLUORESCENT POLYMERS FOR SENSOR APPLICATIONS[♦]

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Abstract: Two soft polyetherurethanes with pyrene or anthracene fluorofore on the quaternary ammonium groups were synthesized and characterized. The properties of these polymers and the corresponding monomers were studied through fluorescence spectroscopy, and for the pyrene-polymer the quenching of fluorescence in film state by nitrobenzene used as efficient quencher was also performed. The fluorescence measurements suggested a hydrophilic environment for pyrene molecule in the polycation, where an increased excimer emission was evidenced. UV photolysis experiments performed with light of 365 nm on one synthesized model containing anthracene in DMF solution showed that the absorption maximum from 367 nm decreased gradually with irradiation time, as the *[4+4]* dimerization process of anthracene occurred. Since the above polymers can form flexible of elastomeric type, it should be possible to develop vapor-based chemical sensors for detection of some analytics.

Keywords: *cationic polyetherurethane, pyrene/anthracene polymer, fluorescence study*

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INTRODUCTION

Molecule-based fluorescent sensors are generally composed of a fluorophore and a binding site, and are incorporated with a signaling mode for the fluorophore in response to the event at the binding sites. A number of fluorescent signaling modes, such as quenching, enhancement, excimers, exciplexes, lifetimes, and anisotropy, are available for sensing. Fluorescence efficiency can be correlated with many structural features of chemicals including π-π* and n-π* transitions, structural rigidity, noncovalent interactions (e.g., hydrogen bonds, π-π interactions, and hydrophilic and hydrophobic interactions), intra or intermolecular energy transfers, and photoinduced electron transfers. These allow the development of fluorescent sensors with very diverse structures as well as specific responses for substrate detection. The high sensitivity of the fluorescence technique requires the use of only very small amounts of sensor molecules and/or analytes. A great number of fluorescent sensors have been constructed to detect protons, metal ions, anions, and neutral molecules [1]. Fluorescent sensors or labels have also been extensively applied in biological studies.

In general, it is assumed that flat highly π-delocalized systems such as pyrene and anthracene show greater tendency to form excimers. An additional requirement for excimer formation is that two monomers need to be in close proximity in order to give stacking interactions and the molecular excimer state. Pyrene has several advantages as a probe molecule. First, as a fluorescence probe, pyrene shows relative changes in the fine structure of the fluorescence spectrum in response to the polarity of the microenvironment [2]. Because the fine structure of the pyrene fluorescence spectrum is not affected by factors other than the polarity of the environment, evaluation of the partition coefficient based on the measurements of the fine structure of the pyrene fluorescence is more reliable than those based simply on the fluorescence intensity. Among other advantages, the high efficiency of excimer formation (which can be monitored by the fluorescence spectrum of pyrene around 480 nm) that allows to determine if a single molecule of pyrene is in a micelle, the small size of pyrene that leads to only small perturbations of the microenvironment and the absence of any hydrophilic parts that would tend to attract it to interfaces can be cited. Pyrene can penetrate into the hydrophobic interior of structures.

Anthracene is a polycyclic aromatic hydrocarbon that has been widely used as a signalling subunit for both cation and anion sensing due to the commercial availability of a large variety of highly fluorescent derivatives and well-known photophysical properties [3]. As a consequence, it represents one of the most important groups extensively analysed due to its peculiar characteristics, e.g. the absence of any specific interaction with most polymers, the relatively small size and symmetric shape. Anthracene-based sensors encompass all areas of molecular recognition; for example, anion sensors, glucose sensors, and metal-organic switches and possess favourable photophysical properties, such as strong absorption and high quantum yield. It is well known that anthracene and its derivatives dimerize photochemically upon long-wave UV irradiation (>350 nm) to give *[4+4]* cycloadducts across the 9,10 positions of anthracene, and the reaction can be reversed by the shorter wavelength irradiation or by heating [4]. If the irradiation is carrying out in aerated solutions, the triplet excited state of anthracene sensitizes the formation of singlet oxygen ($^1\Delta$) O_2, which reacts with the central ring to give a 9, 10-endoperoxide as well as the photodimer. As a result of the aforesaid photochemical reactions considerable changes of absorption, refractive index, degree of solubility are inducing in the polymer matrix. Anthracene containing polymers have been useful to apply various optoelectronic materials, photoluminescent polymer films to act as polariser and colour filter, conventional chemiluminescent fluorophores, electroluminescent devices, photoresist and channel waveguide applications [5], and so on.

