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Structural and Optical Properties of Poly(4-vinyl pyridine)/Pyridine Gels

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Summary: A study of photoinduced processes in pyridine-based gels is presented. Poly(4-vinyl pyridine) dissolved in pyridine with water addition forms a photosensitive material. Under irradiation at the main absorption at 250 nm, a new intense absorption at 360 nm and an emission at 515 nm appeared. Upon continuation of radiation, together with an increase in the intensity of the new absorption, a prolonged tail through the whole visible range is observed. A new far red-shifted emission arises in correlation with the absorption spectrum changes. The presence of lower energy aggregates leads to polymer morphology changes. Short-range aggregates enhance polymer-polymer interactions. Long range aggregates have a tendency to crystallize. The photoinduced morphology changes was studied by transmission electron microscopy (TEM) of the polymer thin film and differential scanning calorimetry (DSC) of the gel. Phase separated species, micelles-like forms with domain size over 200 nm, and nanocrystals with average size 20-30 nm are demonstrated.

Introduction

The presence of the lone pair of sp^2 electrons on the pyridine nitrogen atom influences the photophysical behavior of the molecule. A comparatively weak base with pK_a= 5.21 and hydrogen bond basicity pK_{HB}=1.86,[1] pyridine turns into a strong base when in the photoexcited state. According to semi-empirical calculations[2] the difference in proton affinity between the ground and excited states amounts to 12 kcal/mol. In the presence of water, under UV-irradiation from the main absorption at 254 nm, pyridine is known to undergo photoisomerization to a Dewar pyridine. As the reaction continues, 5-amino-2,4-pentadienal (AP) is produced. AP is not stable and reverts in the dark to pyridine with water elimination.[3-7]

Ten years after its discovery,AP was synthesized.[8] It exists as yellow crystals with maximum absorption at λ_{max}=339 nm (absorption spectrum taken in 0.02 N HCl solution) and extinction coefficient ε=34400. These yellow crystals are also unstable and rapidly turn brownish at room temperature upon exposure to air.[8]

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In pyridine-based polymers the presence of the unshared electron pair of the pyridine N results in a strong flexibility of the optical properties. In poly(*p*-pyridine) and poly(*p*-pyridyl vinylene), additional (n,π*) states result from the promotion of a lone-pair electron from the nitrogen heteroatom to the π* backbone. The optical properties of these polymers were shown to be morphology-dependent. Photoluminescence (PL) of the polymers was red-shifted in thin films compared to in solution, a result that was explained by aggregate formation, where the ground state and excited state wavefunctions are delocalized over several chains. The practical application of these polymers as a symmetrically configured light-emitting device (device which emits light under forward and reverse d.c. bias) was shown.[9]

Recently an unusual novel photosensitive material composed from poly(4-vinyl pyridine)/pyridine (P4VPy/Py) mixture was observed.[10-13] Under UV-irradiation the mixture gels. The photogenerated gel has altered optical properties, especially multicolor emission.[10] FTIR studies of the material reveal the formation of pyridinium ion attached to the polymer backbone immediately after polymer dissolution [13] and hydrogen bond formation during photoinduced gelation.[10]

Here we present the study of the structural and optical properties changes of P4VPy/Py/H_20 mixture caused by irradiation at 250 nm. The P4VPy/Py/H_20 mixture, initially a viscous solution, turns to the chemically crosslinked gel, which is difficult to dissolve even in polar solvents. A new absorption band centered at 360 nm, and intense green and red PL at 515 nm and 640 nm, respectively, accompany the structural changes. We have carried out optical measurements, transmission electron microscopy (TEM), and differential scanning calorimetry (DSC) to study the optical and structural properties of the photoinduced gel. By considering the evolution of the optical properties and comparing the latter with the structural investigations on the nanometer scale, we concluded that under UV-irradiation at 250 nm several photoprocesses occur. One of these is the pyridine ring opening reaction. Another one is the formation of aggregates. The aggregates of the initial stages of irradiation have agreen emission at 515 nm. Upon prolongation of the irradiation another type of the aggregates appears. These aggregates exhibit red emission at 640 nm. Comparison of the parameters of the red (640 nm) and green (515 nm) PL such as: lifetime – 2 ns and 5.5 ns, Stokes losses – 0.09 eV and 0. 29 eV; full width at half maximum (FWHM) – 0.3 eV and 0.55 eV it is suggested that these changes are due to the more rigid and well-defined structures of the red emitting centers.

TEM pictures illustrate modification of the gel. Micelle-like structures with size >200 nm and nanocrystals of size 20-30 nm form under irradiation. The nanocrystals exhibit an electron diffraction pattern with Bragg peaks. A phase transition to the crystal phase can also be seen in a narrow temperature range with T_m=113°C in the calorimetry diagram of the irradiated gel.

The results presented conclude that the nanocrystals mostly involve red emitting centers and the semisolid micelles mostly contain the green emitting centers.

The photoproduct, we believe AP, is much more stable in the viscous media than in a pyridine-water solution. With prolongation of irradiation the concentration of photoproduct increases. The increasing concentration of the photoproduct occurs simultaneously with improvement of the rigidity of the system. Thus we can conclude that AP is an efficient crosslinker in the system.

Experimental Techniques

For this work, poly (4-vinyl pyridine) (P4VPy) with a molecular weight of 50000 (Polyscience Corporation) and gelatin (Aldrich) were used. P4VPy was carefully dried in a vacuum oven (10^{-3} torr), at 90°C for one week before use. P4VPy was dissolved in pyridine-d_5 or in pyridine-h_5 (Py), pK_{HB}=1.86.[5] Both kinds of pyridine were anhydrous (water < 0.003%) and obtained from Aldrich. The ratio between free solvent molecules and polymer side-chain groups was 1:1 in all solutions. Water used was triply distilled with pH=7.0. The water concentration was varied: 0.02, 3, and 50 wt %. Py-d_5 was used for the preparation of the gel with water concentration 0.02 and 3 wt %. Polymer dissolution was carried in a dry box under a N_2 atmosphere. Spectroscopic measurements were performed immediately after preparation of the mixture. Samples were placed in a 2.5-mm quartz cuvette (Starna). For TEM investigation the composition (with water concentration 3 wt %) was dissolved in pyridine so that the P4VPy concentration was 1 wt %. The polymer solution was deposited on 400-mesh copper grids, and then irradiated.

Absorption spectra were recorded on a Shimadzu UV-3101PC scanning spectrophotometer. Excitation and PL spectra were taken on a Shimadzu RF-5301PC spectrofluorimeter. Data were collected at right angles to the excitation beam. UV-irradiation at 250nm (0.5 mW/cm^2) was accomplished by a Xenon short arc lamp (Ushio) inside the Shimadzu RF-5301PC. Periodically, the irradiation was interrupted, and UV-VIS and photoluminescence measurements were performed. The resolution of

the emission and excitation spectra was 1 nm; the resolution of the absorption spectra was 2 nm. PL lifetime measurements were performed by phase modulation with a ISS K-2 unit. The gelation was evaluated visually, depending on the ability of the solution to flow or not. The transmission electron microscope Tecnai-12 (110kV) (Philips) was applied for structural study at the nanometer scale. Differential scanning calorimetry DSC 822 (Mettler Toledo) was used for calorimetry measurements. The CS Chem3D CS ChemOffice Software was used for modeling.

Photophysics of the P4VPY/PY Composition

Figure 1 presents the measured absorption and emission spectra of the composition with water addition in ratio 1:1:0.3 (3 wt %) before and after irradiation at 250 nm for 60 min. The initial absorption spectrum of the gel is almost identical to that of pyridine (curve 1), the PL spectrum is dark blue centered at 450 nm by excitation at 380 nm (curve 3). After irradiation a new absorption centered at 356 nm is observed (curve 4). In conjunction with the absorption spectra change a new green emission peaking at 515 nm (curve 6) by excitation at 468 nm appears in PL spectra.