The present study provides experimental data on some pyrene- and anthracene-polymers, the formation of photochromic species in the latter, into attempt to integrate the investigation in the current research on photosensitive materials. The paper reports the synthesis, characterization and properties of two cationic polyetherurethanes containing pyrene and anthracene anil fluorophores attached on the polymeric backbone by a quaternizing reaction of the aliphatic tertiary amine function nitrogen previously introduced in monomer/precursor. The resulting structures with fluorescent properties could serve as useful spectroscopic probes for sensor applications.

EXPERIMENTAL

A pyrene polyurethane was synthesized by a two step condensation reaction from poly(tetramethylene oxide) diol PTMG, Mn:2000, 0.03 mol), 2,4-toluylene diisocyanate (2,4-TDI, 0.02 mol) and the mixture N-methyldiethanol amine (NMDA, 0.0094 mol), pyrene-diol (Py-D, 0.0006 mol). The NCO-terminated prepolymer was prepared through the reaction between PTMG and 2,4-TDI under dry nitrogen at 65 ^oC for 6 h. After the prepolymer was degassed under vacuum and its temperature was reduced at 50 ^oC, NMDA and Py-D in anhydrous DMF were added. The reaction was carried out at 65 ^oC for 5 h. Similarly, was prepared a precursor based on PTMG, 2,4-TDI and the mixture NMDA, terephthalaldehyd-bis(3-hydroxymethyl)phenylimine (TAM). This precursor was quaternized with 9-chloromethylanthracene in the same medium for 5 h. The resulting polymers (PUC-Py, PUC-AN) were purified by precipitation in diethyl ether, collected by filtration and then dried under reduced pressure.

CHARACTERIZATION

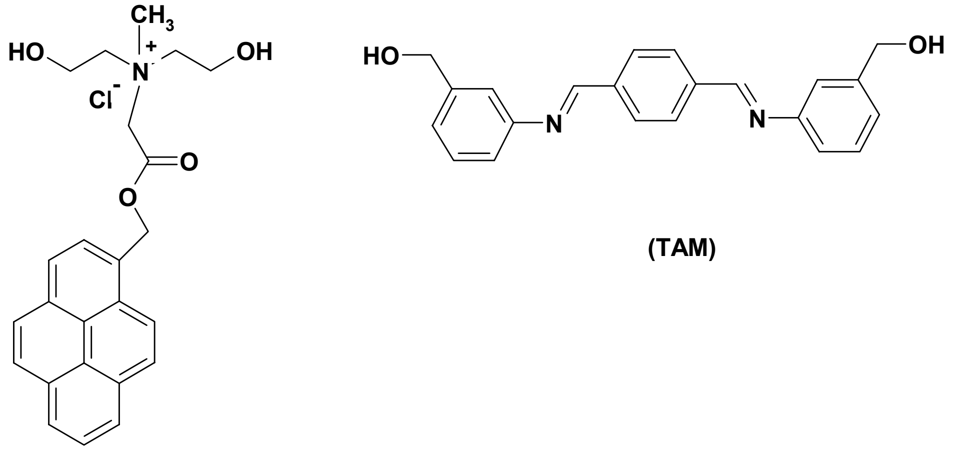
The polymers structures were verified by ^{1}H-NMR, IR and UV spectroscopy using a Bruker 400 MHz spectrometer, a Specord M80 and Specord M42 spectrophotometer, respectively. The thermal stability of the polyurethanes was analysed through thermogravimetry using a derivatograph (MOM Budapest). UV irradiations were performed in DMF solutions and for thin films, using a 500 W high-pressure mercury lamp without wavelength selection, at room temperature. The initial absorbance of the samples in the absorption band maximum was kept between 0.9 – 1.0.

The fluorescence spectra were recorded at room temperature 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. For quenching, the polymer film was introduced in desiccator after a preliminary saturation in vapors of nitrobenzene (about 30 min).

DISCUSSION

Synthesis of polymeric fluorophores involves preparing of diol monomers with pyrene and anil units namely, N-bis(2-hydroxyethyl)methyl-methylenecarbonyloxy-1-pyrene ammonium chloride (Py-D) and terephthalaldehyd-bis(3-hydroxymethylphenylimine) (TAM) as a new meta-substituted aromatic bisazomethine.

The structure of the above mentioned monomers is given in Figure 1.



(Py-D) **(TAM)**

Figure 1. *Structure of the pyrene and anil diol monomers*

Elemental analysis data supported the formation of the expected monomers and confirmed the calculated data. Structural characterization of the synthesized monomers evidenced by ^{1}H-NMR, IR and UV spectroscopy also agreed well with the prediction.

The structural purity was determined by ^{1}H-NMRspectroscopy. In the ^{1}H-NMR spectrum of Py-D can be identified signals for the methyl protons at 2.98 ppm (s), methylene protons at 3.25 ppm (m) and at 7.96-8.38 ppm pyrene protons (Table 1).

The ^{1}H-NMR spectrum of TAM evidenced the presence of one singlet at 8.55 ppm characteristic of the protons in the azomethine group (CH=N) from aromatic diol, while the intensity ratio of azomethine aromatic protons experimentally observed attested the structure of the resulting product.

The IR spectra of aromatic azomethine diol showed characteristic bands due to the presence of CH=N group at 1630 cm^{-1}, hydroxyl group at 3300 cm^{-1} and aromatic ring at 800–1100 cm^{-1}. Moreover, in its UV spectra, two absorption bands centered at 290 and 350 nm assigned to π-π* transitions of the azomethine aromatic diol were observed (Table 1).

Table 1. *Spectral characteristics of pyrene diol and aromatic bisazomethine diol*

Sample	**^{1}H-NMR (ppm)**	**IR (cm^{-1})**	**UV* (nm)**
Py-D	2.98 (s, 3H, CH_3N^+); 3.18 (s, 2H, CH_2N^+); 3.25 (m, 4H, CH_2N^+) 3.75 (m, 4H, HO-C$\underline{H_2}$); 7.96-8.38 (m, 9H, pyrene);	1720 (CO) 820, 710 (pyrene)	275 311 328 345
TAM	8.55 (2H, s, CH=N); 8 (4H, s, 1.6-C_6H_4); 7.2(8H, s, 1.4-C_6H_4); 4.55 (4H, s, CH_2)	3300 (OH); 2875 (CH) 1630 (CH=N); 1600, 1500 (CH–Ar) 750–820 (CH= from Ar)	290 350

*CH_3OH (Py-D); DMF (TAM)

To develop fluorescent ionic polyurethanes with good film forming properties, the first monomer was used as partner in polyaddition reaction between poly(tetramethylene oxide) diol of 2000 average molecular weight (PTMG), 2,4- tolylene diisocyanate (2,4-TDI), Py-D and N-methyldiethanol amine (NMDA), subsequently quaternized with benzyl chloride (PUC-Py). In the case of TAM diol, preparing of such polymers assumes synthesis of polyurethane precursor based on PTMG, 2,4-TDI, NMDA and TAM (molar ratio 1:3:1:1), followed of a quaternization with 9-chloromethylanthracene (PUC-AN). The structure of both fluorescent cationic polyurethanes used in our study is showed in Figure 2.