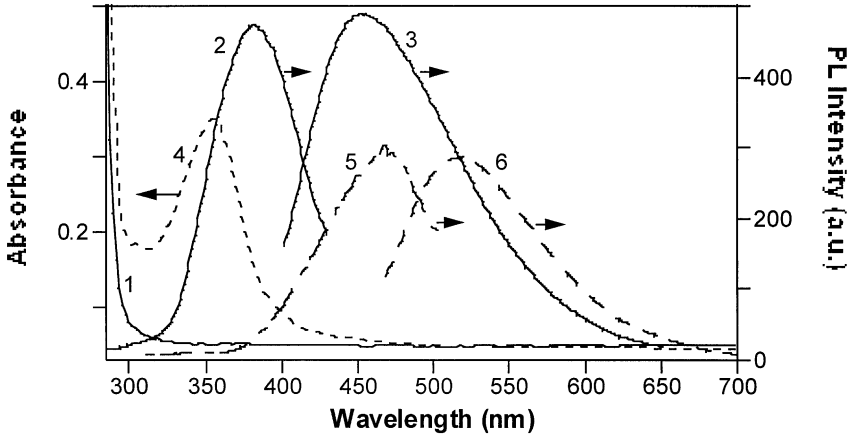

Figure 1. Absorption spectra (1,4); emission (3,6) and excitation (2,5) spectra before irradiation (1,2,3 - solid lines) and after UV-irradiation with 250 nm for 60 min (4,5,6 - dashed lines), for the P4VPy/Py/water composition (mol ratio 1:1:0.3).

The appearance of the absorption at 356 nm can be explained by the presence of some amount of the pyridine open form - AP as a result of the photochemical reaction. As was mentioned above, it is well established that pyridine in the presence of water

undergoes a ring opening reaction under excitation at 250 nm.[3-7]

To elucidate the structure of the green emitting centers, a model system - gelatin/water/pyridine gel at different pH's (5.0, 6.0, 7.0) was studied. The gel was sandwiched between two quartz slides and irradiated with 250 nm wavelength for 30 min.

Figure 2 shows the absorption spectra of the gelatin gel (at pH 5.0, 7.0) before irradiation (1); and absorption (2), excitation (3), and emission (4) spectra after irradiation. As can be seen, the intensity of the pyridine absorption at 250 nm is decreased, and simultaneously an intense new absorption at 360 nm is rising. Moreover, in the absorption spectrum of the gel at pH=5.0 an additional shoulder at 460 nm can clearly be observed.