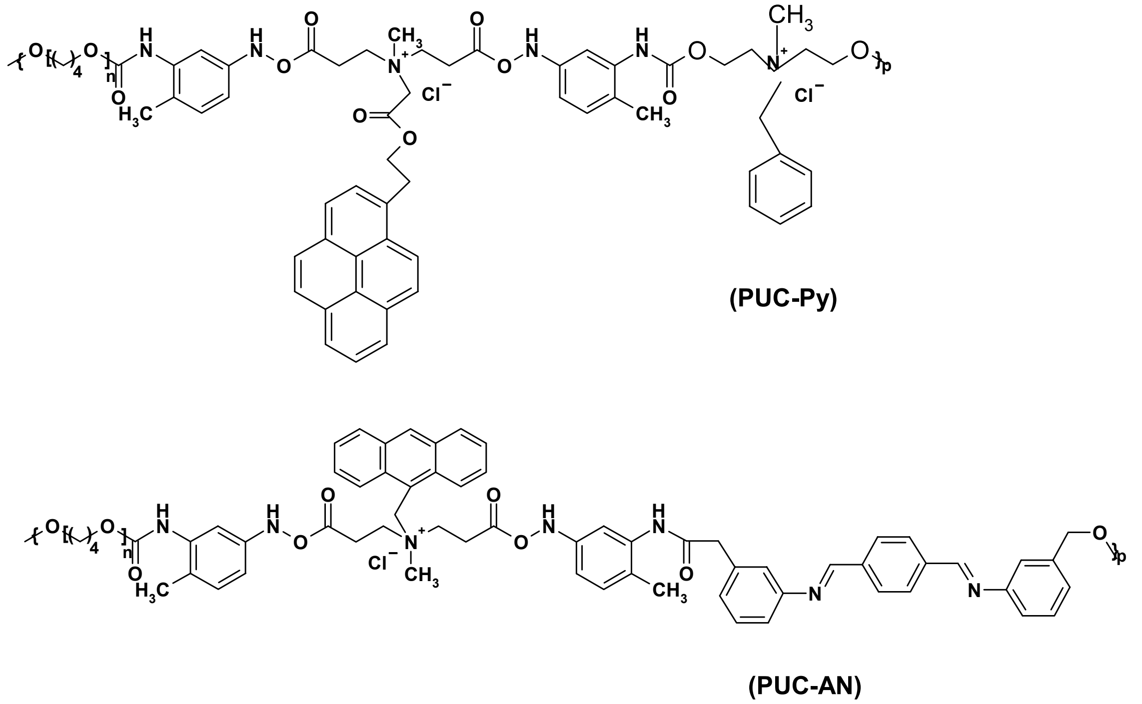


Figure 2. *Structure of fluorescent cationic polyurethanes*

The synthesized polymers are of a block copolymer type with long soft segments including the polyether component and short hard segments containing urethane structures, ammonium groups and azomethine units inserted in the polyurethane backbone besides pyrene or anthracene fluorophore. It was previously demonstrated [6] that the presence of a meta-substituted aromatic monomer prevents close packing of the macromolecular chains and thereby, a higher solubility of the resulting polymer is expected.

The structure of the polymers was determined by elemental analysis, IR, ^{1}H-NMR spectroscopy, TGA and DSC techniques. The elemental analysis data are in agreement with the calculated ones, verifying the expected structure. The pyrene fragment anchored to the macromolecular chain was determined from the ^{1}H-NMR spectrum taking in account the peak intensity ratio of the aromatic protons for the pyrene (7.96-8.38 ppm) to the aromatic protons of the starting diisocyanate (7.3-7.5 ppm). From the evolution of integrated areas around 6 wt% pyrene in PUC-Py was estimated. In the IR spectrum of PUC-Py, the absorption bands near 3300 cm^{-1} are attributed to the stretching vibrations of the NH urethane groups. Also, absorption bands at 1740 cm^{-1} due to the free CO stretching vibrations, at 1710 cm^{-1} from H-bonded carbonyl, at 2880-2950 cm^{-1} assigned to CH_2 groups, and at 1100, 1200 cm^{-1} (C-O-C) can be observed.

The ^{1}H-NMR spectrum of the polymer containing azomethine moiety, together with the assignments of the observed resonances, revealed a singlet at 7.9 ppm, characteristic of the proton in the azomethine units (CH=N), a multiplet at 6.9-7.3 ppm indicating hydrogens atoms in the aromatic ring, while the chemical shifts of the methylene protons from poly(tetramethylene oxide) appeared at 1.5 ppm (CH_2-CH_2). Together with the corresponding signals of the polyurethane precursor, the ^{1}H-NMR spectrum of the anthracene polymer evidenced the presence at 4.97 ppm of methylene protons from chloromethyl anthracene, as well as the ones that belongs to the anthracene structure in the range 6.66-7.07 and 7.54-8.11 ppm, respectively.

Characteristic absorption bands due to N-H stretching at 3400 cm^{-1} (hydrogen unbonded vibration), the C-H vibration in the 2870-2930 cm^{-1} region, the hydrogen-unbonded carbonyl at 1740 cm^{-1} and the hydrogen bonded one at 1630 cm^{-1} , CH=N azomethine stretching bands at 1600 cm^{-1}, as well as of Ar ring at about 1540 cm^{-1} for all films may be identified.

To observe the photobehavior of anthracene structure the UV photolysis experiments on one synthesized model compound (Figure 3) prepared through the quaternization reaction of the nitrogen atom from N-methyldiethanolamine with 9-chloromethylanthracene were firstly followed.

In figure 4, plot (a) is illustrated the UV spectrum of the above model compound with anthracene groups in DMF, with the appearance of a series of vibrationally spaced absorption bands assigned to π-π^* transitions at 318, 333, 350, 367 si 390 nm, indicative for the existence of the majority of molecules in the fundamental state. Upon irradiation of the model compound in DMF solution with UV light of 365 nm, the absorption maximum from 367 nm decreased gradually with irradiation time, providing evidence that the *[4+4]* dimerization process of anthracene took place. After 10 minutes of irradiation, no other modification of spectral intensities were recorded, with the confirmation of total conversion for anthracene moiety and subsequently, corresponding photodimers formation. The photolysis process can be expressed by a first-order rate equation: $ln\ A_0/A_t = kt$, where A_0 and A_t are values of the absorbance at time t_0 and t, respectively, and k is the rate constant. The kinetics of the process is of first order at least for about 75% of photoprocess, with a rate constant value of $5.556 \times 10^{-3}\ s^{-1}$ (Figure 4, plot (b)). In the scheme 1 is illustrated the dimerization reaction for the model compound.

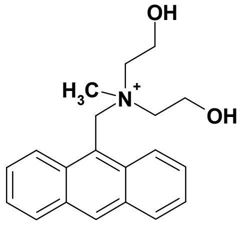


Figure 3. *Structure of model compound with anthracene moiety*

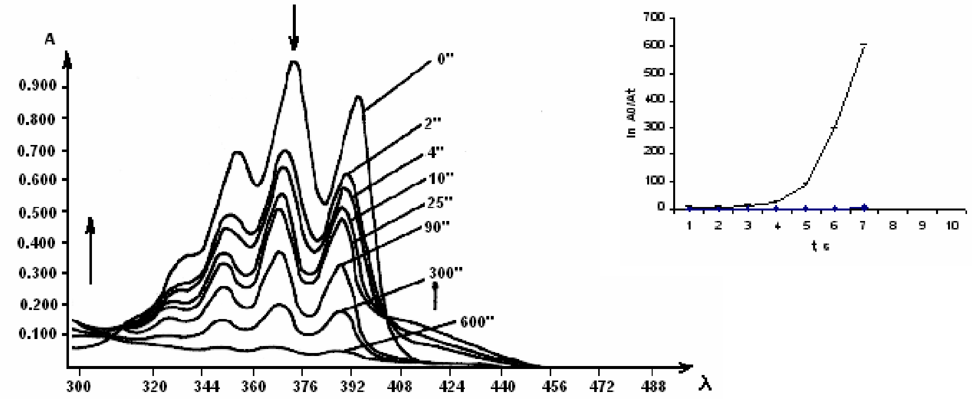
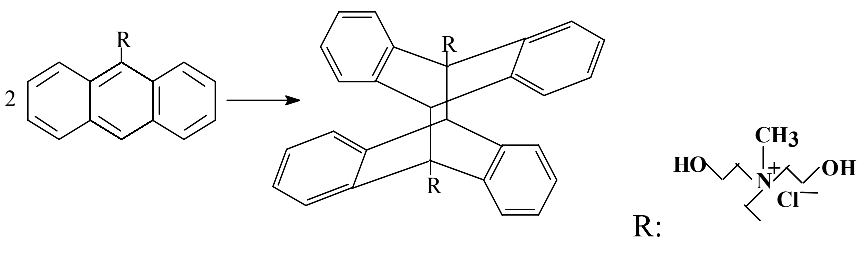