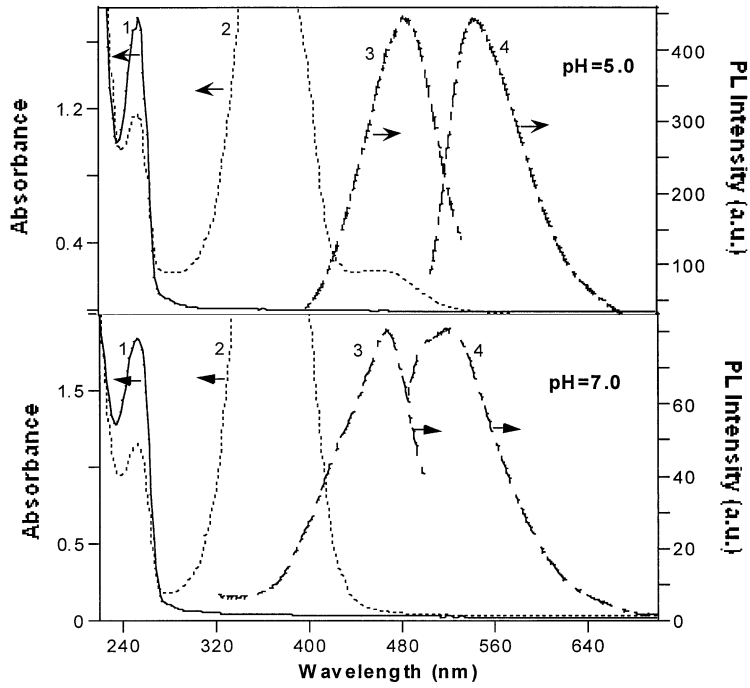

Figure 2. Absorption spectra before irradiation (1); absorption (2), excitation (3) and emission (4) spectra after UV-irradiation with 250 nm for 30 min of the gelatin/Py/water composition with different pH: 5.0 (pH=5.0) and 7.0 (pH=7.0).

The initial the gel practically has no emission. Nevertheless, under irradiation a green emission similar to the one observed in the P4VPy/Py/water (Fig.1) is registered (Fig.2).

The intensity and the peak position of the green emission is observed to be dependent on pH, as shown by Fig.2. The peak position is red-shifted from 517 nm to 542 nm and the intensity increases upon decreasing pH from 7.0 to 5.0.

It is important to note that the appearance of the identical green emission as a result of UV-irradiation in P4VPy/Py gel was observed earlier.[10] Transition energy of the green PL on the transition energy of the initial blue PL depends on the following empirical equation:

$$E_G^{PL} = E_B^{PL} - \Delta_B/2 + C \text{ (eV)} \quad (1)$$

where E_B^{PL} is the energy of blue PL (eV); E_G^{PL} is the energy of green PL (eV); Δ_B denotes the Stokes losses of the blue PL (eV) and C is a constant in the first approximation. (Note that C is a function of the molecular rearrangement in the excited and ground states; in our case it is in the range 15-50 meV).[10] Regarding the classical characterization of the dimer given by Kasha[14] a similar equation describes the "dimer" emitting center structure, where the building block is the emitting center with blue PL.

We now consider the results of the green PL study. Under irradiation in the investigated pyridine-content systems a new aggregate with a radiative energy transition at 2.4 eV (460 nm-520 nm) appears. The appearance of the aggregates occurs as in the P4VPy-based gel as well as in the gelatin gel. In the gelatin gel with low pH the absorption at 460 nm is clearly present in the absorption spectrum after irradiation, which demonstrates a high concentration of the photoinduced aggregates.

At this stage we do not have enough information about the detailed structure of the aggregate. However, flexibility of acid-base properties of pyridine in the excited state, namely, the increase of pyridine basicity in the excited state,[2] and the high concentration of photoinduced aggregates in the gelatin gel at pH=5.0, similar to the "dimer" structure of the emitting center, suggest the following model. A green emitting center appears as a result of photoinduced bonding of two closely located species, which were present in the system before irradiation. An initial building block we believe is the linear pyridine-pyridinium (protonated pyridine) aggregate.[10] Complexation of pyridine-water due to hydrogen bonding was extensively investigated.[15,16]

Continuation of UV-irradiation with 250 nm of the P4VPy/Py samples containing water

for 300 min led to an increase of the intensity of the new absorption at 360 nm and the appearance of the prolonged tail throughout the whole visible range (Fig.3). Simultaneously the new intense red emission at 640 nm by excitation at 610 nm is accompanied by a change in the absorption (Fig. 3).