Figure 4. *(a) Characteristic spectral modifications in UV spectrum of model compound with anthracene unit in DMF solution; (b) process kinetic*



Scheme 1. *Dimerization reaction of model compound*

Fluorescence study

In table 2 are presented the absorption and fluorescence data for pyrene polymer, anthracene-based monomer and the corresponding polymer. In Figure 5 is shown the fluorescence spectrum for PUC-Py in thin film recorded at an excitation wavelength of 344 nm.

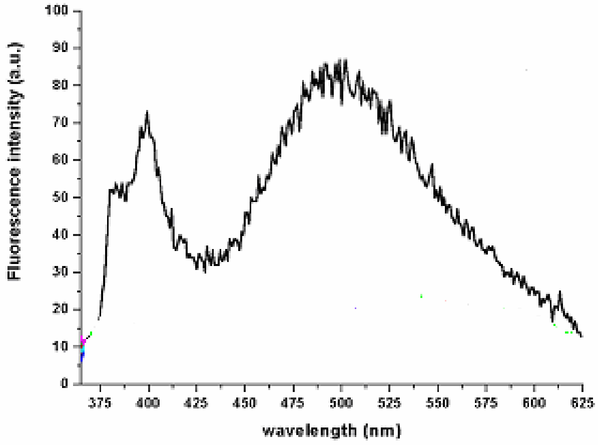


Figure 5. *Fluorescence spectrum for pyrene polyurethane in thin film*

As seen in this figure, the spectrum is typical of pyrene fluorescence [7], where the fluorescence intensities positioned at 380 nm (I_1), 395 nm (I_2), 405 nm (I_3) are assigned to monomer emission, while the intensity at 490 nm (I_4) is attributed to excimer emission. The analysis of spectrum suggests that the ratio the first maxima (I_1) and the third maxima (I_3) for polymeric film (I_1/I_3 = 1.80) determined from deconvolution results is a clear indicator of the polarity. Therefore, the above value sustains that the pyrene molecule is into hydrophilic microdomains. From the ratio of the intensity of the excimer peak (I_E) to that of the monomer (I_M) it was appreciated a value of 3.5, result interpreted as a measure of ability of the polymer to form a higher amount of excimer in film state compared to the monomer emission. One such possibility can be exploited in fluorescence quenching experiments using an efficient quencher of pyrene like nitrobenzene. The effect of nitrobenzene concentration on the fluorescence decay of the pyrene molecule from the polymer film exposed to saturated vapours of nitrobenzene is presented in Figure 6. Monitoring the quenching process of the excited pyrene a gradual decreasing of the fluorescence intensities was registered, with a total quenching of the excimer fluorescence intensity after about 12 min of exposure (monomer fluorescence is quenched around 90 %).

Returning to anthracene fluorophore from monomer, in solid state, a slightly blue shift of the absorption maxima by comparison with the values obtained for anthracene polymer in DMF solution was evidenced, this observation suggesting chromophores interactions in excited state, with excimers formation.

The emission spectrum for the model compound evidence the emission of a blue light, with a maximum centered at 413 nm, as well as a green one attributed to excimer form presence at 476 nm. The polymer fluorescence electronic spectra (λ=280 nm, DMF) (Figure 7) indicated the emission of a blue light with a maximum at 418 nm, the fluorescence maxima of the polymer being shifted over 70 nm to the red zone as compared to the corresponding absorption maximum. For the polymer in the solid state, a hipsochromic shift of fluorescence maximum has been evidenced, due to excimer formation as a consequence of partial overlapping for two anthracene units.

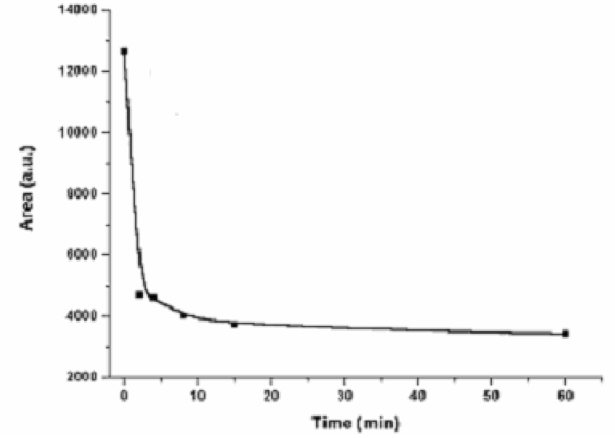


Figure 6. *Quenching effect of the fluorescence decay for PUC-Py in thin film excited with 344 nm and exposed to different times in saturated vapors of nitrobenzene*

Table 2. *Absorption and fluorescence data for pyrene polymer and anthracene-based structures*

Sample	λ_{exc} **(nm)**	λ_A **(nm)**	λ_F **(nm)**	Φ_F
PUC-Py	344	311; 328; 345	380; 395; 405; 490	-
AN	357	318, 333, 350, 367, 390	393, 413, 438, 476	0.007
PUC-AN (DMF)	357	334, 353, 371, 391	400, 418, 442	0.035
PUC-AN (film)	400	331, 352, 370, 390	390, 402, 425, 460	0.01

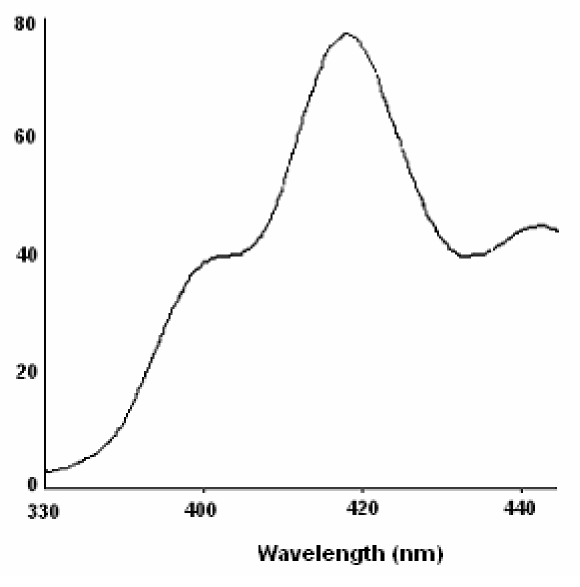


Figure 7. *Fluorescence measurements for PUC-AN polymer in DMF solution*

The less value of quantum yield for polymer film (0.01) by way of comparison with polymer solution in DMF (0.035) may be attributed to PET process efficiency between the donor HOMO orbital and anthracene π-system in the excited state. Generally, the value of fluorescence quantum yield is smaller in a polar solvent due to hydrogen bonding and charge dipole building that induce the increasing of PET intensity [8].

CONCLUSIONS

New segmented cationic polyurethanes of soft elastomer type containing pyrene or anthracene on the quaternary ammonium groups were synthesized and characterized in comparison with model compounds. Deconvolution results sustain the formation of hydrophilic micro domains where the excimer emission is higher than the monomer emission in film state.

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