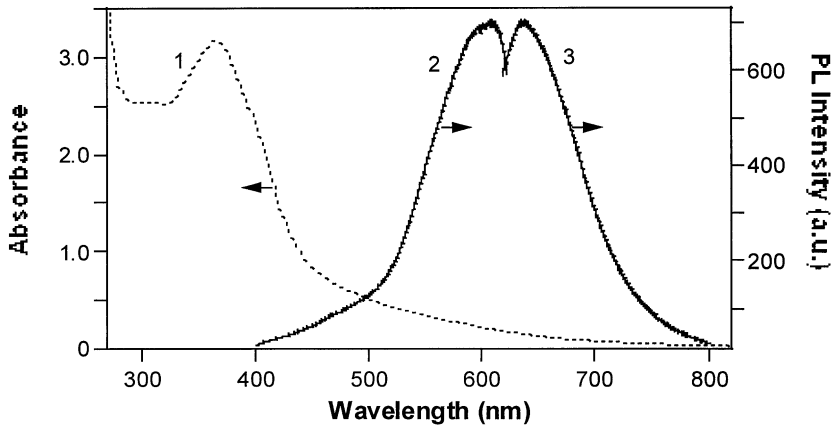

Figure 3. Absorption (1); excitation (2) and emission (3) spectra measured after irradiation of P4VPy/Py/water composition (mol ratio 1:1:10) with 250 nm for 300 min.

The red emission has significantly different properties compared to the green one. Comparing the parameters such as: lifetime – 2 ns and 5.5 ns, Stokes losses – 0.09 eV and 0. 29 eV; FWHM – 0.3 eV and 0.55 eV for red and green PL respectively, argue for a more rigid and well-defined structure of the red emitting centers.

TEM and Differential Scanning Calorimetry Studies

Together with formation of the luminescent aggregates, changes were also observed in the polymer morphology. TEM and calorimetry studies were applied for the polymer morphology investigation.

Transmission electron microscopy (TEM) was carried out on samples obtained from the thin gel film before and after irradiation at 250 nm for 60 min. The TEM image of the gel before irradiation is presented in Fig.4a in two scales: with low and high magnification (Fig.4a, including insert). A homogeneous structure of the polymer film is observed.

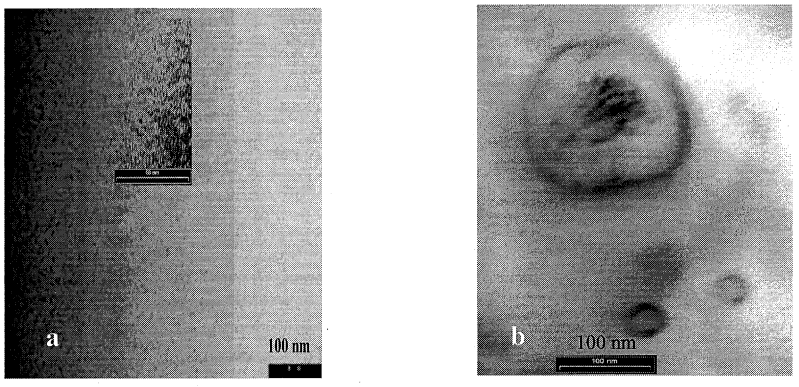

Figure 4. TEM images of the thin gel film before (a) and after UV-irradiation (b) by 250 nm for 60 min.

In support of the results of the optical study (formation of two different types of the aggregates) two new kinds of molecular packing are observed after irradiation (Figs. 4b, 5, 6). The typical region of the irradiated gel film with lower magnification is presented in Fig. 4b.

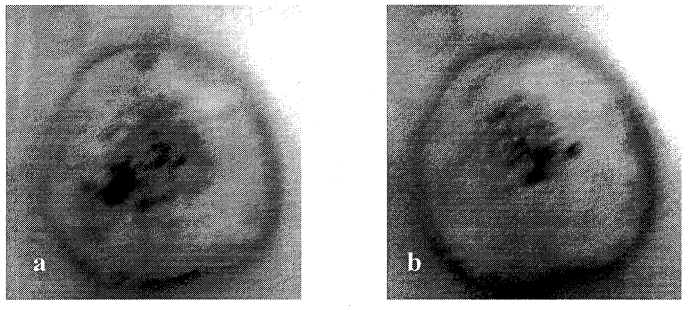

Figure 5. TEM images of the same micelle, taking one (a) after another (b) with the difference in the registration time 2 min.

The micelles with the size in the range of 200 nm (Fig.4 b; 5 a,b), and the nanocrystals with the average size 20-30 nm (Fig. 6) are two kinds of the phase-separated structures, which characterize the gel after UV-irradiation. Interesting behavior of the micelles is shown in Fig. 5a,b. The surface of the micelle has a non-homogeneous structure. The dark spots on the surface belong to the regions with higher electron density. The topography of the darkest areas was constantly changing during the period of the time of

the image registration. We suggest that this observation reflect the isomerization of the inter- or intrachain polymer crosslinking.

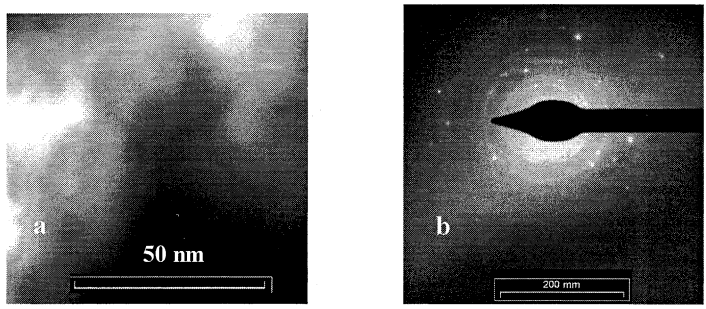

Figure 6. TEM image of a typical nanocrystal (a) and electron diffraction pattern of the same area (b).

The electron diffraction pattern of the typical crystal, shown in Fig. 6b, clearly indicates the concentric ring diffraction pattern and Bragg spots.

Crystalline phase formation in the gel during irradiation with 250 nm also has been confirmed by scanning calorimetry study. Figure 7 presents the calorimetry diagram of P4VPy/Py/water gel before and after UV-irradiation for 300 min in a bulk (the PL and absorption spectra of the same sample are presented in Fig. 3). The sharp peak in the diagram of the irradiated sample demonstrates crystal phase appearance after irradiation.

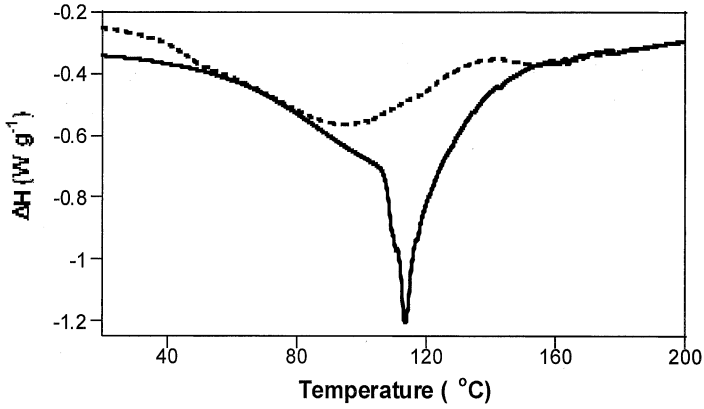

Figure 7. DSC diagram of the gel before (dashed line) and after irradiation with 250 nm for 300 min (solid line) taken at a scan rate of 10^0C/min.

Conclusion

The photophysics of the pyridine-based system P4VPy/Py shows changes in optical properties resulting from the photochemical reaction in the system. The efficiency of the reaction is strongly dependent on the quantity of water in the system. With increasing water content new lower energy aggregates result as the reaction is occurring. The first stage aggregate has a structure similar to the dimer. This photoinduced "dimer" has absorption at 460 nm, and green emission.

Upon continuation the irradiation optical properties change significantly. Longer chain aggregates with lower energy ground and excites states reveal themselves in the prolonged tail throughout the whole visible range and intense red emission.

Short chain and long chain aggregates change the morphology of the gel. Short range aggregates enhance polymer-polymer interaction. Long range aggregates have a tendency towards crystallization. The photoinduced morphology changes were studied by TEM and DSC. Phase separated species of micelles-like form with size over 200 nm, and nanocrystals with average size 20-30 nm are demonstrated. Based on the results of the experiments, and a comparing of our results with the known properties of the aminopentadienal as the product of the open ring reaction, at this stage we can suggest that aminopentadienal acts as the effective crosslinker in the system.

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